
**Water quality — Determination of the
chemical oxygen demand index
(ST-COD) — Small-scale sealed-tube
method**

*Qualité de l'eau — Détermination de l'indice de demande chimique en
oxygène (ST-DCO) — Méthode à petite échelle en tube fermé*

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 3.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this International Standard may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 15705 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

Annexes A to G of this International Standard are for information only.

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Introduction

The chemical oxygen demand, ST-COD value, of water as determined by this dichromate method can be considered as an estimate of the theoretical oxygen demand, i.e. the amount of oxygen consumed in total chemical oxidation of the organic constituents present in the water. The degree to which the test results approach the theoretical value depends primarily on how complete the oxidation is. The ST-COD test is an empirical test and the effects of any oxidizing or reducing agents are included in the result. Under the conditions of the test, many organic compounds and most inorganic reducing agents are oxidized to between 90 % and 100 %. For waters that contain these compounds, such as sewage, industrial waste and other polluted waters, the ST-COD value is a realistic measure of the theoretical oxygen demand. However, for waters that contain large quantities of other substances that are difficult to oxidize under the conditions of the test, such as nitrogenous and heterocyclic compounds (e.g. pyridine and aliphatic and aromatic hydrocarbons), the ST-COD value is a poor measure of the theoretical oxygen demand. This may be the case for some industrial effluents.

The significance of an ST-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.

Detailed testing has shown good comparison between this method and the method of ISO 6060. However, it should not be assumed that this method is comparable in all cases to that of ISO 6060 without testing, particularly when there is a problem in obtaining a 2 ml representative sample (e.g. samples with high content of suspended solids).

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Water quality — Determination of the chemical oxygen demand index (ST-COD) — Small-scale sealed-tube method

WARNING — Persons using this standard should be familiar with normal laboratory practice. This standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

1 Scope

This International Standard specifies a method for the determination of the chemical oxygen demand (ST-COD) using the sealed tube method. The test is empirical and is applicable to any aqueous sample, which includes all sewage and waste waters.

The method is applicable to undiluted samples having ST-COD values up to 1 000 mg/l and a chloride concentration not exceeding 1 000 mg/l. Samples with higher ST-COD values require predilution. For samples with a low COD, the precision of the measurement will be reduced and the detection limit will be poorer.

Samples with a high chloride concentration will need to be prediluted to give a chloride concentration of approximately 1 000 mg/l or less before analysis.

The method oxidizes almost all types of organic compounds and most inorganic reducing agents. It has a detection limit (4,65 times the within-batch standard deviation of a blank or very low standard) of 6 mg/l for photometric detection at 600 nm, and 15 mg/l for titrimetric detection as reported by one laboratory comparing the photometric and titrimetric techniques using a commercial test kit with a range up to 1 000 mg/l.

The titrimetric part of this International Standard is applicable to samples exhibiting an atypical colour or turbidity after the digestion stage.

NOTE A comparison between the full-scale method (ISO 6060) and the method of this International Standard is given in annex A. A discussion of possible hazards is given in annex B. Information on commercial small-scale test kits is given in annex C. The method can be used over a reduced range (see annexes D and E). For checking the chloride concentration, see annex F.

2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this International Standard. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods*

ISO 5667-3:1994, *Water quality — Sampling — Part 3: Guidance on the preservation and handling of samples*

3 Term and definition

For the purposes of this International Standard, the following term and definition applies.

3.1

chemical oxygen demand

ST-COD

mass concentration of oxygen equivalent to the amount of dichromate consumed by dissolved and suspended matter when a water sample is treated under the conditions specified in this International Standard

NOTE 1 Adapted from ISO 6060.

NOTE 2 1 mol of dichromate ($\text{Cr}_2\text{O}_7^{2-}$) is equivalent to 3 mol of oxygen (O).

4 Principle

4.1 Samples are oxidized in a standard manner by digesting with sulfuric acid and potassium dichromate in the presence of silver sulfate and mercury(II) sulfate. Silver acts as a catalyst to oxidize the more refractory organic matter. Mercury reduces the interference caused by the presence of chloride ions. The amount of dichromate used in the oxidation of the sample is determined by measuring the absorbance of the Cr(III) formed at a wavelength of $600 \text{ nm} \pm 20 \text{ nm}$ for a range up to 1 000 mg/l. Absorbance measurements are made in the digestion tube, which acts as a cuvette, and are converted to an ST-COD value.

