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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

Reference number
ISO 15705:2002(E)

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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.

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).

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 ($Cr_2O_7^{2-}$) 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 nm ± 20 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 nm ± 20 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 nm ± 15 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, $c(K_2Cr_2O_7)$ = 0,10 mol/l (range up to 1 000 mg/l ST-COD).

Dissolve 29,418 g ± 0,005 g of potassium dichromate (dried at 105 °C for 2 h ± 10 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, $\rho(H_2SO_4)$ = 1,84 g/ml.

6.4.2 Dilute sulfuric acid, $c(H_2SO_4)$ = 4 mol/l.

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

The solution is stable for 12 months.

6.4.3 Dilute sulfuric acid, $c(H_2SO_4)$ = 1,8 mol/l.

Add cautiously, while swirling, 20 ml ± 1 ml of concentrated sulfuric acid (6.4.1) to 180 ml ± 2 ml of water in a beaker.

The solution is stable for 12 months.

6.5 Mercury(II) sulfate solution, $c(HgSO_4)$ = 1,35 mol/l.

Dissolve 80 g ± 1 g of laboratory grade mercury(II) sulfate in 200 ml ± 2 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, $c(Ag_2SO_4)$ = 0,038 5 mol/l.

Dissolve 24,0 g ± 0,1 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 ml ± 0,01 ml of potassium dichromate (6.3) into individual digestion tubes (7.1.2). Add carefully 0,20 ± 0,01 ml of mercury(II) sulfate solution (6.5), followed by 2,50 ml ± 0,01 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) [$C_6H_4(COOH)(COOK)$], ST-COD = 10 000 mg/l.

Dissolve 4,251 g ± 0,002 g of potassium hydrogen phthalate, previously dried at 105 °C ± 5 °C for 2 h ± 10 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 °C to 8 °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 °C to 8 °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 °C to 8 °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 g ± 0,1 g of iron(II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) in 500 ml of water (6.1).

Add 7,4 g ± 0,1 g of 1,10-phenanthroline monohydrate ($C_{12}H_8N_2 \cdot H_2O$) 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 g ± 0,5 g of ammonium iron(II) sulfate hexahydrate [$(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$] in about 200 ml of water. Cautiously add 20,0 ml ± 0,5 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 ml ± 0,01 ml of 0,1 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, $c(AgNO_3)$ = 0,1 mol/l.

Dissolve 17,0 g ± 0,1 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, [K_2CrO_4], (5 % volumic mass).

Dissolve 5,0 g ± 0,1 g of potassium chromate in 100 ml ± 1 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.

7 Apparatus

7.1 Apparatus for the digestion stage

7.1.1 Heating block, capable of maintaining a temperature of 150 °C ± 5 °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 °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.

7.1.3 **Pipettor**, capable of dispensing 2,00 ml ± 0,02 ml.

7.2 Apparatus for the final measurement stage

7.2.1 Photometric detection apparatus

7.2.1.1 **Photometer**, capable of measuring at 600 nm ± 20 nm.

It is strongly recommended that the photometer be capable of measuring the absorbance of the digested sample directly in the sealed tube, thus eliminating the need to transfer the solution to a separate cuvette (see also annex C).

7.2.1.2 **Suitable storage facilities**, for the used sealed digestion tubes.

The used sealed digestion tubes and their contents shall be disposed of in accordance with national requirements.

7.2.1.3 **Centrifuge**, suitable for holding the digestion tubes (7.1.2).

7.2.2 Titrimetric detection apparatus

7.2.2.1 **Burette**, for example 10 ml with 0,02 ml graduations, or **digital titrator**, for example with a resolution of 0,02 ml or better (for titrating turbid digests from the sealed tubes).

7.2.2.2 **Magnetic stirring titration stand**

7.2.2.3 **Stirrer bar** and **stir bar retriever**

8 Sample collection and preservation

Take samples in accordance with ISO 5667-3.

Take a sample of the water to be tested in a clean glass or polypropene bottle and store at 2 °C to 8 °C in the dark.

Carry out analysis as soon as possible after sampling. If storage is essential, prior to analysis add 10,0 ml ± 0,1 ml of dilute sulfuric acid (6.4.2) per litre of sample to ensure that the pH of the sample is < 2.

