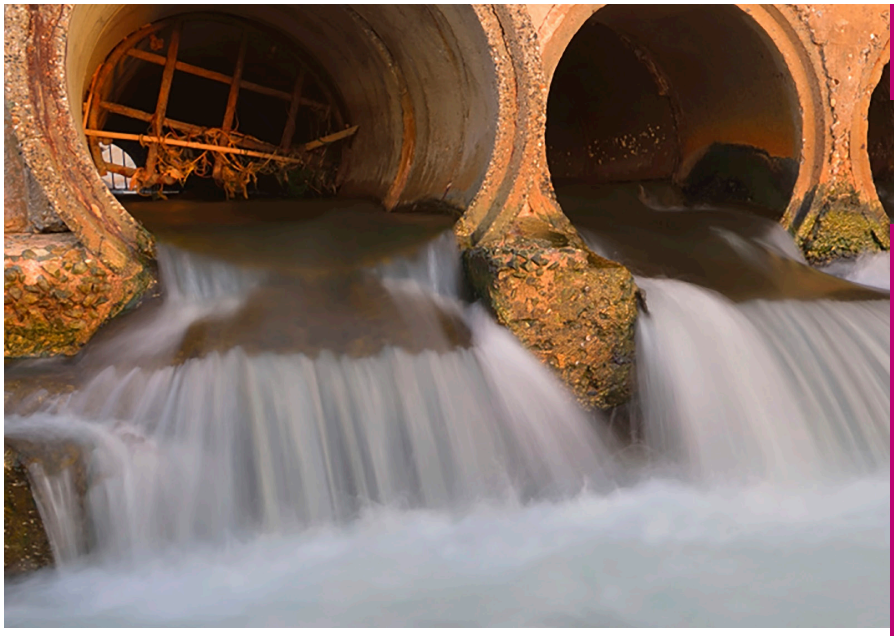

APPLICATION NOTE

Molecular Spectroscopy

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Water Analysis Using LAMBDA UV-Visible Spectrophotometers: Chemical Oxygen Demand Determination

Introduction

Chemical Oxygen Demand (COD) is used as an indirect measurement of the sum of oxidizable matter in water and measures the equivalent amount of oxygen required to oxidize organic compounds. Wastewater commonly contains organic compounds, as a result of industrial processes, which can oxidise in the presence of dissolved oxygen in the water. Low levels of dissolved oxygen can be detrimental to aquatic life but high levels may cause corrosion of metal pipes. It is important to use COD as an indicator of water quality.[1]

In this application, quantitative analysis of COD was performed using the LAMBDA 265™ UV-Vis spectrophotometer and Merck Spectroquant® COD mercury free cell test.

Principle

When oxidizable compounds in water are heated at 148 °C for two hours in an acidic solution of potassium dichromate and in the presence of a silver sulphate catalyst, mainly organic constituents are oxidized. The yellow dichromate ($Cr_2O_7^{2-}$) acts as an oxidizing agent and is reduced to the green chromic ion (Cr^{3+}) during the reaction. The decrease in dichromate ion is measured spectrophotometrically at 445 nm and is directly proportional to the mass of oxygen consumed per litre of solution (mg/L COD is equivalent to mg/L O_2).

This mercury free method is suitable for the concentration range 0 – 150 mg/L COD in drinking water, wastewater, ground water, and surface water, allowing its concentration to be determined by multiplying the absorbance at 445 nm with a known factor. Most COD test kits use mercury sulfate to mask chloride ions. Mercury free test kits are appropriate when high chloride levels are not of concern as chlorides are oxidized by dichromate, resulting in a positive interference.

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Reagents and apparatus

1. Merck Spectroquant® COD cell test (Hg-free) – (1.109772.0001) containing reaction cells with sulfuric acid, potassium dichromate and silver sulfate catalyst
2. PerkinElmer LAMBDA 265 PDA UV-Visible Spectrophotometer
3. UV Lab™ software
4. COD standard solution in water - certified reference material (100 +/- 3 mg/L O_2) supplied by VWR (1.25029.0100)
5. Deionised (DI) water
6. 10 mm quartz cuvette
7. Thermoreactor/Oven
8. Micropipette

Method

A COD standard solution (100 mg/L) in water obtained from VWR was used to test the accuracy and precision of this method. An oven (or thermoreactor) was preheated to 148 °C. After removing the screw cap from a COD vial, 2.0 ml of the 100 mg/L COD standard was placed in the vial, the cap replaced, and the contents mixed vigorously. The vial was then placed in the preheated oven and heated for two hours at 148 °C. This technique was also carried out for a reagent blank using DI water. After allowing to cool for 10 minutes the vials were shaken, placed in a test tube rack, and allowed to cool for a further 30 minutes to room temperature.

Using the UV Lab™ software, the LAMBDA 265 instrument parameters were set, as shown in Figure 1, to measure the absorbance at 445 nm. An equation was set up to calculate the COD, as shown in Equation 1. All samples were transferred to 10 mm cuvettes. Following measurement of the blank, the absorbance of the known COD solution was recorded. The method was further repeated for a homogenised and filtered surface water sample and a tap water sample. A 1:2 dilution using DI water was performed on the surface water sample due to sample turbidity. Measurement of turbid solutions results in a higher baseline leading to false-low COD readings.

