Chemical Oxygen Demand (Dichromate Value) of Polluted and Waste Waters 1977

(Two methods, one tentative)

Methods for the Examination of Waters and Associated Materials

Contents

London Her Majesty's Stationery Office

Warning to users

The analytical procedures given in this booklet should only be carried out by competent trained persons, with adequate supervision when necessary. Local Safety Regulations must be observed. Laboratory procedures should be carried out only in a properly equipped laboratory. Field operations should be conducted with due regard to possible local hazards, and portable safety equipment should be carried. Care should be taken against creating hazards for others. Lone working, whether in the laboratory or field, should be discouraged. Reagents of adequate purity must be used, along with properly maintained apparatus and equipment of correct specification. Specification for reagents, apparatus and equipment are given in manufacturers' catalogues and various published standards. If contamination is suspected, reagent purity should be checked before use.

There are numerous handbooks on first aid and laboratory safety. One such publication is 'Code of Practice for Chemical Laboratories' issued by the Royal Institute of Chemistry, London. Where the Committee has considered that a special unusual hazard exists, attention has been drawn to this in the text so that additional care might be taken beyond that which should be exercised at all times when carrying out analytical procedures. It cannot be too strongly emphasised that prompt first aid, decontamination, or administration of the correct antidote can save life, but that incorrect treatment can make matters worse. It is suggested that both supervisors and operators be familiar with emergency procedures before starting even a slightly hazardous operation, and that doctors consulted after any accident involving chemical contamination, ingestion, or inhalation, be made familiar with the chemical nature of the injury, as some chemical injuries require specialist treatment not normally encountered by most doctors. Similar warning should be given if a biological or radiochemical injury is suspected. Some very unusual parasites, viruses and other micro-organisms are occasionally encountered in samples and when sampling in the field. In the latter case, all equipment including footwear should be disinfected by appropriate methods if contamination is suspected.

The best safeguard is a thorough consideration of hazards and the consequent safety precautions and remedies well in advance. Without intending to give a complete checklist, points that experience has shown are often forgotten include: laboratory tidiness, stray radiation leaks (including ultra violet), use of the correct protective clothing or goggles, removal of toxic fumes and wastes, containment in the event of breakage, access to taps, escape routes, and the accessibility of the correct and properly maintained first aid, fire-fighting, and rescue equipment. If in doubt it is safer to assume that a hazard may exist and take reasonable precautions than to assume that no hazard exists until proved otherwise.

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About this series

This booklet is one of a series intended to provide recommended methods for the determination of water quality. In the past, the Department of the Environment and its predecessors, in collaboration with various learned societies, has issued volumes of methods for the analysis of water and sewage culminating in '*Analysis of Raw, Potable and Waste Waters*'. These volumes, inevitably, took some years to prepare, so that they were often partially out of date before they appeared in print. The present series will be published as individual methods, thus allowing for the replacement or addition of methods as quickly as possible without need of waiting for the next edition. The rate of publication will also be related to the urgency of requirement for that particular method, tentative methods being issued when necessary. The aim is to provide as complete and up to date a collection of methods and reviews as is practicable, which will, as far as possible, take into account the analytical facilities available in different parts of the Kingdom, and the quality criteria of interest to those responsible for the various aspects of the water cycle. Because both needs and equipment vary widely, where necessary a selection of methods may be recommended for a single determinand. It will be the responsibility of the users – the senior analytical chemist, biologist, bacteriologist etc, to decide which of these methods to use for the determination in hand. Whilst attention of the user is drawn to any special known hazards which may occur with the use of any particular method, responsibility for proper supervision and the provision of safe working conditions must remain with the user.

The preparation of this series and its continuous revision is the responsibility of the Standing Committee of Analysts (to review Standard Methods for Quality Control of the Water Cycle). The Standing Committee of Analysts is one of the joint technical committees of the Department of the Environment and the National Water Council. It has nine Working Groups, each responsible for one section or aspect of water cycle quality analysis. They are as follows:

1.0 General principles of sampling and accuracy of results
2.0 Instrumentation and on-line analysis
3.0 Empirical and physical methods
4.0 Metals and metalloids
5.0 General non-metallic substances
6.0 Organic impurities
7.0 Biological methods
8.0 Sludge and other solids analysis
9.0 Radiochemical methods

The actual methods etc are produced by smaller panels of experts in the appropriate field, under the overall supervision of the appropriate working group and the main committee. The names of those associated with this method are listed inside the back cover.

