Chemical Oxygen Demand (Dichromate Value) of Polluted and Waste Waters 1986 (Second Edition)

Methods for the Examination of Waters and Associated Materials

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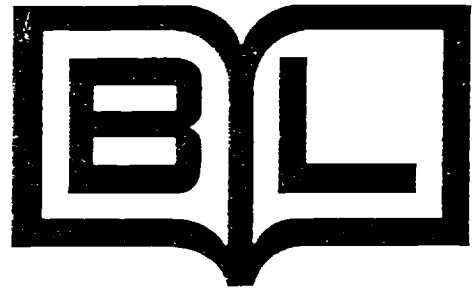

Chemical Oxygen Demand (Dichromate Value) of Polluted and Waste Waters 1986 (Second Edition)

(A reference method, some alternative routine control methods and notes on silver recovery. The 1977 flask digestion — titration method has also been included for information)

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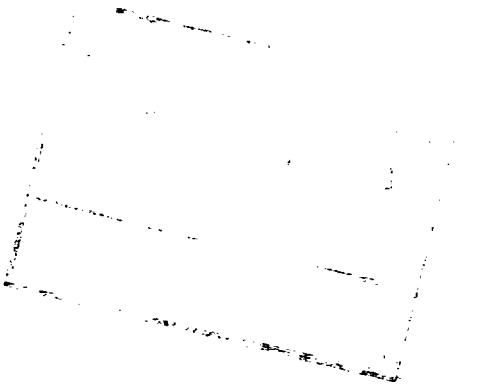
Contents



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Preface

The methods in this second edition, which have been evolved and tested by members of the DOE Standing Committee of Analysts, all give results comparable with those given in the 1977 booklet (4), but without the use of any mercury salts.

The methods given in the earlier booklet, which all used mercury, are now, in consequence, not recommended, even though they do give valid results (see text data in the Appendix). The flask-titrimetric version given in the 1977 booklet is appended for information purposes as it is the method with which the methods given in this booklet have, even if indirectly, been compared. Typical comparative test data are also included.

This booklet contains:

A. A reference large scale (10 ml sample) flask digestion procedure with 0.02083M (M/48) potassium dichromate solution.

B. Small scale open and closed tube (2.0 ml sample) routine control procedures using 0.02083M (M/48) potassium dichromate solution.

C. A small scale open tube (2.5 ml sample) routine control procedure using 0.03473M potassium dichromate solution.

A note on automation of the method
A note on mixed reagents
A note on application of the method for the analysis of solid samples
A note on waste disposal and silver recovery
Notes on the use of Block Digesters and Heating Mantles
Notes on Analytical Quality Control
An Appendix giving the method in the earlier booklet with which ultimately these methods were compared.

Because of the importance of this determination for industrial effluent charging purposes, and for the monitoring of water and effluent quality changes, an introduction and a sampling section precede the methods. These indicate ways in which seemingly insignificant changes can affect the result. When laboratories wish to agree on analyses for the same sample, it is essential that they agree on the details of the procedure beforehand, carry out co-operative interlaboratory comparison studies, and practise good analytical quality control thereafter. When a Referee Method is required the fullscale titrimetric Method A should be used without modification.

Throughout this booklet, Chemical Oxygen Demand (COD) is expressed as oxygen consumed.

About this Series

This booklet is part of a series intended to provide both recommended methods for the determination of water quality, and in addition, short reviews of the more important analytical techniques of interest to the water and sewage industries.

In the past, the Department of the Environment and its predecessors, in collaboration with various learned societies, have 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 series of booklets on single or related topics; 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 and notes 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 technical staff to decide which of these methods to use for the determination in hand. Whilst the 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 a committee of the Department of the Environment set up in 1972. Currently it has seven 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
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
9.0 Radiochemical methods

The actual methods and reviews 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.

Whilst an effort is made to prevent errors from occurring in the published text, a few errors have been found in booklets in this series. Correction notes and minor additions to published booklets not warranting a new booklet in this series will be issued periodically as the need arises. Should an error be found affecting the operation of a method, the true sense not being obvious, or an error in the printed text be discovered prior to sale, a separate correction note will be issued for inclusion in that booklet.

L R PITTWELL
Secretary

1 July 1986

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 properly equipped laboratories.

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 one's self, one's colleagues, those outside the laboratory or work place, or subsequently for maintenance or waste disposal workers. Where the Committee have 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. Reagents of adequate purity must be used, along with properly maintained apparatus and equipment of correct specifications. Specifications 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.

Lone working, whether in the laboratory or field, should be discouraged.

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 correct protective clothing and 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. Hazardous reagents and solutions should always be stored in plain sight and below face level. Attention should also be given to potential vapour and fire risks. If in doubt, it is safer to assume that the hazard may exist and take reasonable precautions, rather than to assume that no hazard exists until proved otherwise.

There are numerous handbooks on first aid and laboratory safety. Among such publications are: 'Guide to Safe Practice in Chemical Laboratories' and 'Hazards in the Chemical Laboratory' issued by the Royal Society of Chemistry, London; 'Safety in Biological Laboratories' (Editors Hartree and Booth), Biochemical Society Special Publication No 5, The Biochemical Society, London, which includes biological hazards; and 'The Prevention of Laboratory Acquired Infection', Public Health Laboratory Service Monograph 6, HMSO, London.

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 radio-chemical 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. If an ambulance is called or a hospital notified of an incoming patient give information on the type of injury, especially if poisoning is suspected, as the patient may be taken directly to a specialized hospital.

Introduction to this Booklet

The tests given in this booklet which are all empirical, are based on the oxidation of organic matter by dichromate in acid solution followed by measurement of the residual dichromate. The amount of oxidation which has taken place is then determined by difference. The oxidation potential of the dichromate ion varies proportionally to the logarithm of its concentration and is also dependent on the acidity; while the oxidizability of organic compounds varies widely. Inorganic reducing agents usually react with dichromate faster than organic matter, and so contribute to the oxygen demand. If present in large amounts, they can rapidly reduce the dichromate concentration and so affect the oxidizability of organic matter in this test. Similarly, while difficulty oxidizable organic compounds may react when alone and dilute, their oxidation may only be partial when mixed with readily oxidized organic substances which react more rapidly with dichromates. Chloride can cause complex interference effects leading to falsely high results. Chlorine may be formed, which although an oxidizing agent, can be lost by volatilization, as also can many organic compounds and their partially oxidized intermediates. In the presence of large amounts of chloride, the presence of ammonia and amines can also cause high results (3). The chlorine formed reacts with the nitrogen compounds to form chloramines which decompose, reforming chloride which is then reoxidized to chlorine. Reaction temperature, which is dependent on many variables, including reaction mixture composition, apparatus design, the degree of immersion of the digest in the heater and draughts, is important as it affects the reaction rates, oxidation potential and volatilization capability.

Many variants of the method exist (1, 2, 3, 4, 5, 6, 7, 10, 13, 16, 17, 18, 19, 21, 22, 24, 25, 26, 27) hence users must agree their procedure with each other if comparisons are to be made.

Procedure A below, using direct titrimetric determination of the residual dichromate, is the reference method. Silver ions are used as a catalyst, using extra silver and chromium III ions to repress the effect of chloride (24). The method with mercury II sulphate (7,4) which has heretofore been used as the chloride suppressant is now no longer recommended as comparable results can be obtained without the use of mercury, though extra care is necessary if low COD values are expected in the presence of much chloride.

For routine laboratory analysis, open and closed tube variants have been developed, although in order to simplify the preparation of tubes, the volumes and strengths of some solutions have been changed slightly. As closed tubes prevent loss of volatiles, for some samples, values obtained by this technique may be slightly higher than those with open tubes or flasks. Automatic potentiometric titrators have been used successfully for the dichromate titration.

The final determination of excess dichromate can readily be adapted to titrimetric autoanalyser techniques. The digestion stage is difficult to automate, but with equipment now available, reaction tubes can be loaded, transferred to a second stage for the much slower digestion and finally, at completion of the digestion time, transferred to a more conventional stage for the titrimetric measurement of excess dichromate. Even sealing and unsealing or the emplacement and removal of condensors can be carried out by robots if the number of samples is large enough to justify the high capital cost.

It is not possible to adapt this method for accurate colorimetric determination of the residual chromium due to the high levels of chromium III and to turbidity which cause problems with both the direct and diphenylcarbazide methods, resulting in loss of precision. Likewise, it is not possible to detect samples with either negligible or very high COD contents by eye.

