International Standard 6060

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Water quality — Determination of the chemical oxygen demand

Qualité de l'eau — Détermination de la demande chimique en oxygène

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Foreword

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Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

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Users should note that all International Standards undergo revision from time to time and that any reference made herein to any other International Standard implies its latest edition, unless otherwise stated.

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Water quality — Determination of the chemical oxygen demand

0 Introduction

The chemical oxygen demand, COD, of water as determined by this dichromate method can be considered as an approximate measure of the theoretical oxygen demand, i.e. the amount of oxygen consumed in total chemical oxidation of the organic constituents to inorganic end products (see also clause 10). The degree to which the test results approach the theoretical value depends primarily on how complete the oxidation is. A great number of organic compounds are oxidized to an extent of between 90 and 100 %, and for waters where these compounds predominate, such as municipal effluents, the COD value is a realistic measure of the theoretical oxygen demand. For other waters which contain large quantities of certain substances that are difficult to oxidize under the conditions of the test (see clause 10), the COD value is a poor measure of the theoretical oxygen demand. This may be the case for some industrial effluents.

The significance of a COD value thus depends on the composition of the water studied. This should be borne in mind when judging results obtained by the method specified in this International Standard.

1 Scope and field of application

This International Standard specifies a method for the determination of the chemical oxygen demand, COD, of water.

It is applicable to most kinds of waters having a COD value higher than 30 mg/l (see also the note in clause 10). The maximum COD value that can be determined on an undiluted sample is 700 mg/l. It is not applicable to highly saline waters containing (after dilution) more than 2 000 mg/l of chloride, such as sea and oilfield waters.

NOTE — An International Standard that covers a lower range is under consideration.

For interferences, see clause 10.

2 References

ISO 385/1, *Laboratory glassware — Burettes — Part 1: General requirements.*

ISO 5790, *Inorganic chemical products for industrial use — General method for determination of chloride content — Mercurimetric method.*

3 Definition

chemical oxygen demand (COD): The mass concentration of oxygen equivalent to the amount of dichromate consumed by dissolved and suspended matter when a water sample is treated with that oxidant under defined conditions.

4 Principle

Reflux in the presence of mercury(II) sulfate of a test portion with a known amount of potassium dichromate and silver catalyst in strong sulfuric acid for a fixed period of time, during which part of the dichromate is reduced by the oxidizable material present. Titration of the remainder of the dichromate with ammonium iron(II) sulfate. Calculation of the COD value from the amount of dichromate reduced.

1 mole of dichromate ($Cr_2O_7^{2-}$) is equivalent to 1,5 moles of oxygen (O_2).

5 Reagents and materials

WARNING — This method involves the handling and boiling of strong solutions of sulfuric acid and dichromate. Protective clothing, gloves and full face protection are necessary. In the event of spillage immediate washing with a copious volume of clean water is the simplest and most effective remedy.

Addition of concentrated sulfuric acid to water must always be carried out with care and with gentle swirling of the contents of the flask.

Care is required when preparing and handling solutions containing silver sulfate and mercuric sulfate as these substances are toxic.

Used reagents contain mercury, silver and chromium salts. Mercury salts discharged into receiving streams may be converted to very toxic methyl mercury compounds by bacterial action. Used reagents shall be handled or treated before disposal, according to national or local regulations. (See also ISO 5790, annex B.)

During the analysis, use only reagents of recognized analytical grade and only distilled water or water or equivalent purity.

NOTE — The quality of the water is of great importance for the precision of the results. Check the quality of the water by running blanks (described in 8.2 and 8.4) and similar parallel tests without any boiling, but otherwise exactly as stated. Note the consumption of ammonium iron(II) sulfate solution (5.3) in both cases. A difference of more than 0,5 ml indicates poor water quality. For determination of COD values below 100 mg/l the difference shall not exceed 0,2 ml. The quality of distilled water can often be improved by redistilling it from an acidified solution of potassium dichromate or potassium permanganate, using all-glass distillation equipment.

5.1 Sulfuric acid, $c(H_2SO_4) = 4$ mol/l.

Add to about 500 ml of water, 220 ml of sulfuric acid ($\varrho = 1,84$ g/ml) in portions and with caution. Allow to cool and dilute to 1 000 ml.