Publication of new or revised methods will be notified to the technical press, whilst a list of Methods in Print is given in the current HMSO Sectional Publication List No 5, and the current status of publication and revision will be given in the biennial reports of the Standing Committee of Analysts.

TA DICK
Chairman

LR PITTWELL
Technical Secretary

20 July 1977

Chemical Oxygen Demand (Dichromate Value) of Polluted and Waste Waters (1977 Version)

The method consists of a common digestion procedure with either a titrimetric or spectrophotometric final determination. The spectrophotometric method is tentative.

Note: Throughout this method Chemical Oxygen Demand (COD) is expressed as oxygen consumed.

1 Performance Characteristics of the Method

(For further information on the determination and definition of performance characteristics see another publication in this series).

1.1 Titrimetric Method

1.1.1	Substances determined	Almost all types of organic compounds, and most inorganic reducing agents.
1.1.2	Types of sample	Sewages, trade wastes and other polluted waters.
1.1.3	Basis of the method	Oxidation in a standard, arbitrary manner with sulphuric acid and potassium dichromate; the residual dichromate is measured titrimetrically.
1.1.4	Range of application	Up to 400 mg/1 COD; the range can be extended by pre-dilution with water.
1.1.5	Calibration curve	Linear.
1.1.6	Standard deviation (a)	Sample / COD (mg/1) / Standard deviation (mg/1) Synthetic solution (b) / 64 / 1.7–6.6 Synthetic solution (b) / 400 / 1.4–6.2 Sewage effluent / 64 / 2.3–5.2 Trade effluent / 312 / 3.5–9.8
1.1.7	Limit of detection (c)	6 to 15 mg/l (9 degrees of freedom).
1.1.8	Sensitivity	1 ml of 0.025M ferrous ammonium sulphate is equivalent to 20 mg/l COD.
1.1.9	Bias	No evidence of bias using potassium hydrogen phthalate.
1.1.10	Interferences	Chloride interferes though for many applications the effect will be unimportant. See Section 3.5. Oxidizing agents diminish the COD values of samples.
1.1.11	Time required for analysis	Typical total analytical time for one to ten samples is about 3 hours.

(a) The range of estimates from 10 laboratories in the Severn-Trent Water Authority is given[1]; each estimate has approximately 4–9 degrees of freedom.

(b) A solution of potassium hydrogen phthalate in distilled water.

(c) The range of estimates from 8 laboratories in the Severn-Trent Water Authority is given[1].

1.2 Spectrophotometric Method (tentative)

1.2.1	Substances determined	Almost all types of organic compounds, and most inorganic reducing agents.
1.2.2	Types of sample	Sewages, trade waste and other polluted waters.
1.2.3	Basis of the method	Oxidation in a standard, arbitrary manner with sulphuric acid and potassium dichromate; the residual dichromate is measured spectrophotometrically.
1.2.4	Range of application	Up to 400 mg/l COD; the range can be extended by pre-dilution with water.
1.2.5	Calibration curve	Linear up to 400 mg/COD.
1.2.6	Standard deviation (a)	Sample / COD (mg/l) / Standard deviation (mg/l) Synthetic solution (b) / 100 / 3.2 Synthetic solution (b) / 400 / 3.7 (9 degrees of freedom).
1.2.7	Limit of detection (a)	16 mg/l (9 degrees of freedom).
1.2.8	Sensitivity	100 mg/l COD gives an absorbance of approximately 0.125 at 440 nm using a cell with a path length of 20 mm.
1.2.9	Bias	No evidence of bias using potassium hydrogen phthalate
1.2.10	Interferences	Chloride interferes though for many applications the effect will be unimportant. See Section 3.5. Oxidizing agents diminish the COD values of samples.
1.2.11	Time required for analysis	Typical total analytical time for one to ten samples is about 3 hours.

(a) Within-batch standard deviations from one laboratory in the Severn-Trent Water Authority are given[2]

(b) A solution of potassium hydrogen phthalate in distilled water.