The reproducibility and reliability of an analysis is dependent on the representativeness of the initial sample and its subsequent subdivision. Use of 10 ml samples is suggested if suspended solids are present. Effluents and sewages are notoriously inhomogeneous, but attempts to homogenize the sample may sometimes result in loss of volatiles or formation of films on the sampling equipment. Because of the sensitivity of this test to variations in procedure, users are reminded that, when agreement on results is essential, agreement on procedural details including sampling and interlaboratory tests are a prerequisite. It is suggested that samples which almost exhaust the dichromate be diluted and reanalysed.

Chemical Oxygen Demand tests are now required as part of the initial evaluation of some materials for compliance with certain EC directives. For water soluble substances, standard solutions can be examined by any of these procedures, but this is not possible for insoluble and sparingly soluble substances; a procedure for carrying out meaningful COD determinations on such materials has been included in Part D3.

Sampling, Sample Preservation and Storage

(with a note on Settled and Filtered COD)

It is as essential to agree sampling procedures as it is to agree the details of the analytical method.

S1. Sampling

S1.1 Samples should be as representative as possible.

S1.2 For very inhomogeneous material, the initial sample should either be large enough to be approximately representative or a composite so designed that a representative analysis can be made. (See also suggestion at C5.1 (note c).)

S1.3 If sampling for an investigation, consideration should be given to whether or not anomalous material should be included, sampled separately or excluded.

S1.4 More specific information on sampling and sampling techniques will be found in the following booklets already published in this series or in preparation:

i. The sampling and initial preparation of sewage and waterworks' sludges, soils, sediments and plants and wild life prior to analysis 1986.
ii. General Principles of Sampling and Accuracy of Results 1980.
iii. Sampling of oils, fats, waxes and tars in aqueous and solid systems 1983.
iv. Sampling of Rivers and Streams 1983.

Other specialized sampling booklets for ground waters, lakes and reservoirs, piped water effluents, precipitation and marine and estuarine waters are in preparation.

S1.5 Care should be taken to ensure that sampling equipment does not react with or contaminate the sample.

S1.6 Settled and Filtered COD determination.

For some effluents, COD measurements specifically exclude material which will subsequently settle out or be filtered off. In such cases, there must be agreement between the parties concerned on the procedure to be used and the action to be taken if problems occur.

For example, the supernatant liquid (taken below any floating solids), filtrate or centrifugate, with or without pH adjustments (see Ref. 11) may be used for the COD determination.

If there is difficulty with samples that do not settle, but which would settle on mixing with other materials, filtration, dilution or pH adjustment are usually considered. Agreement must be obtained and correction made for any volume changes.

S2. Sample Preservation and Storage

S2.1 THE ACIDIFICATION OF SAMPLES CONTAINING CYANIDE OR SULPHIDE SHOULD ALWAYS BE CARRIED OUT IN A FUME CUPBOARD.

S2.2 Failure to store samples correctly or analyse quickly may lead to either erroneously high or erroneously low results, depending on sample type. The analysis must be carried out as soon as possible after sampling. Samples should be stored in glass bottles. Changes can be retarded by refrigerating the sample at 2–5°C or often by reducing the pH to 1–2 with sulphuric acid. The time for which preservation is effective must be established for each type of sample, and may vary from a few hours to several days. Sample preservation procedures should also be checked before being used routinely or for important special samples. A note should be made on the sample label of any preservative added.

S2.3 In order to ensure that aliquots are representative of the whole, samples containing large amounts of solids should be homogenized before any portion is removed. Take care to prevent loss of volatiles either by cooling or by careful choice of the design of the equipment. If solid material which is not subject to secondary treatment is present, it should be separated from the sample (see S1.6 above). If a COD is needed on the solid, see Section D3.

S2.4 Oily samples, especially emulsions, have a tendency to leave a grease film on the sample bottle and sampling equipment. Careful temperature control and the possibility of conditioning the glassware by prerinsing may sometimes avoid significant losses. Free oil layers which are normally separated off prior to treatment should not be included in the sample. If a COD is needed on the oil, see Section D3.

S2.5 For dissolved COD, samples should be filtered before preservation, taking precautions to avoid contamination from the filter paper or the atmosphere. Glass fibre papers or frits without plastic reinforcement should be used. If volatiles are expected, suction should not be used. If necessary, the fitration rate should be increased by inert gas pressure on the unfiltered sample. A safety shield must be used. Presettling may be useful; but only if microbial action is not taking place.

S2.6 Samples for tube scale digestion. Due to the smaller sample size the ability to take a representative aliquot of a non-homogenous sample is reduced. Homogenization may be used to pretreat the sample provided it is shown not to cause an unacceptable bias; prolonged homogenization has generally been shown to reduce the value of the COD obtained. (It has been found that an homogenizer fitted with a 20 mm dispersing shaft operating at about 8000 rpm gives a satisfactory dispersion of solids in 10 seconds. The period of homogenization should not exceed 20 seconds). Dead air space above the sample should be kept as small as possible.

Hazards

H1 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.

H2 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.

H3 The method involves the handling of boiling, 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. Absorbants are also available which facilitate removal of the bulk of the spill. Inhalation of dichromate dust can cause ulcers in the nose, hence inhalation and ingestion should be avoided.

H4 In the sealed tube method, the tubes used will be under pressure during and immediately after the heating stage. Care must be exercised in handling, sealing and unsealing the tubes which should always be pointed away from the operator and everyone else in the room. The closure, heating, removal from the heating block and subsequent opening of sealed tubes after cooling should be carried out behind a protective screen in a well ventilated hood. Care should be taken in opening the tube so that any built up pressure is released gently in a controlled manner. 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.

Do not put sealed tubes containing only water, without added reagents, in the heating block. Pressures of up to 10 atmospheres can be generated. The contents will boil explosively if the tube is opened or bursts, and the steam will be superheated.

H5 Care is required when preparing and handling strong solutions containing either silver salts or dichromates as these are toxic. In the event of these chemicals being swallowed give water to dilute and milk as a soothing and buffering agent. Seek medical advice at once. When calling an ambulance or notifying a hospital of an incoming case, mention that a poison is involved, giving details. Such patients are usually taken immediately to hospitals with special facilities.

H6 In the event of an accident, expert medical advice should be obtained as quickly as possible.

Reagents

Not all solutions are needed for every method. Check which are required prior to preparation. See also Section D2.

R1 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. Proprietary mixtures are available for many of these methods, see Section D2.

R1.1 Acceptability of Blank Water and Reagents. Unacceptable blanks are usually caused by:

oxygen demand in the water;
oxygen demand in the sulphuric acid;
dirty apparatus (traces of detergent, lint and grease).

See steps A5.2.2, A5.2.3 and note (i), B4, B5.2.2 notes (e) and (g). See Section R2.

Reagents Common to most Methods

R2 Water

All blank and reagent water must have a conductivity of less than 2 microSiemens per centimetre, a Total Organic Carbon content of less than 1 mg/l C and be free from reducing agents.

R2.1 Preparation of COD-free water

Glassware used for the preparation and storage of COD-free water must be cleaned with chromic acid (see Hazards Section H3) and materials used should be of analytical reagent grade.

Reflux a solution of 20 ± 1 g sodium hydroxide and 25 ± 1 g potassium permanganate in 2 litre $\pm$ 20 ml of distilled or de-ionized water for 30 ± 10 minutes under a soda-lime trap. Distil over 1.5 litre $\pm$ 50 ml water during 1 hour in a closed system, again under a soda-lime trap. To the distillate add 400 ± 20 ml sulphuric acid (d_{20}1.84) and 25 ± 1 g potassium dichromate, dissolve and reflux under a soda-lime trap for 30 minutes. Arrange the apparatus for distillation and steam out for 10 ± 2 minutes. Fit the soda-lime trap and collect 200 ± 20 ml distillate. Discard the first distillate and then collect 1 litre $\pm$ 50 ml product water over 1 hour $\pm$ 10 minutes. Store the product water under a soda-lime trap in a glass aspirator.

R3 Sulphuric acid (d_{20} 1.84)

R3.1 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. When a satisfactory batch has been found it should be reserved for COD use only.

R4 Standard reference solution of potassium dichromate, 0.02083M (M/48)

Dissolve 6.129 ± 0.001 g of potassium dichromate, previously dried for one hour at 140–150°C in water, quantitatively transfer and dilute with water to 1 litre in a calibrated flask.

R 1:10 phenanthroline ferrous complex ('Ferroin') (see also sections B6.5, 6.5 and D1)

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.

R6 Standard solutions of ferrous ammonium sulphate

R6.0.1 Before making up these reagents it is advised that the following assay (R6.1) of the solid ferrous ammonium sulphate reagent is carried out. It is then not necessary to standardize the working solution if used the same day; but solutions kept for reuse must be restandardized before use, see section R6.3. If the solid ferrous ammonium sulphate is not assayed, then the prepared solution must be standardized (R6.3) before use. (Note, experience has shown that this reagent is more resistant to oxidation in the solid state than ferrous sulphate heptahydrate.)