4.2 For the reduced calibration range up to 150 mg/l, an alternative wavelength $440 \text{ nm} \pm 20 \text{ nm}$ may be used (see annexes D and E). For a further reduced calibration range up to 50 mg/l, an alternative wavelength of $348 \text{ nm} \pm 15 \text{ nm}$ may be used. At 348 nm and 440 nm, the absorbance of the remaining chromium(VI) is measured.

4.3 For turbid and atypically coloured digested samples, titration with standardized ammonium iron(II) sulfate is used.

5 Interferences

5.1 High concentrations of chloride give a positive bias caused by the oxidation of chloride ions to chlorine. The interference from chloride ions is reduced but not totally eliminated by the addition of mercury(II) sulfate. This binds the chloride ions as a soluble chloromercurate(II) complex.

5.2 Manganese can give a positive bias using photometric detection at 600 nm. Using a 0 mg/l to 1 000 mg/l commercial test kit, duplicate analysis of a 500 mg/l manganese solution (as sulfate) gave ST-COD results of 1 080 mg/l and 1 086 mg/l and of a 50 mg/l manganese solution gave ST-COD results of 121 mg/l and 121 mg/l. The effect is much less with lower range (0 mg/l to 150 mg/l) kits at 440 nm (5.1). At this wavelength the interference is expressed as a negative bias. For a 0 mg/l to 150 mg/l commercial test kit, duplicate analysis of a 500 mg/l manganese solution (as sulfate) gave ST-COD results of -7 mg/l and -8 mg/l . See also note in C.6.

5.3 Many aromatic hydrocarbons and pyridine are not oxidized to any appreciable extent. Some volatile organic substances may escape the oxidation by evaporating.

5.4 Ammonium ions are not oxidized (organic nitrogen is normally converted to ammonium ions).

6 Reagents

6.1 **Water**, complying with ISO 3696:1987, Grade 3.

6.2 ST-COD sealed tubes

Whenever possible it is recommended to use ST-COD sealed tubes purchased ready for use. This minimizes the handling of toxic chemicals by laboratory staff. Commercial tubes can be purchased covering different analytical ranges (e.g. up to 50 mg/l, 160 mg/l, 1 000 mg/l or 1 500 mg/l). If tubes cannot be purchased already prepared, then prepare them within the laboratory as described in 6.7, for an analytical range of up to 1 000 mg/l. In this instance the user shall ascertain the reproducibility of optical transmission of the tubes or transfer the contents after digestion to a glass cuvette of 10 mm optical path length.

The ST-COD concentration range of commercial tubes will be specified by the manufacturer and shall not be exceeded. If this occurs, the sample should be suitably diluted to within the specified concentration range.

It is essential that the purchased sealed tubes contain mercury(II) sulfate for suppression of chloride interference. See note in C.6.

6.3 Standard reference solution of potassium dichromate, $c(\text{K}_2\text{Cr}_2\text{O}_7) = 0,10 \text{ mol/l}$ (range up to 1 000 mg/l ST-COD).

Dissolve $29,418 \text{ g} \pm 0,005 \text{ g}$ of potassium dichromate (dried at $105 \text{ }^\circ\text{C}$ for $2 \text{ h} \pm 10 \text{ min}$) in about 600 ml of water in a beaker. Carefully add 160 ml of concentrated sulfuric acid (6.4.1) with stirring. Allow to cool and make up to 1 000 ml in a graduated flask.

The solution is stable for 6 months.

6.4 Sulfuric acid

6.4.1 Concentrated sulfuric acid, $\rho(\text{H}_2\text{SO}_4) = 1,84 \text{ g/ml}$.

6.4.2 Dilute sulfuric acid, $c(\text{H}_2\text{SO}_4) = 4 \text{ mol/l}$.

Add to about 500 ml of water (6.1) in a beaker, $220 \text{ ml} \pm 10 \text{ ml}$ of concentrated sulfuric acid (6.4.1) cautiously with stirring. Allow to cool and dilute to $1\ 000 \text{ ml} \pm 10 \text{ ml}$ in a measuring cylinder. Transfer to a glass bottle.