2 Principle

2.1 Samples are oxidized in a standard, arbitrary manner by refluxing with sulphuric acid and potassium dichromate. The amount of dichromate reduced is expressed in the form of milligrams of oxygen consumed per litre of sample; this is the Chemical Oxygen Demand or COD.

2.2 The test is empirical and is applicable to almost any aqueous sample. It is an index of pollution not subject to inhibition by toxic components which would affect tests dependent upon biochemical oxidation.

2.3 An aliquot of the sample is mixed with the required amount of mercuric sulphate to reduce chloride interference.

2.4 Potassium dichromate, concentrated sulphuric acid and silver sulphate (to catalyse the oxidation of alcohols and low molecular weight acids) are then added. The mixture is refluxed for two hours and the residual dichromate is determined either by titration with standardized ferrous ammonium sulphate or by spectrophotometry.

2.5 Blank determinations must be undertaken with every batch of samples.

2.6 Reactions

2.6.1 Oxidation reaction

$$Cr_2O_7^{2-} + 8H^+ \rightarrow 2Cr^{3+} + 4H_2O + 3O$$

2.6.2 The ferrous iron/dichromate titration

$$6\ Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$

2.6.3 Chloride interference reaction

$$Cr_2O_7^{2-} + 6Cl^- + 14H^+ \rightarrow 2Cr^{3+} + 3Cl_2 + 7H_2O$$

3 Field of Application and Interferences

3.1 The test as described is suitable for undiluted samples having COD values up to 400 mg/l. Samples with higher COD values require pre-dilution.

3.2 The ammonium ion is not oxidized in this test. Organic nitrogen is normally released as ammonium ion.

3.3 Some compounds possessing a benzene ring structure *may* show only partial and non-reproducible oxidation. Certain heterocyclic compounds, for example pyridine, are strongly resistant to oxidation.

3.4 Inorganic reducing agents such as nitrites, sulphites, ferrous iron etc will contribute to the COD. Oxidizing agents can give negative results in the titrimetric procedure and false (low) results in both the titrimetric and spectrophotometric procedures.

3.5 Chloride causes positive interference the magnitude of which depends on the concentration of chloride and the COD value of the sample. In tests of this effect, using potassium hydrogen phthalate, varying degrees of interference have been observed in four or more different laboratories [3]. The minimum and maximum effects are shown in the table below. The results were obtained with the amount of mercuric sulphate specified in Section 8 and the ratio of mercuric sulphate: chloride ion is 40:1, 30:1, 20:1 and 10:1 respectively reading from left to right.

Increment due to Chloride

COD mg/l	Deviation in mg/l COD			
	5mg Cl^- in 10ml aliquot	10mg Cl^- in 10ml aliquot	15mg Cl^- in 10ml aliquot	20mg Cl^- in 10ml aliquot
0*	10	23	41	59
100	1–4	2–8	2–16	7–34
200	2–10	1–28	1–30	5–50
300	4–12	6–10	8–14	8–28
400	4	4	4–20	12–26

* Measurements made by only one laboratory

It can be seen that the effect will often be unimportant, but each analyst must judge this for his own applications. For a fuller discussion see Section 9.

4 Hazards

Poisonous gases may be emitted from the sample on acidifying. This operation should be conducted in a fume cupboard. Hydrogen sulphide gas is highly toxic at low concentrations and also paralyses the sense of smell.

Addition of sulphuric acid (d_{20} 1.84) to water must always be carried out with care and gentle swirling of the contents of the flask.

The method involves the handling of boiling and strong solutions of sulphuric acid and dichromate. Protective clothing, gloves and full face protection are essential. In the event of spillage immediate copious washing with clean water is the simplest and most effective remedy.

Care is required when preparing and handling solutions containing silver sulphate and mercuric sulphate as these are toxic. In the event of either of these chemicals being swallowed give water to dilute and milk as a soothing and buffering agent. Do not delay seeking medical advice.

In the event of an accident, expert medical advice should be obtained as quickly as possible.

5 Reagents

5.1 Except where otherwise stated, analytical reagent grade chemicals are to be used. Reagents should be stored in glass bottles. All reagents, with the exception of ferrous ammonium sulphate, are stable for at least one month.