R6.0.2 The indicator solution R5 transfers a minute amount of ferrous ion to the titration flask, but the effect is minimal and compensated for by the end point colour itself. Ideally titrations should be made to the same colour and point as the equivalent amount of indicator diluted to the same volume as the reacted sample, but other factors such as digested sample colour other than dichromate may cause problems.

R6.1 Assay of the ferrous ammonium sulphate hexahydrate reagent

Transfer 4–6 g of accurately weighed solid reagent (M grams) into a 100 ml calibrated flask, add 90 ± 5 ml water, 2.0 ± 0.1 ml sulphuric acid (R.3), mix and swirl to dissolve the solid, dilute to the mark and mix well. Add 2 drops of indicator solution (R5) to a 350 ml conical flask, add 20.00 ± 0.03 ml of the standard reference solution of potassium dichromate (R.4) and titrate with the prepared ferrous ammonium sulphate solution using a 25 ml burette. Record the volume used, T ml.

Then P, the percentage of ferrous ammonium sulphate hexahydrate in the solid reagent is given by

$$P = \frac{9800}{T \times M}$$

The solid reagent is reasonably stable if stored in a well-closed bottle in a cool, dark place. It should be assayed from time to time (e.g. once a month) and it is strongly recommended that the bottle and the flask used are reserved solely for COD determinations. If there is any doubt, restandardize.

R6.2 Standard ferrous ammonium sulphate solution (0.025M)

Weight out $\frac{980}{P} \pm 0.001$ g of the ferrous ammonium sulphate, assayed in (R6.1) and quantitatively transfer to a 1 litre calibrated flask, add 100 ± 0.5 ml of water and 20 ± 0.5 ml sulphuric acid (R3) swirl to mix and dissolve the solid, cool and dilute to mark with water, stopper and mix again. This solution is not very stable and should be prepared freshly each day, or restandardized (see R6.3).

R6.3 Restandardization of ferrous ammonium sulphate solutions

Standardize solutions, each day before use, against 0.02083M potassium dichromate solution as follows: take 5.00 ± 0.05 ml of 0.02083M 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 (R6.2). For a description of the end point see step A5.2.1, note (g) and R6.0.2. Use of a narrow bore burette calibrated in steps of 0.05 or preferably 0.01 ml is recommended.

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

$$M = \frac{0.02083}{V} \times 30 \text{ (or more exactly } M = \frac{5}{8V}\text{)}$$

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

R7 Premixed reagent. Measure 250 ± 10 ml of water into a 2 litre flat-bottomed borosilicate flask. 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. Add 1.53 ± 0.01 g of potassium dichromate and 7.5 ± 0.5 g of silver sulphate to the water in the flask.

Cautiously add, with frequent swirling, 750 ± 25 ml of sulphuric acid (d_{20} 1.84). The contents of the flask should be well swirled, in order to dissolve the silver sulphate completely. Allow the mixture to stand overnight in the dark and then swirl again the following morning, or before use. This mixed reagent is stable for at least 3 months if stored in a stoppered bottle 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 A5.1.3. Use as detailed in Section 7. This reagent is available commercially. See also Section D2 and A7.2.

R8 250g/l Chromium III potassium sulphate ($KCr(SO_4)_2\ 12H_2O$)

Dissolve 25 ± 0.1 g of chromium potassium sulphate dodeca hydrate (potassium chrome alum) in 100 ± 1 ml of *hot* (over 50°C) distilled water. This solution is saturated at 30°C. Stored in a stoppered glass bottle with a PTFE sleeve or stopper, this solution should keep indefinitely.

Warm to 50°C and stir before use, to redissolve any solids.

R9 1200 g/l Silver nitrate solution

Dissolve 120 ± 1 g of silver nitrate (GPR is acceptable) in about 80 ml of distilled water by warming in a beaker. Using a previously placed mark on the beaker, make up to 100 ml by addition of water; cool and make up to 100 ± 5 ml with water. Do not cool below about 10°C; this solution is saturated at 0°C. Stored in the dark in a stoppered glass bottle this solution should keep indefinitely.

R10 50g/l Silver sulphate in sulphuric acid

Dissolve 50.0 ± 0.1 g of silver sulphate in a 1 litre ± 10 ml of sulphuric acid (d_{20} 1.84) (R3). To obtain a satisfactory solution the initial mixture should be swirled, allowed to stand overnight and then swirled again until all the silver sulphate has dissolved. Stored in the dark in a stoppered glass bottle, this solution should keep indefinitely.

R11 10 g/l Silver sulphate in sulphuric acid

Prepare as R10 but use 10.0 ± 0.1 g of silver sulphate. Store as R10.

R12 500 g/l Silver nitrate solution

Prepare as in R9 but use 50 ± 0.5 g of silver nitrate. Store as R9.

R13 1000 g/l Silver nitrate

Prepare as in R9 but use 100 ± 0.5 g of silver nitrate. Store as R9.

R14 0.03473M Potassium dichromate digest solution

Dissolve 10.216 ± 0.001 g of potassium dichromate, previously dried for one hour at 140–150°C, in 500 ± 1 ml of water; add with external cooling and stirring 167 ± 1 ml of concentrated sulphuric acid (R3), cool and make up to 1 litre in a graduated flask with water. Mix thoroughly.

This mixed reagent is stable for at least 3 months if stored in a stoppered bottle in the dark.

R15 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 graduated flask. The standard should be stored, without freezing, in a refrigerator and renewed monthly.

R16 Standard reference solution of potassium hydrogen phthalate, COD of 800 mg/l

Procedure as in R15 but use 0.680 ± 0.001 g of potassium hydrogen phthalate.

A. Large-Scale (10ml sample) Flask Digestion Procedure with titrimetric determination of residual dichromate

The method consists of a digestion procedure with a titrimetric final determination of residual dichromate.

Silver should be recovered from the final solutions and residues and not thrown away. See Section W1, given after the Appendix at the end of this book.

A1. Performance Characteristics

(For further information on the determination and definition of performance characteristics see Ref. 15.)

A1.1	Substances determined	Almost all types of organic compounds, and most inorganic reducing agents.
A1.2	Types of sample	Sewages, trade wastes and other polluted waters.
A1.3	Basis of the method	Oxidation in a standard, arbitrary manner with sulphuric acid and potassium dichromate; the residual dichromate is measured titrimetrically.
A1.4	Range of application	Up to 400 mg/l COD; the range can be extended by pre-dilution of the sample with water.
A1.5	Standard deviation	See Tables 1 and 2
A1.6	Limit of detection	mg/l COD — degrees of freedom 4.0 — 9 4.4 — 4 7.8 — 4
A1.7	Sensitivity	1 ml of 0.025M ferrous ammonium sulphate corresponds to 20 mg/l COD.
A1.8	Bias	Although some laboratories on certain types of sample do get a slight positive bias, the general concensus of tests indicates a slight negative (−1 to −2%) bias using potassium hydrogen phthalate; this bias is dependent on laboratory. See data under A1.5 above.
A1.9	Interferences	Chloride interferes though for many applications the effect will be unimportant. See Section A3.5. Oxidizing agents diminish the COD values of samples. Ammonia can cause high values if the chloride is unsuppressed.
A1.10	Time required for analysis	Typical total analytical time for one to ten samples is about 3 hours.
A1.11	comparison with the 1977 method	See Table 15.

Table 1. Flask digestion procedure (Method A)

Standard deviation and bias on standard potassium hydrogen phthalate solutions

COD	Standard deviation (within batch)		Bias of the mean		No. of Laboratories	Batch Size
mg/l	Range mg/l	Mean for test mg/l	Range mg/l	Mean bias* mg/l		
0	0.05 to 3.3	0.88	−1.6 to 1.6	+0.9	5	5–10
100	0 to 3.4	1.46	−13.4 to 4.8	−2.16	6	5–10
200	1.40 to 3.29	2.40	−12.2 to 0.6	−3.88	6	5–10
300	1.37 to 5.0	3.0	−14.6 to 5.0	−9.6	6	4–10
400	0 to 7.2	3.14	−23.4 to 0.6	−8.5	7	2–10

*The average mean bias is approximately −2%.