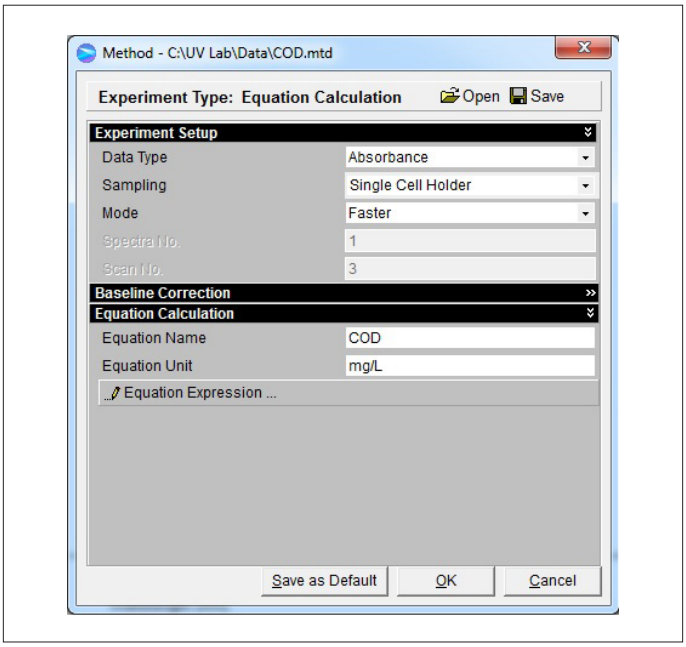

Figure 1. Instrument parameters and method setup.

Equation 1.

COD (mg/L) = Abs445 * (-321)

Results

Figure 2 shows spectra from five repeat runs of the 100 mg/L COD sample, with the results shown in Table 1. The mean absorbance at 445 nm was determined to be -0.320, which corresponded to a calculated concentration of 102.7 mg/L COD using Equation 1. The results obtained had a high level of accuracy and repeatability with a relative standard deviation of 0.17%.

Table 2 shows the results of five repeat measurements of the tap water and surface water samples. The mean absorbance of the surface water sample at 445 nm was determined to be -0.054, which corresponded to a calculated concentration of 17.3 mg/L COD using Equation 1. The surface water sample involved a 1:2 dilution due to sample turbidity. By accounting for the dilution factor, the mean corrected concentration was 34.6 mg/L COD. The mean absorbance of the tap water sample was determined to be -0.012, which corresponded to a calculated concentration of 3.9 mg/L COD using Equation 1. Both tap and surface water sample results showed a high level of repeatability with a relative standard deviation of 2.96 % and 2.25% respectively.

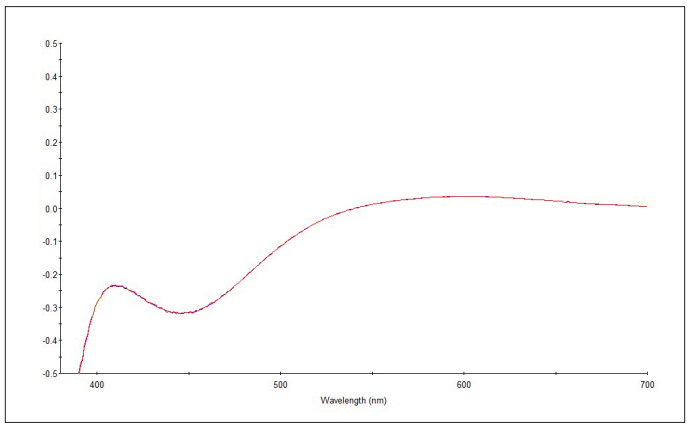

Figure 2. Overlaid UV-Vis spectra of repeat measurements of COD standard.

Table 1. Results for repeat measurements of standard solution.

COD Standard Solution	Absorbance at 445 nm	COD Concentration (mg/L)
Repeat 1	-0.320	102.7
Repeat 2	-0.319	102.3
Repeat 3	-0.319	102.5
Repeat 4	-0.320	102.7
Repeat 5	-0.320	102.6

Table 2. Results for repeat measurements of water samples.

	Tap Water Sample		Surface Water Sample		
	Absorbance at 445 nm	COD Concentration (mg/L)	Absorbance at 445 nm	COD Concentration (mg/L)	Corrected COD concentration (mg/L)
Repeat 1	-0.012	3.8	-0.053	16.9	33.9
Repeat 2	-0.012	3.9	-0.056	17.9	35.7
Repeat 3	-0.013	4.1	-0.054	17.3	34.7
Repeat 4	-0.012	3.9	-0.053	16.9	33.8
Repeat 5	-0.013	4.1	-0.054	17.2	34.4

Conclusion

Quantitative analysis of Chemical Oxygen Demand in water was achieved rapidly with a high level of repeatability and accuracy using the LAMBDA 265 UV-Vis spectrophotometer and UV Lab™ software. The Merck Spectroquant® mercury free cell test allows for simple determination of Chemical Oxygen Demand in the range 0-150 mg/L, avoiding exposure to hazardous chemicals and measurement of calibration standards.

References

1. Sincero, A., *'Physical-chemical treatment of water and wastewater'*, London: IWA Pub., 2003

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