Reagents Common to both Methods

5.2 Water

Either distilled or de-ionized water can be used provided the blank value remains acceptable (see steps 8.2.2, 8.2.3 and note i).

5.3 Sulphuric acid (d_{20} 1.84)

Unacceptable blank values can be caused by minute amounts of contaminants in the reagents. The major cause is the sulphuric acid used—analytical reagent grade is not necessarily better than ordinary acid, and when a satisfactory batch has been found it should be reserved for COD use only.

5.4 1% m/V Silver sulphate in sulphuric acid

Dissolve 10.0±0.1 g of silver sulphate in 1 litre of sulphuric acid (d_{20} 1.84). To obtain a satisfactory solution the initial mixture should be shaken, allowed to stand overnight and then shaken again in order to dissolve all the silver sulphate. Store in a dark brown glass bottle out of direct sunlight.

5.5 20% m/V Mercuric sulphate solution

Prepare 10% V/V sulphuric acid by adding cautiously, with swirling, 50±2 ml of sulphuric acid (d_{20} 1.84) to 450±5 ml of water. Dissolve 100±1 g of laboratory grade mercuric sulphate in 500±5 ml of 10% V/V sulphuric acid. The micro analytical reagent grade of mercuric sulphate is advised when measuring very low COD values.

5.6 Standard reference solution of potassium dichromate, 0.020833M (M/48)

Dissolve 6.129 g of potassium dichromate, previously dried for one hour at 140–150°C, in water and dilute with water to 1 litre in a calibrated flask.

For the Titrimetric Determination

5.7 1:10 phenanthroline ferrous complex ('Ferroin')

This reagent is commercially available in either plastic or glass bottles; both are acceptable. If necessary a suitable indicator can be prepared as follows. Dissolve 3.5±0.1 g

of ferrous sulphate heptahydrate in 500±1 ml of water. Add 7.4±0.1 g of 1:10 phenanthroline monohydrate and shake until dissolved.

5.8 Standard solution of ferrous ammonium sulphate 0.025M

Dissolve 9.8±0.1 g of ferrous ammonium sulphate hexahydrate in about 100 ml of water, cautiously add 20.0±0.5 ml of sulphuric acid (d_{20} 1.84), oool and dilute with water to 1 litre in a calibrated flask.

Standardize the solution, each day before use, against 0.020833M potassium dichromate solution as follows: take 5.00±0.05 ml of 0.020833M potassium dichromate solution and dilute with water to approximately 60 ml; carefully add 15.0±0.5 ml of sulphuric acid (d_{20} 1.84) and cool; add not more than two drops of 'Ferroin' indicator and titrate with the ferrous ammonium sulphate solution. For a description of the end point see step 8.2.1, note g.

The molarity M of the ferrous ammonium sulphate solution is given by

$$M=\frac{0.020833\times 30}{V} \text{ or more exactly } M=\frac{5}{8V}$$

where V is the volume (in ml) of ferrous ammonium sulphate solution titrated.

For the Spectrophotometric Determination

5.9 Standard reference solution of potassium hydrogen phthalate, COD of 400 mg/l

Dissolve 0.340±0.001 g of potassium hydrogen phthalate, previously dried at 120°C for 2 hours, in water and dilute with water to 1 litre in a calibrated flask. The standard should be stored, without freezing, in a refrigerator and renewed monthly.

6 Apparatus

High blank values may be the result of minute amounts of contaminants in the oxidation flask, the reflux condenser or on the anti-bumping aid. Apparatus should be cleaned by repeatedly boiling fresh dichromate/sulphuric acid/silver sulphate mixture in the apparatus until low and consistent blank values are obtained. Apparatus should be reserved solely for COD determinations.

6.1 Glassware should have standard ground glass joints where appropriate; grease must not be used.

Apparatus Common to both Methods

6.2 150-ml boiling flask and a distillation tray capable of holding all the contents of the boiling flask in the event of breakage during the digestion stage.

6.3 Automatic dispensing pipette or burette for the 1% m/V silver sulphate in sulphuric acid. (A tilt type dispenser is not suitable).

6.4 Water-cooled condenser, at least 150 mm long, capable of being easily rinsed as required in step 8.1.5.

6.5 Protective cap for the reflux condenser to keep dust out of the apparatus when not in use. A small beaker is satisfactory.