Table 2. Flask digestion procedure (Method A)

Relative standard deviations on real samples

Sample type	Mean COD mg/l	Relative standard deviation %	Degrees of freedom
Crude sewage	47.6	3.6	4
	48	0	4
	205.8	0.68	4
	268.7	2.90	4
	346	1.68	4
	388.1	1.86	4
	480	3.06	4
	611	1.52	4
	617	2.20	4
	656	0.14	4
	679	0.97	4
Industrial effluents	9.8	9.2	4
	71.5	1.40	4
	74.4	2.96	4
	95.4	9.0	4
	146	1.37	4
	186.8	1.39	4
	216	1.11	4
	310.7	0.48	4
	420.4	2.47	4
	567	2.11	4
	1017.6	7.13	4
	1041	1.24	4
	2828	2.74	4
	2840	0.50	4
Sewage works effluents	36.7	8.17	4
	39.0	4.62	4
	41.9	4.77	4
	47.6	3.57	4
	50	1.80	4
	55.3	1.45	4
	121.4	1.40	4

A2. Principle

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.

Samples are oxidized in a standard, arbitrary manner by refluxing with sulphuric acid and potassium dichromate with a silver salt to catalyse the oxidation of alcohols and low molecular weight acids. Chromium III is added as potassium chromium sulphate dodecahydrate, which along with excess silver salt suppresses chloride interference and with it the effect due to ammonia. The mixture is refluxed for two hours and the residual dichromate is determined by titration with standardized ferrous ammonium sulphate solution. 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.

Blank determinations must be undertaken with every batch of samples.

A2.1 Reactions

A2.1.1 Oxidation reaction

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

A2.1.2 The ferrous iron/dichromate titration

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

A2.1.3 Chloride interference reactions

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

A2.1.4 Chloride interference is suppressed by precipitation with silver and complexation with chromium III:

$$Cr^{3+} + 6Cl^- \rightarrow CrCl^{3-}_6$$

$$Ag^+ + Cl^- \rightarrow AgCl$$

A3. Field of Application and Interferences

A3.1 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.

A3.2 The ammonium ion is not oxidized in this test unless chloride is present in sufficient amount to cause interference. Some ammonium ion is then oxidized. Organic nitrogen is normally released as ammonium ion.

Table 3. Flask digestion procedure (Method A)

Chloride interference effects with spiked standards and real samples

Sample type	Actual COD mg/l	Chloride mg/l	Mean deviation due to chloride mg/l COD	Degrees of freedom
Phthalate standards	0	500	4.68	4
	100	500	6.18	4
	200	500	−0.53	4
	300	500	−0.62	4
	400	500	0.46	4
	0	1,000	13.48	6
	100	1,000	5.68	4
	200	1,000	−0.76	4
	300	1,000	5.54	4
	400	1,000	0.63	6
	0	2,000	11.49	6
	100	2,000	6.4	4
	200	2,000	1.6	4
	300	2,000	4.7	4
	400	2,000	1.57	5
	0	5,000	42.53	6
	100	5,000	14.54	4
	200	5,000	8.76	4
	300	5,000	12.32	4
	400	5,000	11.91	6
	0	10,000	94.1	8
	100	10,000	62.6	5
	200	10,000	34.7	5
	300	10,000	23.8	5
	400	10,000	24.7	6
Industrial effluent	186.8*	3,500	3.2	4
	567*	3,480	10	4
Phthalate standard + 100 mg/l NH_3	0	5,000	45.4	2

*These samples initially had negligible chloride, were analysed, spiked with chloride and reanalysed.

A3.3 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, 7, 18, 21, 25) (see also Table 15).

A3.4 Inorganic reducing agents such as nitrites, sulphites, ferrous salts etc. will contribute to the COD. Oxidizing agents can give false negative and low results.

A3.5 If not suppressed, chloride would cause positive interference the magnitude of which would depend on the concentration of chloride and the COD value of the sample. In tests of this effect, using potassium hydrogen phthalate, the interference reduces as the COD strength increases. This is due to the reduction in the amount of residual dichromate in the refluxing mixture. Typical results are shown in table 3. The results were obtained with the amount of chromium potassium sulphate specified in Sections A5 and A6.

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 A6.

A3.6 Sample instability can cause low results see Section 2.2.

A4. Apparatus

4.1 High blank values may result from minute amounts of contaminant in the oxidation flask, the reflux condenser or on the anti-bumping aid. Apparatus should be cleaned by repeatedly boiling with fresh dichromate/sulphuric acid/silver sulphate mixture R7. in the apparatus until low and constant blank values are obtained. Apparatus should be reserved solely for COD determinations.

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

Volumetric glassware should be grade B or better.

If rinsed with water between use, digestion apparatus must be drained and dried at 105°C. Use of wet apparatus causes loss of precision.

Digestion Apparatus

A4.2 150 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.

A4.3 Automatic dispensing pipette or burette for the 1% m/V silver sulphate in sulphuric acid. (A tilt type dispenser is not suitable).

A4.4 Water-cooled condenser, at least 150 mm long, capable of being easily rinsed as required in step A5.1.5.

A4.5 Protective cap for the reflux condenser to keep dust out of the apparatus when not in use. A small beaker is satisfactory.

A4.6 Predigested anti-bumping granules All anti-bumping granules and aids should be precleaned by digestion for 2 hours as described in Section A5.

A4.7 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.

Titration

A4.8 25 ml burette

A5. Analytical Procedure

A5.0.1. READ THE SECTION 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.

A5.0.2 Some laboratories use automatic potentiometric titrators for the determination of the dichromate residual. As the actual end point potential has been found to vary with trade effluent type, the instruments are programmed to indicate the point of inflection of the titration curve using the second differential of the plot. See Section D1.

A5.0.3 Determine the chloride content in the sample (see the appropriate publications in this series (8)) and, if greater than 2 g/l, see Section A6.

A5.0.4 For a modified procedure for large numbers of samples, see Section A7.

A5.0.5 Experience has shown that departure from the concentrations, temperatures and other details specified in both the digestion and titration stages of this procedure can lead to inaccurate results. The tolerances given and notes (b) and (g) must be adhered to.

Step	Procedure	Notes
A5.1	**Digestion**	
A5.1.1	Insert the anti-bumping aid or granules into the boiling flask (note (a)). Then add 0.6 ± 0.02 ml of 1000 g/l silver nitrate solution (R13).	(a) Once in position they need not be removed between determinations.
A5.1.2	Measure 10.0 ± 0.1 ml of sample into the flask (notes (b) and (c)). Swirl to mix and stand for not less than 2 minutes.	(b) If the chemical oxygen demand exceeds 400 mg/l oxygen, the sample should be quantitatively diluted by a suitable factor and a 10 ml aliquot of the diluted sample taken for oxidation. This diluted sample should consume dichromate equivalent to between 5 and 20 ml of 0.025M ferrous ammonium sulphate (R6). This dilution factor must be taken into account when making the final calculation.
		Expected COD mg/l — **Dilution** 0–400 — none 200–800 — 1 vol made up to 2 vols 500–2 000 — 1 vol made up to 5 vols 1 000–4 000 — 1 vol made up to 10 vols 2 000–8 000 — 1 vol made up to 20 vols 5 000–20 000 — 1 vol made up to 50 vols 10 000–40 000 — 1 vol made up to 100 vols 20 000–80 000 — 1 vol made up to 200 vols
		(c) If the sample (after any necessary dilution) contains more than 2 g/l of chloride ion, see Section A6.
A5.1.3	Add 0.40 ± 0.05 ml of chromium III potassium sulphate solution (R8) and swirl to mix; add 5.00 ± 0.03 ml of 0.02083M potassium dichromate (R4). Using an automatic dispensing pipette or burette add 15.0 ± 0.5 ml of 1% m/v silver sulphate in sulphuric acid (R11) (note (d)).	(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.
A5.1.4	Fit the condenser and swirl the flask and its contents, then boil gently under reflux for $2\,h \pm 10$ min (note (e)).	(e) Excessive reflux times will result in high blank values.
A5.1.5	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	

Step	Procedure	Notes
	a manner as to rinse the condenser. Disconnect the flask from the condenser and cool the flask to below 20°C in running water. Proceed to section 5.2. (See note (g)).	
A5.2	**Determination of Residual Dichromate** (see also A5.0.2 and D1)	
A5.2.1	Add not more than two drops of 'Ferroin' indicator (R5) to the flask and titrate the residual dichromate with standardized 0.025M ferrous ammonium sulphate (R6) (notes (f) and (g)).	(f) 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. This is especially common with samples high in chloride.
A5.2.2	**Blank determination** The blank value should be the mean of at least two, preferably more, 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, additional determinations being made if necessary.	(g) The end point fades unless digests are titrated at between 15 and 20°C.
A5.2.3	The blank value is determined as described in steps 5.1.1 to 5.2.1 inclusive, replacing the 10 ml of sample by the same amount of water (R2) (notes (c) and (h)).	(h) An acceptable blank determination should require at least 23.5 ml of 0.025M ferrous ammonium sulphate, or its equivalent, in the titration. (See Sections R1.1, R2 and R2.1). In addition, the difference between a refluxed blank value (apparatus plus reagent blank) and an unrefluxed blank (reagent blank) should not exceed 1.5 ml of 0.025M ferrous ammonium sulphate or its equivalent.
A5.2.4	**Calculation of results** If it was necessary to pre-dilute the sample, the appropriate factor must be included in the calculation. $COD = 800\ M(V - V_s)$ mg/l Where V = average number of ml ferrous ammonium sulphate (R6.2) used in titrating the blank (steps 5.2.2); V_s = number of ml ferrous ammonium sulphate (R6.2) used in titrating the sample: M = molarity of standard ferrous ammonium sulphate solution, as determined in Section R6 (note (i)).	(i) Ferrous ammonium sulphate solutions do not retain their titre. If not freshly prepared and standardized that day, they should be restandardized (see Sections R6, R6.1, R6.2 and R6.3).