This sample is stable for 5 days. After freezing at − 20 °C, samples are stable for 1 month.

9 Preparation of tubes and instrument set-up

9.1 Checking tubes for optical performance (where the absorbance is measured directly in the digestion tube)

Take a random sample (5 to 10) of empty tubes from a batch prior to preparation. Add 5 ml of water (6.1) to each tube. Replace the caps and ensure that no air bubbles are visible. (Tap gently to dislodge any air bubbles.) Measure the absorbance values at 600 nm using the photometer (7.2.1.1). These values shall not differ from each other by more than ± 0,005 absorbance units.

9.2 Tube preparation

See 6.7.

9.3 Instrument calibration/sensitivity check

To check the sensitivity of the instrument, prepare calibration standards as in 6.8.

Digest and measure as for samples in accordance with 10.1 and 10.2.

Record these results, verifying that there is no deterioration of sensitivity of the instrument and that a linear response of absorbance versus ST-COD concentration is obtained by plotting a manual calibration graph using a measured value Y, in system (absorbance) related units, of the potassium hydrogen phthalate calibration standards against X, the nominal chemical oxygen demand (ST-COD).

If the instrument calibration falls outside laboratory set tolerances, carry out manual absorbance measurements of the calibration standards and input a new calibration factor according to the manufacturer's instructions.

10 Analytical procedure for measurement of samples

10.1 Digestion stage

10.1.1 Carefully inspect all new sealed digestion tubes to see if there are any defects. Check whether the solution in the tube shows any hint of a green colour; if so, reject the tube.

10.1.2 The method is suitable for chloride concentrations up to 1 000 mg/l. A method for checking the chloride concentration is given in annex F. Users are advised to check the maximum acceptable chloride concentration for their system, for example by spiking a standard solution with an ST-COD value of 20 mg/l (potassium hydrogen phthalate) with chloride ion (NaCl)

10.1.3 Turn on the heating block (7.1.1) and preheat to 150 °C.

10.1.4 Remove the cap from a digestion tube (7.1.2).

10.1.5 Thoroughly shake and homogenize the sample and immediately pipette (7.1.3) 2,00 ml of the sample into the digestion tube. For any sample expected to have an ST-COD value greater than 1 000 mg/l, pipette (7.1.3) into the digester tube 2,00 ml of an appropriately diluted portion of the sample. Carry out a blank determination using water (6.1) with every batch of analysis.

10.1.6 Replace the cap firmly and mix the contents by gently inverting the tube several times.

10.1.7 Wipe the outside of the tube with a paper tissue.

10.1.8 Place the tube in the heating block (7.1.1). Reflux the contents at 150 °C for 2 h ± 10 min.

10.1.9 Remove the tubes from the heating block and allow them to cool to 60 °C or less. Mix the contents by carefully inverting each tube several times while still warm. Then allow the tubes to cool to ambient temperature before measuring the absorbance.

10.2 Photometric detection

10.2.1 If the cooled digested samples appear to be clear (i.e. absence of any visible turbidity), measure the absorbance at 600 nm using the photometer (7.2.1.1). Obtain results by direct readout from the instrument or by comparison against a calibration graph (see 9.3).

NOTE If the photometer or the tubes are not suitable for measuring the absorbance of the solution directly in the sealed tube, then it is necessary to take care not to disturb any sediment at the bottom of the tube when transferring some of the contents to a 10 mm path length cuvette for measuring the absorbance.

10.2.2 If any of the cooled digested samples appear to be turbid, centrifuge them at $4\,000g \pm 200g$ for 5,0 min ± 0,5 min. If the digestion solution is no longer turbid, measure the absorbance at 600 nm using the photometer as outlined in 10.2.1.

Exercise caution when centrifuging sealed tubes.

10.2.3 If the solution after the digestion stage and the centrifuge treatment is still turbid, or if the digest possesses an atypical colour, proceed as in 10.3.

10.3 Titrimetric determination

10.3.1 Carefully remove the cap of a tube containing the digested sample. Rinse the inside walls with less than 1 ml of water (6.1) or, alternatively, quantitatively transfer to another suitable container.