6.6 Predigested anti-bumping granules or an aid, as shown in figure 1, constructed of glass and PTFE*. The rod should be of sufficient length to keep the aid upright in the boiling flask. All anti-bumping granules and aids should be precleaned by digestion for 2 hours as described in Section 6.

* PTFE (Polytetrafluoethylene)

6.7 Uniform heating is essential to maintain gentle boiling. For safety reasons this is best achieved by using a heated sand tray. Point sources of heating are considered unsatisfactory. No part of the flask should be heated to a temperature in excess of the liquid boiling therein since decomposition of dichromate commences at a few degrees Celsius above the reflux temperature and will lead to high results.

For the Titrimetric Determination

6.8 25-ml burette, grade B or better.

For the Spectrophotometric Determination

6.9 100-ml calibrated flask.

6.10 A spectrophotometer of prism or grating type or using narrow band pass optical filters.

7 Sampling and Sample Preservation

7.1 THE SAFETY WARNING AT THE BEGINNING OF SECTION 4, RELATING TO ACIDIFICATION OF SAMPLES CONTAINING CYANIDE OR SULPHIDE, SHOULD BE OBSERVED WHEN PRESERVING SAMPLES

7.2 The analysis must be carried out as soon as possible after sampling. Samples should be stored in glass bottles. Whilst complete and unequivocal preservation of samples is a practical impossibility, changes can be retarded by refrigerating the sample at 2–5°C or by reducing the pH to 1–2 with sulphuric acid. The time for which preservation is effective must be established for the type of sample involved, and may vary from a few hours to several days. A note should be made on the sample label of any preservative added.

Samples containing large amounts of solids should be homogenised before an aliquot is taken for the subsequent analysis.

For soluble COD, samples should be filtered before preservation, taking precautions to avoid contamination from the filter paper or the atmosphere.

8 Procedure

8.0.1 READ SECTION 4 ON HAZARDS BEFORE STARTING THIS PROCEDURE

All operations should be carried out with care.

Dangers of spillage obviously arise if the sample contains carbonate, or any other substance which will emit a gas. Poisonous gases may be emitted if, for example cyanide or sulphide is present; hence addition of sulphuric acid to the samples should be carried out in a fume cupboard. Caution in the initial mixing of sulphuric acid with unknown samples must always be the rule.

8.0.2 Both the spectrophotometric and the titrimetric procedures measure the residual dichromate ion $Cr_2O_7^{2-}$; the spectrophotometric procedure is particularly suitable for the analysis of large numbers of samples and can easily be automated with suitable apparatus.

8.0.3 Determine the chloride content in the sample (see the appropriate publications in this series) and, if greater than 500 mg/l, see Section 9.