A6. Procedure for High levels of Chloride Interference

see also A7.3

(Samples containing more than 2 g/l of chloride)

A6.1 It is recommended that, where possible, the chloride ion concentration of the sample aliquot taken for the test be limited to a maximum of 2 g/l and in such cases the procedure given above is applicable.

A6.2 However, it may not always be possible to limit this value because of the low organic content of the original sample. In which case, at step A5.1.1 use 1.2 ± 0.05 ml of 1000g/l silver nitrate (R13) instead of 0.6 ± 0.05 ml and at step 5.1.3 instead of 0.40 ± 0.05 ml reagent R8 add 0.80 ± 0.05 ml of reagent R8.

A6.3 Above 4 g/l chloride, further increments of silver nitrate solution R13 and chromium III solution R8 should be considered.

A6.4 Blanks should be treated in the same way as samples.

A6.5 If the colour change at the end point to the titration is now less easy to see, use of a potentiometric titrator is suggested. See Part D1.

A7. 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. Premixed reagents (R7) are commercially available.

READ SECTION ON HAZARDS BEFORE STARTING THIS PROCEDURE

Step	Procedure	Notes
	At step A5.1.3.	
A7.1	**Either**	
	Replace the separate additions of 5.00 ± 0.03 ml of reagent R4 and 15.0 ± 0.5 ml of reagent R11 by a single addition of 18.5 ± 0.05 ml of reagent R7.	
	Or,	
A7.2	If many analyses are made routinely, it may be convenient to also include reagent R8 in the mixed reagent, as this mixed reagent is not so prone to crystallize as R8 alone. To every 185.0 ± 0.2 ml of prepared R7 add 4.00 ± 0.05 ml of R8 and mix well before use. Use 18.9 ± 0.2 ml instead of separate additions of R7 and R8. Alternatively, dissolve 1.000 ± 0.005 g of potassium chromium alum in every 185.0 ± 0.2 ml of R7 and use 18.5 ± 0.05 of this reagent at step A5.1.3 instead of adding the three reagents R8, R4 and R11. Then use 0.40 ± 0.05 ml of water R2 to rinse in the initial silver nitrate solution R13 at step A5.1.1.	
A7.3	If the high chloride procedure A6 is used regularly, it is less likely to cause confusion if the extra silver nitrate and chromium potassium sulphate are added separately at steps A5.1.1 and A5.1.3 before adding either combined reagent. Use of excess chromium and silver appears to have negligible effect on the COD values obtained.	

B. Small-Scale Open and Closed Tube Digestion Procedures with 0.02083M (M/48) potassium dichromate and a titrimetric determination of the residual dichromate.

Two alternative digestion procedures are given, differing only in whether the digestion tubes are open and fitted with an air condenser or are sealed to prevent loss of volatile substances until the oxidation is completed. The residual dichromate is determined titrimetrically using a small-volume burette.

Silver should be recovered from the final solutions and residues and not thrown away. See Section W1 given after the Appendix at the end of this booklet.

B1. Performance Characteristics of the methods [15].

Distinction will only be made where data varies between the various procedures.

B1.1	Substances determined	Almost all types of organic compounds and most inorganic reducing agents.
B1.2	Types of sample	Sewages, trade wastes and other polluted waters.
B1.3	Basis of the method	Oxidation in a standard, arbitrary manner with sulphuric acid and potassium dichromate. The residual dichromate is determined titrimetrically.
B1.4	Range of application	Up to 400 mg/l COD; the range can be extended by pre-dilution of the sample with water.
B1.5	Standard deviation	See Tables 4, 5, 6 and 7.
B1.6	Limit of detection	
B1.6.1	Open tube method	10 mg/l (17 degrees of freedom)
B1.6.2	Sealed tube method	9.0 mg/l (15 degrees of freedom)

Table 4. Open tube 0.02083 M (M/48) dichromate (Method B)

Standard deviation and bias on potassium hydrogen phthalate standard samples

COD	Standard deviation within batch mg/l	Bias of the mean mg/l	No. of laboratories	Batch size
0	4.3	−2	1	5
100	3.0	−2	1	5
200	4.5	−2	1	5
300	4.1	−3	1	5
400	4.5	−4	1	5

Table 5. Open tube 0.02083M (M/48) dichromate (Method B)

Relative standard deviations on real samples

Sample type	Mean COD mg/l	Relative standard deviation %	Degrees of freedom
Industrial effluent	142	4.6	4
Industrial effluent	293	5.2	4
Sewage works effluent	44	2.6	4

Table 6. Closed tube 0.02083M (M/48) dichromate (Method B)

Standard deviation and bias on potassium hydrogen phthalate standard samples

	Standard deviation within batch		Bias of the mean			
COD	Range mg/l	Mean mg/l	Range mg/l	Mean mg/l	No. of laboratories	Batch size
0	1.9 to 5	3.2	−5 to 12.5	3.2	3	5
100	1.2 to 3.9	2.65	−1.7 to +2	1.1	4	5
200	3.8 to 6.5	5.3	1 to 7	3.2	3	5
300	3.6	3.3	−4 to 1	−1.6	3	5
400	2.3 to 4.5	3.5	−14.6 to −8.0	−10.8	4	5

Table 7. Closed tube 0.02083M (M/48) dichromate (Method B)

Relative standard deviations on real samples

Sample type	Mean COD mg/l	Relative standard deviation %	Degrees of freedom
Crude sewage	38.0	8.02	4
	66.5	2.10	4
	169	2.24	4
	208	1.49	4
	209	1.77	4
	902.9	1.84	4
Industrial effluent	39.3	7.12	4
	44	5.91	4
	95.4	9.01	4
	142	3.24	4
	184	3.59	4
	188	5.42	4
	212	1.79	5
	272	0.81	5
	279	1.40	5
	293	1.77	4
Sewage works effluent	60	8.5	4
	62	6.77	4
	79	3.73	4

B1.7 Sensitivity
Both digestions

1 ml of 0.025M ferrous ammonium sulphate solution corresponds to 100 mg/l COD.

B1.8 Bias

B1.8.1 Open tube digestion

The bias is negligible but variable with laboratory and with sample type. Although a few laboratories may find very slight positive bias, the general tendency is for a small negative bias of about 1 to 2% when using potassium hydrogen phthalate.

B1.8.2	Sealed tube digestion	There is no evidence for any bias when using potassium hydrogen phthalate standards.
B1.9	Interferences	As Method A. See also Tables 8 and 9
B1.10	Time required	
	Both digestions	Typical total analytical time for from one to thirty-six samples is about 3½ hours.

B2. Principle

See Part A Section A2. The only differences are in scale and equipment used. The principles are identical.

B3. Field of Application and Interferences

B3.1 In most respects these procedures are similar to those in Part A. Sections A3.1 to A3.5 also apply here. For data on chloride interference see Tables 8 and 9.

B3.2 For sampling problems see Sampling Section S2.6.

B3.3 The possible loss of volatile components, or volatile intermediate compounds during mixing and refluxing in the standard procedure, may be reduced or eliminated in the sealed-tube procedure, resulting in higher COD values for some samples when using this variant.

Comparisons have been made between this method and the 1977 flask method indirectly via Method A. See Table 15.

B4. Apparatus

High blank values may be the result of minute amounts of contaminants in the glassware, and digestion tubes. All new or contaminated glassware should be soaked for 24 hours in dichromate/sulphuric acid reagent (R7) and well rinsed out with water. The digestion tubes should be cleaned by boiling the dichromate/sulphuric acid mixture (R7) in them as in the procedure, and checking that low blank values are obtained. All apparatus should be reserved solely for COD determinations. Grease must not be used. All apparatus should be dry before use.