10.3.2 Whilst swirling, add one drop of the ferroin indicator solution (6.9.1). If the colour of the solution immediately changes from blue-green to orange-brown, the ST-COD value of the original sample will be above the range of the method. The sample shall be further diluted and the digest repeated.

10.3.3 If the colour remains lime green, titrate whilst swirling the solution with FAS (6.9.2) until the sample colour changes sharply from greenish-blue to orange-brown. Record the volume of FAS required (V_2 ml). Then titrate a digested blank using water instead of test sample and record the volume of FAS required (V_1 ml).

Transfer the sample to the digestion tube. Recap the tube and dispose of it in accordance with national or local regulations.

NOTE A low range (up to 150 mg/l) titrimetric procedure is given in annex E.

11 Calculation of results

11.1 Photometric procedure

Obtain the results of the measurements (10.2.1) by direct readout from the photometer or from the calibration graph (see 9.3). Record these results. If any result is outside this working range, repeat the analysis by dilution of the original sample.

Calculate the ST-COD, expressed in milligrams of oxygen per litre, up to three significant figures as read off from the calibration graph, depending upon the concentration found (see clause 12).

11.2 Titrimetric procedure

Calculate the chemical oxygen demand, ST-COD, expressed in milligrams of oxygen per litre, using the equation:

$$\text{ST-COD} = \frac{8\,000\, c(V_1 - V_2)}{V_0} \qquad (2)$$

where

c is the concentration of the ammonium iron(II) sulfate as calculated in 6.9.2, in moles per litre (mol/l);

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

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

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

8 000 is the molar mass of ½ O_2 (i.e. O), in milligrams per mole (mg/mol).

12 Expression of results

Report the ST-COD results up to three significant figures, depending on the concentration found and the validation data of the method.

NOTE Appropriate reporting is required for analyses carried out for European Directive applications.

13 Test report

The report shall give reference to this International Standard and contain the following details:

a) precise identification of the sample;

b) results as stated in clause 12;

c) method of pretreatment of sample;

d) any deviations from this test method and details of all circumstances that may have affected the result.

14 Precision

For precision data, see annex G.

Annex A
(informative)

Comparison between the COD method according to ISO 6060 and the method described in this International Standard

A.1 The small-scale method uses five times less mercury than the full-scale method. Mercury is a very toxic priority pollutant substance and it is important to minimize the amount used.

A.2 The small-scale method also uses proportionally less other toxic/hazardous reagents than the full-scale method.

A.3 All the reagents for the small-scale method are pre-dispensed into sealed glass digestion tubes. These tubes have a minimum shelf-life of 1 year. The reagents for the full-scale method are sequentially added to each reaction flask or tube at the time of analysis.

A.4 The small-scale method uses a photometric measurement of the digested sample rather than a conventional titration with ammonium iron(II) sulfate. For all commercially prepared tubes, the photometric measurement can be performed by simply placing the sealed tube, after digestion with the sample, in a specially adapted photometer.

A.5 The small-scale photometric method is especially suitable for laboratories with large ST-COD workloads. It only requires a single volumetric transfer operation (adding for example 2 ml to 3 ml of the sample to the pre-prepared sealed tube). These small-scale pre-prepared sealed tubes are available from a number of commercial suppliers. The full-scale titrimetric method requires four volumetric transfers with the option of manually adding 0,4 g of solid mercury(II) sulfate to each reflux flask or tube.

A.6 With the small-scale method, staff do not have to dispense corrosive and toxic reagents. Thus the risk of accidents from these corrosive/toxic reagents is greatly reduced relative to the full-scale method.

The silver and mercury waste products in the sealed tubes may be recovered or recycled.

However, users need to ensure that they can obtain 2 ml representative aliquots of their samples and that the sample digests are not turbid. Experience with a large number of laboratories has shown that obtaining 2 ml representative samples and the turbidity of the sample digests are not a significant problem for the vast majority of waste water samples.

Annex B
(informative)

Hazards

B.1 The method involves the handling of hot, concentrated solutions of sulfuric acid and potassium dichromate. Protective clothing, gloves and eye protection are essential. It is essential that staff be fully trained with respect to all the hazards associated with this method.