The solution is stable for 12 months.

6.4.3 Dilute sulfuric acid, $c(\text{H}_2\text{SO}_4) = 1,8 \text{ mol/l}$.

Add cautiously, while swirling, $20 \text{ ml} \pm 1 \text{ ml}$ of concentrated sulfuric acid (6.4.1) to $180 \text{ ml} \pm 2 \text{ ml}$ of water in a beaker.

The solution is stable for 12 months.

6.5 Mercury(II) sulfate solution, $c(\text{HgSO}_4) = 1,35 \text{ mol/l}$.

Dissolve $80 \text{ g} \pm 1 \text{ g}$ of laboratory grade mercury(II) sulfate in $200 \text{ ml} \pm 2 \text{ ml}$ of dilute sulfuric acid (6.4.3).

WARNING: This reagent is very toxic. For hazards, see annex B.

The solution is stable for 12 months.

6.6 Silver sulfate in sulfuric acid, $c(\text{Ag}_2\text{SO}_4) = 0,038\ 5 \text{ mol/l}$.

Dissolve $24,0 \text{ g} \pm 0,1 \text{ g}$ of silver sulfate in 2 litres of concentrated sulfuric acid (6.4.1).

To obtain a satisfactory solution, shake the initial mixture. Allow it to stand overnight and then shake it again in order to dissolve all the silver sulfate.

Store in a dark brown glass bottle out of direct sunlight. The solution is stable for 12 months.

6.7 Dispensed premixed reagent (ST-COD range up to 1 000 mg/l).

Dispense $0,50 \text{ ml} \pm 0,01 \text{ ml}$ of potassium dichromate (6.3) into individual digestion tubes (7.1.2). Add carefully $0,20 \pm 0,01 \text{ ml}$ of mercury(II) sulfate solution (6.5), followed by $2,50 \text{ ml} \pm 0,01 \text{ ml}$ of silver sulfate (6.6).

Swirl cautiously to mix, then cap the tubes. Allow to stand overnight to cool. Swirl again before use.

This dispensed reagent is stable for 1 year if stored in the dark at ambient temperature.

A large batch of digestion tubes (7.1.2) may be prepared in advance, using the reagents as specified here.

Sealed tubes containing mercury(II) sulfate, concentrated sulfuric acid, potassium dichromate and silver sulfate may be prepared in-house or purchased commercially, if available.

These sealed tubes should be stored in the dark at ambient temperatures. They should be stable for at least 1 year. It is essential that tubes that have passed their expiry date are not be used and are discarded.

6.8 Reagents for photometric detection

6.8.1 Stock calibration standard solution of potassium hydrogen phthalate (KHP) [$\text{C}_6\text{H}_4(\text{COOH})(\text{COOK})$], ST-COD = 10 000 mg/l.

Dissolve $4,251 \text{ g} \pm 0,002 \text{ g}$ of potassium hydrogen phthalate, previously dried at $105 \text{ }^\circ\text{C} \pm 5 \text{ }^\circ\text{C}$ for $2 \text{ h} \pm 10 \text{ min}$, in approximately 350 ml of water (6.1). Dilute with water to 500 ml in a volumetric flask.

Store the solution in a refrigerator at $2 \text{ }^\circ\text{C}$ to $8 \text{ }^\circ\text{C}$ and prepare fresh each month.

An alternative to storage by refrigeration is to add 2 ml of dilute sulfuric acid (6.4.2), prior to diluting to 500 ml, to inhibit microbiological degradation.

6.8.2 Instrument calibration standard solutions, ST-COD of 200 mg/l, 400 mg/l, 600 mg/l, 800 mg/l and 1 000 mg/l.

Separately, dilute 20 ml, 40 ml, 60 ml, 80 ml and 100 ml of the stock 10 000 mg/l calibration solution (6.8.1) together with 4 ml of dilute sulfuric acid (6.4.2) to 1 000 ml with water.

Store these solutions at $2 \text{ }^\circ\text{C}$ to $8 \text{ }^\circ\text{C}$ and prepare fresh each month.

For a low concentration range [e.g. up to 150 mg/l (O)], standards of 30 mg/l, 60 mg/l, 90 mg/l, 120 mg/l and 150 mg/l may be prepared (see annex C). Store these solutions at $2 \text{ }^\circ\text{C}$ to $8 \text{ }^\circ\text{C}$ and prepare fresh each month.