If digestion tubes are sealed with metal or plastic caps these must not be so cleaned but must not come into contact with the reaction mixture during the analysis.

Volumetric glassware should be grade B or better unless grade A is specified.

Open Tube Digestion Apparatus

B4.1 Digestion tubes. Borosilicate glass tubes 16 mm diameter with a 14/23 ground glass socket and a total volume of not less than 15 ml. Other tube sizes may be used but the performance characteristics quoted in Section B1 may not apply. Tubes with any slight noticeable defect (e.g. surface scratches) should be discarded.

B4.2 Air condenser 13 mm diameter not less than 150 mm long with 14/23 cone, or similar.

Sealed Tube Digestion Apparatus

B4.3 Many types of tube have proved suitable. The main criteria are that with the facilities available the tubes can be heated, cooled, removed from the heater and opened without risk of bursting or spillage which could cause injury.

The test data in the tables was obtained using borosilicate-glass culture vials, 125 × 16 mm and plastic screw-caps with PTFE liners (or metal caps if an oven is used as the heating source). Other tube sizes may be used but the performance characteristics quoted in Section B1 may not apply. **Tubes with any slight noticeable defect (e.g. surface scratch) should be discarded.**

Other proven alternatives are Carius tubes, flame sealed and flame opened after use and tubes with ground glass stoppers or caps held in place by springs or clamps.

Table 8. Open tube 0.02083 M (M/48) dichromate (Method B)

Chloride interference effects with spiked standards and real samples

Sample type	Actual COD mg/l	Chloride mg/l	Mean deviation due to chloride mg/l COD	Degree of freedom
Phthalate standards	0	500	5	4
	100	500	4	4
	200	500	4	4
	300	500	3	4
	400	500	−6	4
	0	1,000	7	4
	100	1,000	9	4
	200	1,000	10	4
	300	1,000	4	4
	400	1,000	−3	4
	0	2,000	9	4
	100	2,000	16	4
	200	2,000	9	4
	300	2,000	3	4
	400	2,000	2	4
Industrial effluent	164*	3,500	10	4
Phthalate standard + 100 mg/l NH_3	0	5,000	97	1

*This sample initially had negligible chloride, was analysed, spiked with chloride and reanalysed.

Table 9. Closed tube 0.02083 M (M/48) dichromate (Method B)

Chloride interference effects with spiked standards of real samples

Sample type	Actual COD mg/l	Chloride mg/l	Mean deviation due to chloride mg/l COD	Degrees of freedom (in each of 2 laboratories)
Phthalate standards	0	500	5.6	4
	100	500	6.6	4
	200	500	10.5	4
	300	500	5.5	4
	400	500	4.4	4
	0	500	13	4
	100	500	14	4
	200	500	13	4
	300	500	12	4
	400	500	−5	4
	0	1,000	2.6	4
	100	1,000	19.6	4
	200	1,000	8	4
	300	1,000	33	4
	400	1,000	−5	4
	0	2,000	8	4
	100	2,000	19	4
	200	2,000	16	4
	300	2,000	12	4
	400	2,000	−2	4
	0	5,000	86	4
	100	5,000	25	4
	200	5,000	7	4
	300	5,000	7	4
	400	5,000	−5	4
	0	10,000	86	4
	100	10,000	92	4
	200	10,000	81	4
	300	10,000	12	4
	400	10,000	19	4
Industrial effluents	167.8*	3,370	−16.2	4
Phthalate standards + 100 mg/l NH_3	0	5,000	20	1

*This sample initially had negligible chloride, was analysed, spiked with chloride and reanalysed.

Apparatus common to all methods

B4.4 Heating source. Thermostatically controlled heating block drilled to accommodate the 16 mm tubes such that the level of the liquid in the tube is level with the surface

of the block. It is recommended that the holes be drilled out to 0.75 mm diameter greater than the average diameter of the tubes to accommodate variations in tube diameter (sand may be added to the holes if they are too deep). The block should be controlled to give a digest temperature of 150° ± 3°C.

Care should be taken to ensure that the temperature of the block does not rise above 153°C. It is recommended that the temperature reached by tubes in all positions in the block be checked periodically and that any position outside the specification be not used. See the Note on use of block digesters in Part N of this booklet. Block capacity should be sufficient to accommodate blanks along with the samples.

An alternative heating source is a suitable air oven, controlled so as to give a digest temperature of 150° ± 3°C.

B4.5 2 ml pipette. For ease of operation and safety an automatic pipette is recommended. The tip should be able to accept suspended matter and there should be little or no drainage period. Precision and accuracy checks should be carried out at regular intervals.

B4.6 1 ml graduated pipette, or preferably, dispensers capable of dispensing 0.1 ± 0.005 ml and 0.2 ± 0.01 ml.

B4.7 A dispenser capable of dispensing 3.7 ml ± 0.02 ml.

B4.8 A 5 or 10 ml burette calibrated in 0.02 ml steps

Alternatively, Conway micro-burettes are commercially available but may need some modification, and piston-burettes are also readily available and are perfectly suitable provided they are not greater than 5 ml capacity graduated in 5 µl steps.

The accuracy of any burette should be checked by the user.

B4.9 1 ml pipette Class A or suitable dispenser

B4.10 Pre-digested anti-bumping granules. These should be pre-cleaned by digestion for 2 hours as described at the start of section B4.

B5. Analytical Procedure

Read the Section on Hazards before starting this procedure.

B5.0 Preliminary operations

B5.0.1 All operations should be carried out with care. Caution must always be the rule in the initial mixing of sulphuric acid containing reagents with unknown samples. Point the tube outwards when mixing, swirling the contents and adding the acid very slowly; otherwise samples containing a lot of carbonate may froth and spill. Poisonous gases may be evolved if substances such as cyanide and/or sulphide are present.

B5.0.2 The digestion procedure described is based on a 1:5 scale down of the flask procedure A. The oxidizing reagent (R7) used is exactly as described in the modified flask procedure for large numbers of samples A7. If it is preferred to use the reagents specified in the unmodified standard procedure, this can be done by substituting 1.0 ± 0.01 ml of the 0.02083M standard reference dichromate solution (R4) and 3.0 ± 0.1 ml of a 10 g/l solution of silver sulphate (R11) in concentrated sulphuric acid in place of the 3.7 ml oxidizing reagent (R7).

B5.0.3 Determine the chloride content of the sample (8) and if greater than 2 g/l see Section B6.

B5.0.4 Experience has shown that departure from the concentrations, temperatures and other details specified in both the digestion and titration stages of this procedure can lead to inaccurate results. The tolerances given and note (g) must be adhered to.

Step	Procedure	Notes
B5.1	**Digestion**	
	Steps B5.1.1, B5.1.3 and B5.1.9 apply only to the open tube digestion procedure.	See A5.1.2 note (b) for dilution information when samples are expected to exceed a COD value of 400 mg/l COD.

Step	Procedure	Notes
	Steps B5.1.4 and B5.1.8 apply only to the closed tube digestion procedure. All other steps are common to both procedures. Only four blanks are required per digestion batch of samples.	
B5.1.1	If an open tube digestion is used, add two preferably six boiling granules to each of the digestion tubes.	**Open tube only.**
B5.1.2	Measure 2.00 ± 0.02 ml of sample into a digestion tube, add 0.10 ± 0.005 ml of silver nitrate solution (R9), swirl to mix and allow to stand for at least 2 minutes. Add 0.10 ± 0.005 ml of chromium III potassium sulphate solution (R8). Then add 3.70 ± 0.02 ml of oxidizing mixture (R7) and swirl to mix. Allow any evolved gas to escape. (See notes (a) and (b)).	(a) If large numbers of samples are analysed regularly see Part D2. (b) There is some evidence that use of a 10.0 ± 0.1 ml sample with 50ml digestion tubes gives improved precision with samples containing much suspended matter. Use with the sealed tube varient needs thorough checking as some such varients have a high positive bias. Reagent additions for the digestion should be increased fivefold.
B5.1.3	For an open tube digestion, place the condenser on top of the tube.	**Open tube only.**
B5.1.4	If using a closed tube digestion, close the tube and secure the stopper.	**Sealed tube only.**
B5.1.5	Prepare four blank solutions in exactly the same way using 2.00 ml water in place of 2.00 ml sample. (Note (c)).	(c) If experience shows that the blank results are very consistent, some laboratories use fewer blanks. However, sufficient blank samples should be run to guarantee the accuracy at step B5.2.3. If this cannot be achieved, investigate, run extra blanks and if necessary repeat the whole analysis.
B5.1.6	Place the sample tube and the blank tubes in the heating source and allow to digest at 150 ± 3°C for 2 h ± 10 mins (note (d)).	
B5.1.7	Remove the tubes and allow to cool in the air for 5 minutes then cool preferably under running water or in an ice bath to below 20°C. (Note (g)).	(d) A tube containing a thermometer placed in a spare blank sample should be placed in the heating block during use. Measure actual digest temperatures. Do not rely on block settings. For sealed tubes use a cap with a tight fitting hole in it, or similar device. See also Part N and Ref. 23 on checking tube and block positions.
B5.1.8	**Either** Cautiously unseal the digestion tubes. (See Hazards Section H4 for safety precautions).	**Sealed tube only.**
B5.1.9	**Or** Remove the condensers from the digestion tubes. Rinse the condensers into the titration flask (used in B5.2.1) with 2 ± 0.1 ml of water. (Note (e)).	**Open tube only.**
B5.2	**Titrimetric Determination of Residual Dichromate**	
B5.2.1	Transfer the contents of the tubes into a 250 ml conical flask. (Note (e)). Rinse the residual dichromate into the flask using 10 ± 1 ml of water. Ensure that the sample is still at less than 20°C. Cool if necessary.	(e) Use of a 100 ml disposable white plastic cup instead of a flask may sometimes facilitate end point detection.