8.0.4 For a modified procedure for large numbers of samples see Section 10.

Step	Experimental Procedure	Notes
8.1	**Digestion**	
8.1.1	Insert the anti-bumping aid or granules into the boiling flask (note a).	(a) Once in position they need not be removed between determinations.
8.1.2	Measure 10.0±0.1 ml of sample into the flask (notes b and c).	(b) If necessary, the sample should be diluted accurately and a 10 ml aliquot taken for oxidation, which should consume dichromate equivalent to between 5 and 20 ml of 0.025M ferrous ammonium sulphate. (c) If the 10 ml taken for oxidation contains more than 5 mg of chloride ion, see Section 9.
8.1.3	Add 1.0±0.2 ml of 20% m/V mercuric sulphate solution and swirl to mix; add 5.00±0.03 ml of 0.020833M potassium dichromate. Using an automatic dispensing pipette or burette add 15.0±0.5 ml of 1% m/V silver sulphate in concentrated sulphuric acid (notes d and e).	(d) Run the acid down the side of the flask whilst gently swirling and cooling the flask under running cold water. This procedure minimizes loss of volatiles. (e) The amount of mercuric sulphate in this mixture will suppress, but not entirely eliminate, the effect of chloride ion. For example, 20 mg of chloride ion in the absence of organic matter will produce an apparent COD of about 60 mg/l (See Sections 3.5 and 9).
8.1.4	Fit the condenser and swirl the flask and its contents, then boil gently under reflux for 2 h±10 min (note f).	(f) Excessive reflux times may result in high blank values.
8.1.5	Remove the flask from the source of heat and allow to cool for approximately 10 min, then add 25±5 ml of water via the condenser in such a manner to rinse residual dichromate from the condenser. Disconnect the flask from the condenser and cool the flask to room temperature in running water. Determine the residual dichromate by either steps 8.2.1 to 8.2.4. or 8.3.1 to 8.3.7 inclusive.	
8.2	**Titrimetric Determination of Residual Dichromate**	
8.2.1	Add not more than two drops of 'Ferroin' indicator to the flask and titrate the residual dichromate with standardized ferrous ammonium sulphate (note g).	(g) After the first addition of ferrous iron solution the indicator is blue-green in colour and the end point occurs when the colour changes sharply through deep blue to pink. The blue colour may reappear a few minutes later but this phenomenon should be ignored.
	Blank determination	
8.2.2	Ideally the blank value should be the mean of at least three determinations, but if any value differs by more than ±0.5 ml from the mean value it must be rejected and a new mean recalculated from the acceptable blank values.	
8.2.3	The blank test is carried out as described in steps 8.1.1 to 8.2.1. inclusive, replacing the 10 ml of sample by the same amount of water (notes h and i).	(h) When more than 5 mg of chloride ion is found in 10 ml of test sample, see Section 9. (i) An acceptable blank test should require at least 23.5 ml of 0.025M ferrous ammonium sulphate, or its equivalent, in the titration.

Step	Experimental Procedure	Notes
	Calculation of results	
8.2.4	If it was necessary to pre-dilute the sample, the appropriate factor must be included in the calculation. $COD = 800\ M\ (V_B - V_S)$ mg/l Where V_B = average number of ml ferrous ammonium sulphate used in titrating the appropriate blank (step 8.2.3. or step 9.5). V_S = number of ml ferrous ammonium sulphate used in titrating the sample. M = molarity of standard ferrous ammonium sulphate solution, as determined in Section 5.8.	
8.3	**Spectrophotometric Determination of Residual Dichromate (tentative)**	
8.3.1	Set up the spectrophotometer according to the manufacturer's instructions. Adjust the zero of the instrument with water in the reference cell and re-check the zero after each sample or as often as experience indicates.	
8.3.2	Quantitatively transfer the solution from the oxidation flask to a 100-ml calibrated flask and dilute with water to volume and mix thoroughly. This solution is stable for at least 30 days (note j).	(j) If a rapidly settling, crystalline precipitate develops, allow it to settle before measuring the absorbance. If a turbidity appears, insufficient mercuric sulphate has been used. Start again with a fresh aliquot and use the procedure given in Section 9.
8.3.3	Measure the absorbance of the solution in a 20-mm cell at a wave-length of 440 nm. The COD value of the sample is read directly from a calibration graph prepared as in steps 8.3.4 to 8.3.6 below (note k).	(k) The absorbance measurement decreases in value with increase in the COD value. As a guide the absorbance of the blank is approximately 0.70 and of a 400 mg/l COD standard about 0.20.
	Calibration graph	
8.3.4	Dilute the standard reference solution of potassium hydrogen phthalate to give solutions having COD values of 100, 200 and 300 mg/l. Use water to give the 0 mg/l COD (notes l and m).	(l) When more than 5 mg of chloride ion is found in 10 ml of test sample, refer to Section 9. (m) Using the procedure specified the slope of the graph should remain reproducible for a particular spectrophotometric system. The position of the graph will, however, vary with any variation in the absorbance reading of the blank solution. Because of this possible variation in the blank value it is necessary to re-establish the calibration graph for each daily set of analyses. See steps 8.3.4 to 8.3.6.
8.3.5	Take 10 ml aliquots of solutions with COD values of 0, 100, 200, 300, 400 mg/l and carry out steps 8.1.1. to 8.1.5, 8.3.2 and 8.3.3.	
8.3.6	Plot the individual absorbance readings against the respective COD values in mg/l to give the required graph.	

Step	Experimental Procedure	Notes
	Calculation of results	
8.3.7	The COD value of the sample is read directly from the prepared calibration graph (step 8.3.6). If it is necessary to pre-dilute the sample, the appropriate factor must be included in the calculation.	