B.2 Poisonous gases may be emitted from samples on acidifying and therefore all operations should be carried out in a well-ventilated area, preferably a fume cupboard. It is advisable that unknown samples be acidified in a fume cupboard because of the possible release of hazardous gases such as HCN and H_2S.

B.3 All digestion tubes contain toxic mercury(II) sulfate and silver sulfate. Extra care is required when handling solutions containing mercury(II) sulfate and silver sulfate dissolved in concentrated sulfuric acid. These solutions are both toxic and highly corrosive.

B.4 Digestion tubes will be under pressure during and immediately after the heating stage. Tubes should be carefully inspected before use. Any tubes found with cracks, flaws, or indications of contamination should be discarded.

B.5 Sealed tubes containing water and no other reagents should not be placed in heating blocks set at 150 °C as excessive pressures can be generated. This method utilizes a 50 % (by volume) sulfuric acid matrix which has a boiling point of about 150 °C.

B.6 Sealed digestion tubes that contain samples which exhaust all the potassium dichromate will contain mercury vapour. Hence, the top from such a digestion tube should not be removed.

B.7 Used sealed tubes should remain capped and should be disposed of in accordance with documented procedures.

WARNING — Used sealed tubes should not be opened. Tubes should be disposed of in accordance with national requirements.

B.8 Commercial test tubes must have a label so that they can be identified when users remove them from the storage box and possibly use them with other tube tests. (e.g. a different concentration range). Also the tubes should incorporate a suitable hazard-warning label placed on the side of the tube.

Annex C
(informative)

Information on the use of commercial small-scale ST-COD test kits utilizing photometric detection

C.1 There are a number of small-scale sealed-tube proprietary ST-COD test kits with photometric detection. A nominal sample volume of 2 ml to 3 ml is normally used. It is essential to precisely follow the manufacturer's instructions supplied with the test kit when using these test kits.

C.2 Users of these kits should ensure that the version used contains mercury(II) sulfate for the suppression of chloride interference, and silver sulfate as an oxidation catalyst. Most manufacturers also supply mercury-free kits. These are not considered suitable for monitoring waste water ST-CODs. It has been found that commercial test kits that use mercury(II) sulfate give good chloride suppression for chloride concentrations up to 1 000 mg/l.

C.3 Each digestion tube supplied should be fit for purpose and should withstand the pressures generated. After the digestion step is completed, the tube is allowed to cool down (as described in the manufacturer's operating instructions) and is directly inserted into a specially adapted photometer. No physical transfer of the sample into a photometer cell is required. Thus there is minimal risk of contamination of the environment by the toxic and corrosive chemicals used in this method.

C.4 Users should validate these test kits using

— a blank,

— a range of potassium hydrogen phthalate standards,

— a sodium acetate standard with an ST-COD of 70 % to 80 % of the calibration top standard (to ensure oxidation of refractory compounds),

— a range of chloride standards of up to 1 000 mg/l chloride, and

— a range of typical samples.

NOTE Solutions containing 160 mg/l and 900 mg/l of anhydrous sodium acetate have theoretical CODs of 125 mg/l and 702 mg/l. Mean ST-COD results of 120 mg/l and 672 mg/l (five measurements) have been observed using the method of this International Standard.

C.5 Commercial manufacturers supply test kits for low (typically up to 50 mg/l or 150 mg/l) and high (typically up to 1 000 mg/l or 1 500 mg/l) ranges. The low-range kits monitor the decrease of chromium(VI) absorbance at 348 nm ± 20 nm or 440 nm ± 20 nm, whilst the high-range kits monitor the increase of chromium(III) absorbance at 600 nm ± 20 nm. The user should select the appropriate calibration range to use.

C.6 The photometric endpoint measurement should not be used for any digested samples that exhibit visible turbidity and/or atypical colours. In these cases, the alternative titrimetric endpoint determination should be used. For the vast majority of wastewater samples, photometric endpoint measurement has been found to be suitable.