Step	Procedure	Notes
B5.2.2	Add not more than two drops of 'Ferroin' indicator (R5) to the flask and titrate the residual dichromate with standardized ferrous ammonium sulphate (R6) (notes (f) and (g)).	(f) 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 should be ignored. This is especially common with samples high in chloride. (g) The end point fades unless tubes are kept at between 15 and 20°C. Use of a bubble mixer is suggested.
B5.2.3	Repeat steps B5.2.1 and B5.2.2 with the blanks. (Notes (e), (f) and (g)). Calculate the mean value for the blank but if any value differs by more than ± 0.1 ml from the mean it must be rejected and a new mean recalculated from the acceptable blanks. Let V_b be the average number of ml of ferrous ammonium sulphate used in titrating the appropriate blanks. Let V_s be the number of ml of ferrous ammonium sulphate used in titrating the sample.	
B5.2.5	**Calculation of results** If it was necessary to pre-dilute the sample, the appropriate dilution factor must be included in the calculation. $COD = 4000M\ (V_b - V_s)$ mg/l where M = molarity of the ferrous ammonium sulphate solution, as determined in section R6.3 (or R6.2 if freshly prepared).	

B6. Procedure for High Levels of Chloride Interference (Samples containing more than 2 g/l of chloride).

B6.1 It is recommended that, where possible, the chloride ion concentration of the sample aliquot taken for the test be limited to a maximum of 2 g/l and in such a case the procedure given above is applicable.

B 6.2 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. In which case at step B5.1.2, instead of the 0.10 ml additions each of reagents R9 and R8, for samples with between 2 and 4 g/l chloride add 0.20 ± 0.01 ml of each reagent.

B6.3 Above 4 g/l chloride, consider use of a further increment of silver nitrate solution (R13) and chromium III solution R8.

B6.4 Blanks should be treated in the same way as samples.

B6.5 If the colour change at the end point of the titration is now less easy to see, use a potentiometric titrator. See Part D1.

B7. Extension of the COD Range of the Methods

The method has been tested in the COD range 0–400 mg/l. Samples containing more than 400 mg/l are quantitatively diluted with water before analysis. See Part A Section A5.1.2 note (b). The appropriate factor must be included in the calculation. Troubles with end point failure occur at higher levels.

Some laboratories having a majority of samples in the 400–800 mg/l COD range may prefer to use method C for routine control analyses.

C. Small-Scale Open Tube Digestion procedures with 0.03473M potassium dichromate and a titrimetric determination of the residual dichromate.

This method is only recommended for routine control analysis by laboratories analysing large numbers of samples with COD values between 400 and 800 mg/l and is intended to avoid the errors attendant on sample dilution.

Samples are digested in digestion tubes fitted with an air condenser until the oxidation is completed. The residual dichromate is determined titrimetrically using a small-volume burette.

Silver should be recovered from the final solutions and residues and not thrown away. See Section W1 given after the Appendix at the end of this booklet.

C1. Performance Characteristics of the method [15].

C1.1	Substances determined	Almost all types of organic compounds and most inorganic reducing agents.
C1.2	Types of sample	Sewages, trade wastes and other polluted waters.
C1.3	Basis of the method	Oxidation in a standard, arbitrary manner with sulphuric acid and potassium dichromate. The residual dichromate is determined.
C1.4	Range of application	Up to 800 mg/l COD; the range can be extended by pre-dilution of the sample with water.
C1.5	Standard deviation	See Tables 10, and 11.

Table 10. Open tube 0.03473M dichromate (Method C)

Standard deviation and bias on potassium hydrogen phthalate samples

	Standard deviation within batch		Bias of the mean			
COD mg/l	Range mg/l	Mean for test mg/l	Range mg/l	Mean Bias mg/l	No. of laboratories	Batch size
0	0.86 to 4.1	2.45	0 to 6.6	2.6	6	5–10
100	2.76 to 11	4.75	−5.4 to 13	1.66	7	5–10
200	2.37 to 4.08	3.98	−7 to +6	0.37	6	5–10
300	3.26 to 10	4.90	−10.4 to +3	−3.12	6	5– 9
400	2.83 to 6.5	4.10	−6 to +7.2	0.95	6	5–14
800	2.67 to 8.31	4.93	−19 to +1	−6.9	5	5–17
Using mixed reagent prepared as in D2.C						
100		4.0		−1	1	5
200		2.5		6	1	5
200		3.4		2	1	5
400	0	0		−9	1	5
400		4		−4	1	5
800		0.3		−17	1	5

Table 11. Open tube 0.03473M dichromate (Method C)

Relative standard deviation on real samples

Sample type	Mean COD mg/l	Relative standard deviation %	Degrees of freedom
Crude sewage	214	1.73	4
	272.4	3.52	4
	367	1.55	4
	394	1.37	4
	409	1.05	4
	415	0.67	4
	448	7.00	4
	516	0.54	4
	563	1.01	4
	728.4	1.00	4
	1,124	8.02	4
	1,526	1.39	4
Industrial effluent	114	1.92	4
	135.8	4.34	4
	251	1.51	4
	342	2.66	4
	438	1.76	4
	479	1.06	4
	3,686	0.49	4
	3,780	1.00	4
	3,896	0	4
	3,954	0.91	4
	4,300	0.44	4
	4,465	1.38	4
	6,213	0.85	4
	8,322	0.86	4
Sewage works effluent	43.2	7.65	4
	60	6.17	4
	66	5.08	4
	73	3.01	4
	77	4.16	4
	78	4.61	4
	82	5.12	4
	96	3.33	4
	159	3.08	4
	167.4	5.26	8
	241.2	2.74	4
	339	4.33	4

C1.6	Limit of detection	10 mg/l (17 degrees of freedom)
C1.7	Sensitivity	1 ml of 0.025M ferrous ammonium sulphate solution is equivalent to 80 mg/l COD.
C1.8	Bias	The bias is negligible but variable with laboratory and with sample type. Although a few laboratories may find very slight positive bias, the general tendency is for a small negative bias of about 1 to 2% when using potassium hydrogen phthalate.
C1.9	Interferences	As Method A. See also Tables 12 and 13.
C1.10	Time required	Typical total analytical time for from one to thirty-six samples is about 3½ hours.

C2. Principle

See Part A Section A2. The only differences are in scale and equipment used. The principles are identical.

C3. Field of application and interferences

As Method B Section 3. See Tables 14 and 15.

Table 12. Open tube 0.03473M dichromate (Method C)

Chloride interference effects with spiked standards and real samples

Sample type	Actual COD mg/l	Chloride mg/l	Mean deviation due to chloride mg/l COD	Degrees of freedom
Phthalate standards	0	500	11.3	4
	100	500	5.4	5
	200	500	5.7	5
	300	500	0.2	5
	400	500	−4.1	5
	800	500	−5.6	4
	0	1,000	−14.1	5
	100	1,000	9.9	4
	200	1,000	8.4	4
	300	1,000	9.5	5
	400	1,000	3.8	4
	800	1,000	−0.14	3
	0	2,000	16.6	5
	100	2,000	9.8	5
	200	2,000	9.2	4
	300	2,000	5.5	4
	400	2,000	8.9	4
	800	2,000	−6.2	3
	0	3,500	16.8	17
	0	3,500	20.4	4
	0	5,000	34.7	5
	100	5,000	24.2	5
	200	5,000	18.3	5
	300	5,000	17.9	4
	400	5,000	12.5	5
	800	5,000	−5.8	3
	0	10,000	104.6 (41)	5
	100	10,000	65.2 (52)	5
	200	10,000	63.2 (21)	5
	300	10,000	55.3 (25)	5
	400	10,000	27.2 (12)	5
	800	10,000	−5.8 (7)	5
Industrial effluent	42.2*	3,500	−1.6	
	475.7*	3,500	−4.3	
	147*	3,500	+11.2	
	233*	3,685	−18	
	335*	3,570	−4	
Using mixed reagent prepared as in D2.C				
Phthalate standards	0	2,000	12.3	4
	0	3,500	15.7	4
	100	3,500	10	4
	200	3,500	10	4
	0	10,000	96 (28)	4 (4)
	100	10,000	(30)	4
	200	10,000	(29)	4

Figures in brackets were obtained with a double quantity of silver nitrate and chrome alum as repressants.
* These samples initially had negligible chloride, were analysed, spiked with chloride and reanalysed.