6.9 Reagents for titrimetric detection (used for sealed-tube digested samples exhibiting atypical colour and/or turbidity).

6.9.1 Phenanthroline iron(II) sulfate indicator solution (ferroin)

Dissolve $3,5 \text{ g} \pm 0,1 \text{ g}$ of iron(II) sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) in 500 ml of water (6.1).

Add $7,4 \text{ g} \pm 0,1 \text{ g}$ of 1,10-phenanthroline monohydrate ($\text{C}_{12}\text{H}_8\text{N}_2 \cdot \text{H}_2\text{O}$) and shake until dissolved.

The solution is stable for at least 1 month.

6.9.2 Ammonium iron(II) sulfate (FAS) solution, approx. 0,075 mol/l.

Dissolve $30,0 \text{ g} \pm 0,5 \text{ g}$ of ammonium iron(II) sulfate hexahydrate [$(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$] in about 200 ml of water. Cautiously add $20,0 \text{ ml} \pm 0,5 \text{ ml}$ of concentrated sulfuric acid (6.4.1). Cool and dilute with water to 1 000 ml in a volumetric flask.

Prepare each week and standardize on the day of use.

Dilute $0,5 \text{ ml} \pm 0,01 \text{ ml}$ of $0,1 \text{ mol/l}$ potassium dichromate (6.3) to about 5 ml with dilute sulfuric acid (6.4.2). Titrate this solution with the ammonium iron(II) sulfate, using one drop of ferroin (6.9.1) as indicator.

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

$$c = \frac{0,5 \times 0,1 \times 6}{V} = \frac{0,3}{V} \quad (1)$$

where

V is the volume of ammonium iron(II) sulfate solution consumed, in millilitres (ml);

0,5 is the volume of dichromate solution, in millilitres (ml);

0,1 is the concentration of dichromate solution, in moles per litre (mol/l);

6 is a factor: 1 mole of dichromate is equivalent to 6 moles of ammonium iron(II) sulfate hexahydrate.

6.9.3 Silver nitrate solution, $c(\text{AgNO}_3) = 0,1 \text{ mol/l}$.

Dissolve $17,0 \text{ g} \pm 0,1 \text{ g}$ of silver nitrate in 1 000 ml of water (6.1).

Store in a dark glass bottle. This solution is stable for 6 months.

6.9.4 Potassium chromate solution, $[\text{K}_2\text{CrO}_4]$, (5 % volumic mass).

Dissolve $5,0 \text{ g} \pm 0,1 \text{ g}$ of potassium chromate in $100 \text{ ml} \pm 1 \text{ ml}$ of water (6.1). Add silver nitrate (6.9.3) dropwise to produce a slight red precipitate of silver chromate. Filter this solution.

This solution is stable for up to 1 year.

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7 Apparatus

7.1 Apparatus for the digestion stage

7.1.1 Heating block, capable of maintaining a temperature of $150 \text{ }^\circ\text{C} \pm 5 \text{ }^\circ\text{C}$ without causing localized over-heating to the contents of the tubes being tested.

The heating block should have a capacity for holding at least 10 tubes. The holes in the heating block should be of such a diameter that the glass tube wall is in close contact with the metal block. The depth of the holes should be such that adequate heating of the contents occurs.

NOTE Blocks are available that hold more than 50 tubes.

The contents of the tubes shall reach simmering point within 10 min of adding the tubes to the preheated block.

7.1.2 Digestion tubes, made from acid-resistant glass capable of withstanding a pressure resistance of 600 kPa at $150 \text{ }^\circ\text{C}$ (e.g. length 185 mm, external diameter 14 mm, wall thickness 1 mm).

The glass tubes shall fit into the heating block such that the wall is in close contact with the metal block. Before use they shall be inspected to ensure that they are not damaged or cracked in any way, and they shall be discarded if any slight defect is detected. The glass tubes will be supplied with suitable caps.

If the sealed tubes are to be used as the cuvettes for measuring absorbance, then it is essential that the outside of the tubes are scrupulously clean prior to being put into the photometer.

NOTE Annex C gives some information on the use of commercial small-scale ST-COD kits utilizing photometric detection.