5.2 Silver sulfate - sulfuric acid

Add 10 g of silver sulfate (Ag_2SO_4) to 35 ml of water. Add in portions 965 ml of sulfuric acid ($\varrho = 1,84$ g/ml). Allow 1 or 2 days for dissolution. The dissolution is enhanced by stirring.

5.3 Ammonium iron(II) sulfate, standard volumetric solution, $c[(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O] \approx 0,12$ mol/l.

Dissolve 47,0 g of ammonium iron(II) sulfate hexahydrate in water. Add 20 ml of sulfuric acid ($\varrho = 1,84$ g/ml). Cool and dilute with water to 1 000 ml.

This solution shall be standardized daily as follows:

Dilute 10,0 ml of potassium dichromate solution (5.4) to about 100 ml with 4 mol/l sulfuric acid. Titrate this solution with the ammonium iron(II) sulfate to be standardized, using 2 or 3 drops of ferroin (5.6) as indicator.

The concentration, *c*, expressed in moles per litre, of the ammonium iron(II) sulfate is given by the formula

$$\frac{10,0 \times 0,040 \times 6}{V} = \frac{2,4}{V}$$

where V is the volume, in millilitres, of ammonium iron(II) sulfate consumed.

5.4 Potassium dichromate, standard reference solution, $c(K_2Cr_2O_7) = 0,040$ mol/l, containing mercury salt.

Dissolve 80 g of mercury(II) sulfate ($HgSO_4$) in 800 ml of water. Add, with caution, 100 ml of sulfuric acid ($\varrho = 1,84$ g/ml). Allow to cool and dissolve 11,768 g of potassium dichromate, dried at 105 °C for 2 h, in the solution. Transfer the solution quantitatively to a volumetric flask and dilute to 1 000 ml.

The solution is stable for at least 1 month.

NOTE — To minimize use of mercury(II) sulfate, except where absolutely essential, the dichromate solution can be made up without the mercury salt. In this case, add 0,4 g of mercury(II) sulfate to the test portion **before** the addition of the dichromate (5.4) in 8.4 and shake thoroughly.

5.5 Potassium hydrogenphthalate, standard reference solution, $c(KC_8H_5O_4) = 2,082\ 4$ mmol/l

Dissolve 0,425 1 g of potassium hydrogenphthalate, dried at 105 °C, in water and dilute to 1 000 ml.

The solution has a theoretical COD value of 500 mg/l.

This solution is stable for at least 1 week if stored at 4 °C.

5.6 Ferroin, indicator solution.

Dissolve 0,7 g of iron(II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) in water. Add 1,50 g of 1,10-phenananthroline monohydrate, and shake until dissolved. Dilute to 100 ml.

This solution is commercially available.

5.7 Anti-bumping granules

Clean the granules as described in 6.1.

6 Apparatus

Usual laboratory equipment, and

6.1 Reflux apparatus, consisting of a 250 ml flask or tube with ground glass neck connected to a condenser so that there may be no significant loss of volatile material.

Clean the apparatus by repeatedly refluxing with fresh mixtures of 5 ml of potassium dichromate (5.4), 15 ml of silver sulfate-sulfuric acid (5.2) and 10 ml of water until constant blank values (8.2) are obtained.

Reserve this apparatus solely for use in the COD test.

6.2 Heating mantle, hotplate or other heating device, capable of bringing the sample to boiling within 10 min. Ensure that the device works without causing local overheating to solutions being heated.

6.3 Precision burette, of capacity 10 ml, graduated in divisions of 0,02 ml, and complying with ISO 385/1.

NOTE ON THE PREPARATION OF GLASSWARE

The glassware used shall be scrupulously clean and shall be protected from dust. This is particularly important in the case of low COD values.

7 Sampling and samples

Laboratory samples shall be collected preferably in glass bottles, although polyethylene bottles are also suitable. Analyse the samples as soon as possible and not later than 5 days after sampling. If the samples have to be stored prior to analysis, add 10 ml of sulfuric acid (5.1) per litre of sample. Keep them at 0 to 5 °C. Shake the storage bottles and make sure that their contents are well homogenized when withdrawing a test portion for analysis.

8 Procedure

8.1 Test portion

Place 10,0 ml of the laboratory sample (clause 7) into the flask (6.1). If the COD value of the sample is expected to exceed 700 mg/l make a dilution of the original sample with water so that a COD value of between 350 and 700 mg/l is obtained.

8.2 Blank test

Carry out a blank test in parallel with the determination, by the same procedure but replacing the test portion by 10 ml of water.

