

The Determination of Chemical Oxygen Demand in Water Quality Analysis

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Abstract

Chemical oxygen demand is one of the most important items in water quality analysis. The method is mature and the operation is relatively simple. In this paper, several detailed problems in the determination of chemical oxygen demand (GB11914-89 dichromate method) are presented, and solutions are proposed according to the practical analysis and practice.

Keywords Chemical oxygen demand; Determination; Uniformity; Dilution factor; Interference elimination

1. Introduction

A chemical oxygen requirement^[1] is the amount of oxidizing oxidizer that is used as an oxidizer, as an oxidizer, using the amount of oxidants as an oxidizer to process the water as an oxidizer. The amount of chemical oxygen required is a measure of the level of the level of exposure in the water, and as a measure of relative content of organic matter, but it can only reflect the contamination of organic material that can be oxidized, and it can't reflect the contamination of polycyclic aromatic hydrocarbons, PCB, dioxin, etc. Chemical oxygen demand is one of the indicators for China to implement total emission control, and it is also one of the main monitoring projects of the water quality environmental monitoring department.

The chemical oxygen demand in the water can be obtained by adding the kind and concentration of the oxidizing agent, the acidity of the reaction solution, the reaction temperature and time, and the presence of the catalyst, so that the chemical oxygen demand is also a conditional indicator, which must be carried out strictly in accordance with the operation steps^[2].

The determination of chemical oxygen demand is regulated by the dichromate method in China. It's called a reflux device, and in a strong acid solution, a certain amount of sodium dichromate of potassium oxide in the water sample, an overdose of dichromate potassium, which is used as an indicator of the subiron, is used to rehydrate the ammonium sulfuric acid, and then calculate the amount of oxygen used in the water to reduce the amount of oxygen in the water. The reflow time of this method is long, but the measurement result is more accurate^[3].

In recent years, the COD value of water sample has been measured by means of rapid determination of COD, i. e., the water sample reacts fast oxidation reduction reaction in the heating furnace, and the trivalent chromium ion generated after reaction is measured, and its concentration is measured by spectrophotometer. This method is easy to operate, short time, but large error.

COD is a conditional index, no matter which method is used, it must follow the operation steps strictly. However, in the process of analysis, it is only a basic premise to get an accurate result, and it is necessary to carry out the operation according to the operating procedures. More operation, more brain power, good summary and attention to some details are needed. The determination of chemical oxygen demand is based on GB11914-89 dichromate method.

2. The principle of

A known amount of potassium dichromate solution is added to the water sample and the catalyst is used as a silver salt under strong acidic medium, after boiling reflux, after boiling, the ferrous iron sulfate is used to convert the amount of potassium dichromate that is not reduced in the water sample to be reduced to a concentration of oxygen consumed by the consumption of ferrous sulfate as an indicator^[4]. It is difficult to oxidize aromatic hydrocarbon and pyridine under that condition of acidic potassium dichromate, and its oxidation rate is low, and the linear aliphatic compound can be effectively oxidized by the catalysis of sil sulfate.

3. The range of application

The GB11914-89 dichromate method applies to all types of water samples of all types of COD over 30mg/L, and an undiluted water sample has a limit of 700 mg/L, which is not to be used for containing saltwater, which is more than 1,000 mg/L.

4. Precautions in measurement

4.1 Sample collection, transportation and preservation

Water samples should be collected in glass bottles and analyzed as soon as possible. If not immediately analysis, should add sulfuric acid to $\text{pH} < 2$, place under $4\text{ }^{\circ}\text{C}$, but save time not more than five days, the volume of collecting water samples shall not be less than 100 mL.

4.2 Quantitative removal, interference and elimination of samples for testing purposes

4.2.1 Sample uniformity

In certain conditions, the mass concentration of the dissolved oxygen in the water sample corresponding to the dichromate consumed by the suspension is consumed by the oxidation of the potassium dichromate. So when you measure raw water, you have to shake the water sample. The mud-water mixture in the biochemical system was sampled and left at rest for more than 30min, and the determination of supernatant was representative. The uniformity of water samples has great influence on the test results. It is require that that sample before sampling is well mix (the surface water is taken onto the supernatant), especially the water sample whose turbid precipitate is not homogeneously distributed, and the sampling is very influential to the measurement result. At this time, the lower end of the relatively small pipette is selected as far as possible to avoid large and uneven turbidity as the test sample. For this kind of unevenly distributed samples, several samples can be appropriately taken for analysis, and then the data can be processed by statistical methods.

4.2.2 Whether the sample needs to be diluted and determine a reasonable dilution factor

The upper limit for the undiluted water sample is 700 mg/L, which must be determined after dilution beyond this limit. For water samples with high chemical oxygen demand, if a small sample of water and reagent is heated to see whether it turns green, if the solution is green, then reduce the waste water appropriately until the solution is green. Therefore, this "green" is the key to determine whether the samples can be directly analyzed. But you can't analyze it without the solution being green, which is green.

It's called "shallow green" and "dark green" or "dark green", and it's shown in several analysis, that when the water sample is heated with the reagent, the solution is in light green (or yellow green), and the water sample can be analyzed in the water sample, and when the water sample is heated, the remaining quantity of the solution in the solution is 1/5 to 4/5, and when the water sample is heated with the reagent, the solution is dark green (or dark green), and the water sample is not to be analyzed directly, and it needs to be reduced in the water sample, or to be properly diluted to the water sample. In the analysis of the chemical oxygen requirement, don't see the colour of the solution change, it's a waste of time, which is a waste of time and a waste of reagent.