9 Chloride Interference

(Aliquots containing in excess of 5 mg of chloride per 10 ml)

It is recommended that, where possible, the chloride ion content of the sample aliquot taken for the test be limited to a maximum of 5 mg and in such cases the procedure given above is applicable. However, it may not always be possible to limit the chloride ion to this value because of the low organic content of the original sample and in these cases a special procedure can be used. This procedure is applicable to samples for which the aliquot taken for analysis contains more than 5 mg of chloride ion and employs additional mercuric sulphate in a ratio of 40 to 1 mercuric sulphate to chloride ion to suppress the effect of such high chloride concentrations. Even after using this additional amount of mercuric sulphate, there may still be an enhancement of the true COD value, the magnitude of which will depend on the ratio of chloride to COD and the rate of oxidation of the organic material. The actual interference by chloride will be difficult to estimate.

READ SECTION 4 ON HAZARDS BEFORE STARTING THIS PROCEDURE.

Step	Experimental Procedure	Notes
9.1	Determine the chloride concentration in the sample by a suitable procedure.	
9.2	Carry out steps 8.1.1 and 8.1.2.	
9.3	Add to the flask a weight of mercuric sulphate equal to forty times the weight of chloride ion in the sample aliquot. Swirl the flask vigorously for a minimum of one minute.	
9.4	Continue with step 8.1.3 onward beginning at the potassium dichromate addition.	
	Blank determinations	
9.5	Blank determinations are carried out as described in steps 8.2.2 and 8.2.3 replacing the 10 ml sample aliquot with water (note n).	(n) Ensure that the blank solution contains the same amount of mercuric sulphate as used for the sample.

10 Modified Procedure for Large Numbers of Samples

For laboratories dealing with a very large number of samples, the following pre-mixing procedure reduces the manipulative work per sample.

READ SECTION 4 ON HAZARDS BEFORE STARTING THIS PROCEDURE.

Step	Experimental Procedure	Notes
10.1	Measure 250±10 ml of water into a 2-litre flat bottomed borosilicate flask (note o).	(o) Goggles must be worn and the flask should be stood on a rubber mat in a sink partially filled with water during the operations which follow.
10.2	Add 1.53±0.01 g of potassium dichromate and 7.5±0.5 g of silver sulphate.	
10.3	Cautiously add, with frequent swirling, 750±25 ml of sulphuric acid (d_{20} 1.84) (note p).	(p) In order to dissolve the silver sulphate completely, the contents of the flask should be swirled well, allowed to stand overnight and then swirled again the following morning, or before use. The mixed reagent is stable for at least 3 months if stored in the dark, but rapidly deteriorates in daylight. Because of a volume reduction on pre-mixing, 18.5 ml of this solution is equivalent to the separate volumes of reagents described in step 8.1.3.
10.4	The mixture is used as follows.	
10.4.1	Add 10 ml of sample and the required amount of mercuric sulphate to the oxidation flask as described in steps 8.1.2 and 8.1.3.	
10.4.2	Measure 18.5±0.2 ml of oxidizing mixture into the flask using an automatic dispensing pipette or burette.	
10.4.3	Continue onward with step 8.1.4.	

11 Removal of Silver and Mercury from Spent Test Solutions

In order to avoid risks to the environment, eg sewage treatment works and watercourses and to recover some of the cost of expensive reagents, the following procedures are recommended.

11.1 Removal of silver

Place 40 ml of hydrochloric acid (d_{20} 1.18) in a Winchester bottle and add the spent test solutions to the acid. When the Winchester is full allow the silver chloride precipitate to settle overnight. Decant the supernatant liquid which contains mercury into a beaker.

11.2 Removal of mercury

NOTE:

The hydrogen sulphide evolved during this precipitation process is poisonous. All operations, including the decantation of the supernatant liquid should be carried out under a fume hood.

Add between 1 and 3 g of stick ferrous sulphide to the decanted liquid from the silver recovery step. Allow to stand at least 24 hours, occasionally swirling or stirring the solution to disperse the hydrogen sulphide, and finally allow the precipitated mercuric sulphide to settle. Decant the supernatant liquid.