8.3 Check test

Check the technique and the purity of the reagents by analysing 10,0 ml of the standard solution (5.5) by the same procedure as given for the test portion.

The theoretical oxygen demand of this solution is 500 mg/l; the experimental procedure is satisfactory if the result of the check test is at least 96 % of this value.

8.4 Determination

Add 5,0 ml of potassium dichromate (5.4) and a few anti-bumping granules (5.7) to the test portion and mix well.

Add slowly 15 ml of silver sulfate - sulfuric acid (5.2), while swirling and cooling the flask under running water or in an ice-bath to prevent loss of volatile organic material. (Without adequate mixing, local heating may occur at the bottom of the flask, and the mixture may be blown out of the flask.)

Attach the flask to the condenser, and reflux the mixture for 2 h. Allow to cool and wash down any material on the inside of the condenser into the flask with a small volume of water. Remove the flask and dilute the mixture to about 75 ml with water and cool to room temperature.

Titrate the excess dichromate with ammonium iron(II) sulfate (5.3) using 1 or 2 drops of ferroin (5.6) as indicator.

NOTES

1 The reaction mixture has to boil gently without any bumping. Bumping indicates local overheating of the solution, which may lead to false results. Bumping may be caused by intense heating or by inefficient anti-bumping granules.

2 The consumption of ammonium iron(II) sulfate will be 10 ml or less, provided it has not deteriorated. The burette (6.3) should be precise enough to avoid overshooting the end-point.

3 Although the quantity of ferroin added is not critical, it should be kept as constant as possible. Take as the end-point the first sharp colour change from blue-green to reddish brown, even though the blue-green colour may reappear after some minutes.

9 Expression of results

9.1 Calculation

The chemical oxygen demand, COD, expressed in milligrams of oxygen per litre, is given by the formula

$$\frac{8\,000\,c(V_1 - V_2)}{V_0}$$

where

c is the concentration, in moles per litre, of the ammonium iron(II) sulfate as calculated in 5.3;

V_0 is the volume, in millilitres, of the test portion before dilution (if any);

V_1 is the volume, in millilitres, of ammonium iron(II) sulfate used in the titration against the blank;

V_2 is the volume, in millilitres, of ammonium iron(II) sulfate used in the titration against the test portion;

8 000 is the molar mass, in milligrams per litre, of $^1/_2\ O_2$.

Give the result to the nearest milligram per litre. Values below 30 mg/l shall be reported as "< 30 mg/l".

9.2 Reproducibility

Data obtained with a very similar procedure[1] indicate that the standard deviation, when comparing results, obtained for the same trade effluent, by different laboratories, is less than 10 mg/l.

About 40 different laboratories analysed some samples at the level of COD = 500 mg/l. The standard deviation was 20 mg/l for a potassium hydrogenphthalate solution and 25 mg/l for an industrial effluent from a pulp and paper mill. At the level of 50 mg/l the standard deviation was about 10 mg/l for a similar effluent.

In another study two samples of industrial effluent were analysed by 32 laboratories. The COD levels were at 140 and 160 mg/l respectively and the standard deviation between laboratories was near 14 mg/l for both samples.

10 Interferences

The test is sensitive to some interferences, principally chlorides. Inorganic reducing agents, such as nitrites, sulfides, and iron(II), will increase the result. It is acceptable practice to include the oxygen demand from such agents as part of the overall COD value of the sample.

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[1] *Chemical Oxygen Demand of Polluted and Waste Waters.* London, Her Majesty's Stationery Office, 1978.

The interference from chlorides is reduced — but not totally eliminated — by the addition of mercury(II) sulfate to the test portion before refluxing. This binds the chloride ion as a soluble chloromercurate(II) complex (see 8.4).

NOTE — When the chloride content exceeds 1 000 mg/l, the minimum acceptable value for the COD will be 250 mg/l. Results which fall below this level are of doubtful accuracy.

Aromatic hydrocarbons and pyridine are not oxidized to any appreciable extent. Some very volatile organic substances may escape the oxidation by evaporation. Straight chain aliphatic compounds are effectively oxidized by the silver sulfate - sulfuric acid (5.2).

11 Test report

The test report shall contain the following information:

a) reference to this International Standard;

b) precise identification of the sample;

c) the results, expressed in milligrams of oxygen per litre;

d) any departure from the procedure specified or any circumstance which may have affected the results.