NOTE High levels of manganese have been found to result in a positive bias for the high level methods. The formation of a red coloured Mn(III), Mn(VI) or Mn(VII) species is suspected (4.2). The effect (this time as a negative bias) is much less significant with the low range (up to 150 mg/l) kits than with the high range (up to 1 000 mg/l or 1 500 mg/l) kits.

If a sample is to be titrated in the digestion tube, users should ensure that the tube is of sufficient volume to accommodate the maximum required volume of titration solution.

Annex D
(informative)

Low-range sealed-tube photometric method (up to 150 mg/l)

D.1 Samples containing lower concentrations of organic material may be analysed using a more sensitive method. This technique utilizes the same equipment and general instructions as the photometric method (up to 1 000 mg/l), but uses a lower concentration of potassium dichromate. The amount of hexavalent chromium is determined by measuring the yellow colour at 440 nm ± 20 nm.

D.2 The dichromate solution prepared as in 6.3 should be replaced with a 0,015 mol/l solution, prepared as follows.

To approximately 500 ml of water, add 4,413 g ± 0,005 g of potassium dichromate ($K_2Cr_2O_7$), dried at 105 °C for 2 h ± 10 min and 160 ml of concentrated sulfuric acid (6.4.1). Dissolve, cool to room temperature, and make up to 1 000 ml in a graduated flask.

D.3 The premixed reagent is prepared as in 6.7, but substituting the above dichromate solution for the one from 6.3.

The instrument calibration standard solutions (6.8.2) should be replaced with a set of standards at lower concentrations, prepared as follows.

For instrument calibration standard solutions with ST-COD values of 30 mg/l, 60 mg/l, 90 mg/l, 120 mg/l and 150 mg/l of oxygen (O), separately dilute 3 ml, 6 ml, 9 ml, 12 ml and 15 ml of calibration solution (6.8.1) to 1 litre with water. Prior to diluting with water, add 4 ml of dilute sulfuric acid (see note in 6.8.2). Store these solutions at 2 °C to 8 °C and prepare monthly.

The photometer (see 7.2.1.1, 10.2 and 11.1) should be capable of measurements at 440 nm ± 20 nm. Note that the amount of remaining dichromate decreases as the ST-COD value increases. Thus, measurements made versus a reacted blank will yield negative absorbance values. If the instrument in use is not capable of displaying values less than zero, make all measurements versus a tube filled with water (6.1), and prepare a calibration appropriately.

D.4 Follow the procedure given in 10.1 and 10.2.

Annex E
(informative)

Low-range sealed-tube titrimetric method (up to 150 mg/l)

E.1 Samples containing lower concentrations of organic material may be analysed using a more sensitive method. This technique utilizes the same equipment and general instructions as the usual titrimetric method (up to 1 000 mg/l), but uses a lower concentration of potassium dichromate and ammonium iron(II) sulfate.

E.2 The dichromate solution specified in 6.3 should be replaced with a 0,015 mol/l solution, prepared as follows.

To approximately 500 ml of water add 4,413 g ± 0,005 g of potassium dichromate ($K_2Cr_2O_7$), dried at 105 °C for 2 h ± 10 min and 160 ml of concentrated sulfuric acid (6.4.1). Dissolve, cool to room temperature and make up to 1 litre in a graduated flask.

E.3 The premixed reagent is prepared by following the instructions in 6.7, substituting the above dichromate solution for that specified in 6.3.

The ammonium iron(II) sulfate solution prepared as in 6.9.2 should be replaced with a 0,012 mol/l solution, prepared as follows.

Dissolve 4,8 g ± 0,1 g of ammonium iron(II) sulfate hexahydrate [$(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$] in about 200 ml of water. Cautiously add 20,0 ml ± 0,5 ml of concentrated sulfuric acid (6.4.1). Cool and dilute with water to 1 000 ml in a volumetric flask. Prepare the solution fresh each week and standardize it on the day of use.

Dilute 0,50 ml ± 0,01 ml of 0,015 mol/l potassium dichromate 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 equation:

$$c = \frac{0{,}50 \times 0{,}015 \times 6}{V} = \frac{0{,}045}{V}$$

where

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

0,50 is the volume of dichromate solution, in millilitres (ml);

0,015 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.

Otherwise, follow the titrimetric method described in 6.9, 10.3 and 11.2.