

# INTERNATIONAL STANDARD

**ISO**  
**6060**

Second edition  
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## **Water quality — Determination of the chemical oxygen demand**

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



Reference number  
ISO 6060:1989(E)

## 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.

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.

International Standard ISO 6060 was prepared by Technical Committee ISO/TC 147, *Water quality*.

This second edition cancels and replaces the first edition (ISO 6060:1986). Technically the second edition is equivalent to the first edition, but the maximum permissible chloride content of the test portion is now restricted to 1 000 mg/l (first edition 2 000 mg/l).

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## 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.

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# Water quality — Determination of the chemical oxygen demand

## 1 Scope

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

It is applicable to water with a COD value of between 30 mg/l and 700 mg/l. The chloride content must not exceed 1000 mg/l. A water sample which is in accordance with these conditions is used directly for analysis.

If the COD value exceeds 700 mg/l, the water sample is diluted. For greatest accuracy it is preferable that the COD value of the sample is in the range of 300 mg/l to 600 mg/l.

Under the given reaction conditions, organic compounds are extensively oxidized. Excluded are compounds with certain structural elements (e.g. pyridine nucleus, quaternary nitrogen compounds). Volatile hydrophobic substances may evaporate and thus escape the oxidation. Inorganic compounds being oxidized under the reaction conditions are, for example:

- bromide ions, iodide ions;
- certain sulfur compounds;
- nitrite ions; and
- certain metal compounds.

On the other hand, certain compounds may react as oxidizing agents under the reaction conditions. Depending on the use of the test results, these circumstances shall be kept in mind.

For interferences, particularly from chlorides, see clause 10.

## 2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 385-1:1984, *Laboratory glassware — Burettes — Part 1: General requirements*.

ISO 5790:1979, *Inorganic chemical products for industrial use — General method for determination of chloride content — Mercurimetric method*.

## 3 Definition

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

**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 ( $\text{Cr}_2\text{O}_7^{2-}$ ) is equivalent to 1,5 moles of oxygen ( $\text{O}_2$ ).

If the test portion contains more than 1 000 mg/l of chlorides, a modified procedure must be applied.<sup>1)</sup>

## 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 copious volumes 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. Used reagents shall be treated for disposal according to national or local regulations (see also ISO 5790, 1979, annex B).**

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

NOTE 1 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 similar parallel tests without any boiling, but otherwise exactly as stated. Note the consumption of ammonium iron(II) sulfate solution (5.4) 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, $c(\text{H}_2\text{SO}_4) = 4 \text{ mol/l}$ .

Add to about 500 ml of water, 220 ml of sulfuric acid ( $\rho = 1,84 \text{ g/ml}$ ) 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 ( $\text{Ag}_2\text{SO}_4$ ) to 35 ml of water. Add in portions 965 ml of sulfuric acid ( $\rho = 1,84 \text{ g/ml}$ ). Allow 1 or 2 days for dissolution. The dissolution is enhanced by stirring.

### 5.3 Potassium dichromate, standard reference solution, $c(\text{K}_2\text{Cr}_2\text{O}_7) = 0,040 \text{ mol/l}$ , containing mercury salt.

Dissolve 80 g of mercury(II) sulfate ( $\text{HgSO}_4$ ) in

800 ml of water. Add, with caution, 100 ml of sulfuric acid ( $\rho = 1,84 \text{ g/ml}$ ). 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 2 If so desired, the dichromate solution may be prepared 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 solution (5.3) in 8.1 and mix thoroughly.

### 5.4 Ammonium iron(II) sulfate, standard volumetric solution, $c[(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}] \approx 0,12 \text{ mol/l}$ .

Dissolve 47,0 g of ammonium iron(II) sulfate hexahydrate in water. Add 20 ml of sulfuric acid ( $\rho = 1,84 \text{ g/ml}$ ). 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 (5.3) to about 100 ml with sulfuric acid (5.1). 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 expression.

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

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

### 5.5 Potassium hydrogenphthalate, standard reference solution, $c(\text{KC}_8\text{H}_5\text{O}_4) = 2,0824 \text{ mmol/l}$ .

Dissolve 0,4251 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 approximately 4 °C.

### 5.6 Ferroin, indicator solution.

Dissolve 0,7 g of iron(II) sulfate heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) or 1 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 water. Add 1,50 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. Dilute to 100 ml.

1) Modified procedures for samples exceeding 1 000 mg/l chloride content are currently being studied by ISO/TC 147/SC 2. A procedure for low level COD, below 30 mg/l, is also under study.