11.3 SILVER CHLORIDE AND MERCURIC SULPHIDE ARE NOTIFIABLE WASTES AND MUST NOT BE DISPOSED TO LAND WITHOUT CONSENT.

Precious metal refiners may accept silver and possibly mercury for ultimate recovery. The supernatant liquid from step 11.2 contains a relatively high concentration of sulphide. The liquid should be oxidized or diluted 500 to 1 before disposal.

12 References

(1) Department of the Environment, file WS646/19, papers TP 64 and 79.

(2) Department of the Environment, file WS646/19, paper TP 69.

(3) Department of the Environment, file WS646/19, papers TP 71 to 75, and 78a.

Address for Correspondence

However thoroughly a method may be tested, there is always the possibility of a user discovering a hitherto unknown problem. Users with information on this method are requested to write to:

The Technical Secretary
The Standing Committee of Analysts
The Department of the Environment
2 Marsham Street
LONDON SW1P 3EB
England

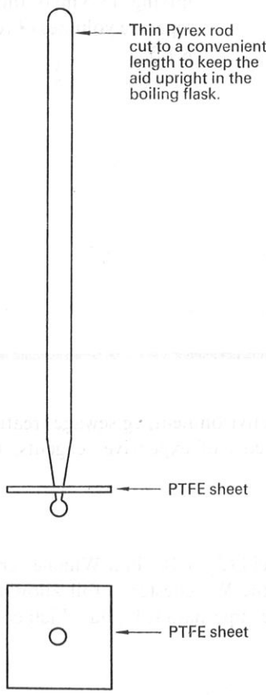

Figure 1 Anti-bumping aid for COD determinations

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Department of the Environment/National Water Council

Standing Committee of Analysts

1 At one time or another a considerable number of people have worked on the drafting and testing of this method, some co-opted only for a few meetings. Work is already in progress to ascertain whether improvement is possible, especially for saline waters. The following list is complete according to the minutes and committee papers relevant to the method as here published. Because members have at various times served in various capacities, dates of service have been tabulated.

2 Members of the committee responsible for this method:

	Main Committee	*Working Group*	*Special COD Panel 1977*
Mr JB Allcroft		occasional attendance	
Mr MA Allen		from November 1975	
Mr DE Bond	until January 1974		
Mr J Borland	after June 1975		
Dr JM Carter	after June 1975		
Mr RV Cheeseman		occasional attendance	
Dr GW Clayfield	from formation	from formation	member
Dr V Collins	from June 1975 until January 1977		
Dr RL Cooper	after June 1975	until November 1974	
Dr J Cope		until December 1975	
Dr BT Croll	after June 1975	until April 1975	
Mr TA Dick	after February 1975		member
Mr GE Eden	until June 1975		
Dr N Harkness	until June 1975		
Mr AE Hey		from formation	member
Mr E Hodges	after June 1975		
Mr GJ Holland	after June 1975		
Dr AJ Howard	from June 1975 until January 1977		
Mr WM Lewis	from formation	until January 1974	
Mr DJ Lloyd		after November 1975	
Mr PJ Long	after June 1975		
Mr GF Lowden		from formation	
Mr JC McCullins	from January 1976		
Mr D Mercer	until January 1974		
Mr P Morries	after June 1975		member
Mr D Myles	after June 1975	after November 1975	member
Mr AH Nield	after January 1976	after November 1975	
Dr JD Norris		from November 1974 until January 1976	
Dr HA Painter	after June 1975		
Mr JF Palframan		until September 1975	
Dr AT Palin	until June 1975		
Dr SJ Patterson	from formation		
Mr AS Pearce		after January 1976	member
Mr B Pettman		from September 1974 until June 1975	
Mr LR Pittwell	from December 1973	occasional attendance	member
Dr JE Portmann	after June 1975		
Mr LD Purdie	after June 1975		
Mr BD Ravenscroft	after June 1975	after November 1975	member
Mr TD Rees		until June 1975	
Mr LA Richards		after November 1975	
Prof JP Riley	after June 1975		
Mr R Sinar	from formation		
Mr A Thompson		until December 1975	
Dr KC Wheatstone		until December 1975	
Mr FJ Whitby		after November 1975	
Mr BT Whitham	after June 1975		
Mr AL Wilson	from formation		member
Dr R Wood	after June 1975		

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