After getting the water sample, the first thing to know is the type of water sample, according to its color, smell and so on, whether the water sample needs to be diluted. One-time dilution, the dilution factor is the key. If the dilution factor is too small, the solution will turn green when heated. If the dilution factor is too large, the amount of ammonium ferrous sulfate solution consumed by the sample solution will be close to the amount of ammonium ferrous sulfate solution consumed by the blank solution by the final titration, which cannot be determined. So, how to determine a more reasonable dilution factor? For wastewater samples with high chemical oxygen demand, the waste water sample and reagent with the required volume of 1/10 can be first taken and shaken evenly in a 15 mm x 150 mm rigid glass tube to see if it turns green after heating. If the solution is green, then the sampling amount of waste water should be appropriately reduced until the solution remains green, so as to determine the volume that should be used for sample analysis of waste water. At the dilution, the sample amount of the waste water shall not be less than 5 mL. If the chemical oxygen demand is high, the sample shall be diluted several times step by step. After multiple dilution, an appropriate amount of water should be taken and placed in the volumetric flask, and distilled water should be diluted to the standard line, so as to obtain a certain dilution factor. Then, 20.00 mL of water should be taken for reflux.

The other way to do that is to take a potassium dichromate of potassium, which is a small amount of sulfuric acid, which is a little bit of silver sulfuric acid, and then it heats up the temperature of the solution, and then you look at the temperature of the water, and you see the colour of the solution, and when the color of the solution turns to brown and yellow, then you write down the volume of the solution, and the dilution is equal to ten and it's ten to the V; Then dilute it with a volumetric flask

4.2.3 Interference and elimination of methods

Acid potassium dichromate oxidation resistance is very strong, but most of the organic matter, oxide to join silver sulfate as catalyst, the linear aliphatic compounds can be oxidized completely, and aromatic organic matter is not easy to be oxidized, would not be pyridine oxidation and volatile linear aliphatic compounds, benzene and other organic matter exists in vapor phase, can't contact with the liquid antioxidant, oxidation is not obvious. The main interferometry of the method is chloride ion, because chloride can be oxidized by heavy chromate, and it can be deposited with the effects of silver sulphate, which can affect the results, so when you add sulfuric mercury to the water before the reflux, it can be redirected to the water, and then the chloride can bind to mercury and sulfuric acid as a soluble chloramalgam hydrate.

For samples with more than 30mg /L chloride ion content, 0.4g mercury sulphate should be added to the reflux conical flask first, followed by water sample, and shake well for analysis. Samples with chloride ion content higher than 1000 mg/L should be first quantitatively diluted so as to reduce the content below 1000 mg/L and then measured. The maximum amount of chloride ion complexed with 0.4g mercuric sulfate can be up to 40mg. If 20.00ml water sample is used, the maximum concentration of chlorine ion can be complexed with 2000 mg/L. If the concentration of chloride ion is low, less mercury sulfate can be added to keep mercury sulfate: chloride ion = 10:1. If there is a small amount of mercury chloride precipitation, the determination will not be affected.

4.3 Selection and calibration of standard solution concentration

For chemical oxygen demand (COD) is greater than 50 mg/L water samples, the application of 0.2500 mol/L potassium dichromate standard solution, back to drops in 0.1 mol/L ferrous ammonium sulphate solution. For water samples with chemical oxygen demand less than 50 mg/L, the standard solution of 0.02500 mol/L of potassium dichromate should be used instead of 0.01 mol/L ammonium sulfate solution. It is necessary to add 20mL of concentrated sulfuric acid to be added for each test, to add 20mL of concentrated sulfuric acid, to be used for calibration with a solution of potassium dichromate daily, especially when that temperature is high, the change of its concentration is to be observed. Silver sulfuric acid - silver sulfuric acid solution must be used to ensure the total dissolution of silver sulfuric acid.

4.4 Control the condensation effect of the reflux

When the chemical oxygen demand is determined, when the test sample and reagent are added, the test sample shall be placed on the reflux unit for 2 HRS. If not, the evaporation loss of the test specimen can be caused. Therefore, the accuracy of test result can be greatly affected. It is connected with distillation unit, and then that condensate water is first open, and then the silver sulfate solution is added to the solution of silver sulfuric acid, and the electric furnace is heated and refluxed for two hours, and the color of the solution is yellow to blue, and then turns to brown after the titration. Blank samples shall be taken every day.

4.5 Hold the titration rate

In the case of the volume method, usually, when you're titrating, you're going to follow the operating principle of "two slow and fast," but when the chemical oxygen requirement is titrated, you don't have to go too slow, and you're going to be able to determine the speed of the titration in terms of the color of the solution. When the solution is added to the substrate, it's red and brown, and it starts to titrate, and it's going to be fast, and it's going to be a little bit faster, and it's going to go from the red brown to the yellow, to the dark green, until it's blue and green, and then it's going to slow down, shake the solution, and change it to the drip. When the color of the solution turns gray, it proves that it is about to reach the end point. At this point, only one or half drops are needed to reach the reddish brown color, and titration is completed. The accuracy of the titration endpoint control directly affects the size of the reading and the accuracy of the calculation results. Grasp the titration speed, should be fast, should be slow, to achieve fast and accurate. During titration, the conical bottle should not be shaken violently, and the reagent in the bottle should not splash water, otherwise, the measurement results will be affected.

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