Table 13. Open tube 0.03473M dichromate (Method C)

Ammonia + chloride effects

Sample type	Mean COD mg/l	Ammonia mg/l	Chloride mg/l	Mean deviation mg/l	Degrees of freedom
Phthalate standard	0	100	5,000	34	2
	0	100	5,000	48.9 (9)	4
Glutamic acid 500 mg/l	490	—	0	15	3
$(HO_2C.CH(NH_2)$	490	—	2,000	31	3
$(CH_2)_2CO_2H)$	490	—	3,500	30	3
	490	—	5,000	41	3

The figure in brackets was obtained using a double quantity of silver nitrate and chrome alum as repressants.

Table 14. Open tube 0.03433M dichromate (Method C)

Recovery tests

Substance	Concentration mg/l	Theoretical COD mg/l	Found COD mg/l	% Recovery	Degrees of Freedom
Glutamic acid	500	490	505	103.1	3
Sodium benzoate	250	416	416	100.0	4
Pyridine	200	445	< 10	< 2.2*	4
3 Picoline	200	481	144	29.9*	4
Nicotinic acid	200	286	40	14.0	4
Acetic acid	508	542	543	100.2	4
Methanol	300	450	436	96.9	4
Sodium dodecylsulphate	250	499	498	99.8	4
Benzene	176	541	318	58.8	3
Toluene	173	542	320	59.1	5
Oxalic Acid	1530	280	272	102.9	3

*For similar data using mercury under similar conditions but in a sealed tube (28)

C4. Apparatus

As Method B Section 4 except for the following changes.

As Section B4.5 instead of a 2.0 ml pipette a 2.5 ml pipette is required;

As Section B4.7 the dispensers required are 1.5 ± 0.01 ml and 3.5 ± 0.05 ml; at Section B4.8 a 15 or 25 ml burette is required but otherwise with similar specifications.

C5. Analytical procedure

Read the Section on Hazards before starting this procedure.

C5.0 Preliminary operations

C5.0.1 All operations should be carried out with care. Caution must always be the rule in the initial mixing of sulphuric acid containing reagents with unknown samples. Point the tube outwards when mixing and swirling the contents, and adding the acid very slowly; otherwise samples containing a lot of carbonate may froth and spill. Poisonous gases may be evolved if substances such as cyanide and/or sulphide are present.

C5.0.2 The digestion procedure described is based on the open tube procedure in Part B; but the oxidizing reagent used is stronger.

C5.0.3 Determine the chloride content of the sample (8) and if greater than 2 g/l see Section C6.

C5.0.4 Experience has shown that departure from the concentrations, temperatures and other details specified in both the digestion and titration stages of this procedure can lead to inaccurate results. The tolerances given and notes (b), (c), (e), (f) and (i) must be adhered to.

Step	Procedure	Notes
C5.1	**Digestion**	
C5.1.1	Add at least two boiling granules to each of the digestion tubes. (Note (a)).	(a) Some laboratories find six granules to be the optimum number.
C5.1.2	Measure 2.50 ± 0.02 ml of sample into a digestion tube, (notes (b), (c) and (d)) add 0.100 ± 0.005 ml of reagent R12 and 0.100 ± 0.005 ml of reagent R8. Mix well and stand for at least 2 minutes. Add 1.5 ± 0.01 ml of reagent R14 and 3.5 ± 0.05 ml of reagent R10 and swirl to mix. Allow any evolved gas to escape. (Note (d)).	(b) If necessary samples should be prediluted as follows:

Expected COD mg/l	Dilution
0–800	none
400–1600	1 vol made up to 2 vols.
1000–4000	1 vol made up to 5 vols.
2000–8000	1 vol made up to 10 vols.
4000–16000	2 vol made up to 20 vols.
10000–40000	1 vol made up to 50 vols.
20000–80000	1 vol made up to 100 vols.

Step	Procedure	Notes
C5.1.3	Place the condenser on top of the tube. (note e)	(c) For samples with high suspended solids contents, use of 10.0 ± 0.1 ml samples greatly increases the precision. Use 50 ml digestion tubes. Reagent additions should be increased fourfold. Titrate as in A5.2
C5.1.4	Prepare four blank solutions in exactly the same way using 2.50 ml water in place of 2.50 ml sample. (Note (f)).	(d) If many samples are analysed see also Part D2.
		(e) Avoid wetting the top of the tube or joint. See also Section D2 for an alternative way of adding the silver catalyst.
		(f) See B5.1.5 note (c).
C5.1.5	Place the sample tube and the blank tubes in the heating source and allow to digest at $150 \pm 3°C$ for $2\,h \pm 10$ mins (note (g)).	(g) A tube containing a thermometer placed in a spare blank sample should be placed in the heating block during use. Measure actual digest temperatures. Do not rely on block settings. See also Part N and Ref. 23 on checking tube fit for all block positions.
C5.1.6	Remove the tubes and allow to cool in the air for 5 minutes then cool preferably under running water or in an ice bath, to below 20°C. (Note (h)).	
C5.1.7	Remove the condensers from the digestion tubes. Rinse the condensers into the titration flask (used in C5.2.1) with 2.0 ± 0.1 ml of water (note (h)).	
C5.2	**Titrimetric Determination of residual dichromate**	
C5.2.1	Transfer the contents into a 250 ml conical flask. (Note (h)). Rinse the residual dichromate into the flask using 10 ± 1 ml of water. Ensure that the sample is still at less than 20°C. Cool if necessary.	(h) Use of a 100 ml disposable white plastic cup instead of a flask may sometimes facilitate end point detection.
C5.2.2	Add not more than two drops of 'Ferroin' indicator (R5) to the flask and titrate the residual dichromate with standardized ferrous ammonium sulphate (A6) (notes (i) and (j)).	(i) 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 should be ignored. This is especially true for samples high in chloride.
		(j) The end point fades unless tubes are kept at between 15 and 20°C.
C5.2.3	Repeat steps C5.2.1 and C5.2.2 with the blanks (notes (g), (h) and (i)). Calculate the mean value for the blank but if any value differs by more than ± 0.1 ml from the mean it must be rejected and a new mean recalculated from the acceptable blanks. Let V_b be the average number of ml of ferrous ammonium sulphate used in titrating the appropriate blanks. Let V_s be the number of ml of ferrous ammonium sulphate used in titrating the sample.	

Step	Procedure	Notes
C5.2.5	**Calculation of results** If it was necessary to pre-dilute the sample, the appropriate dilution factor must be included in the calculation. $COD = 3200M\ (V_b - V_s)$ mg/l where M = molarity of the ferrous ammonium sulphate solution, as determined in Section R6.3 (or R6.2 if freshly prepared).	

C6. Procedure for High Levels of Chloride Interference.

(Samples containing more than 2 g/l of chloride.)

C6.1 It is recommended that, where possible, the chloride ion concentration of the sample aliquot taken for the test be limited to a maximum of 2 g/l and in such a case the procedure given above is applicable.

C6.2 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. In which case at step C5.1.2 for samples with between 2 and 5 g/l chloride use double the quantities of reagents R12 and R8.

C6.3 Blanks should be treated in the same way as samples.

C6.4 If the colorimetric end point to the titration is now less easy to see, use a potentiometric titrator. See Part D1.

C7. Extension of the COD range of the methods

Samples containing more than 800 mg/l should be quantitatively diluted. See C5.1.2 note (a). The appropriate factor must be included in the calculation.

Table 15. Comparison with former (1977) Flask Titrimetric Method
Method A

Sample type	COD mg/l	
	New Method	Old Method
Industrial effluent	8	6
	63	55
	63	60
	94	92
	137	128
	174	162
	258	308
	310	309
	403	387
	557	547
	1,003	988
	1,011	982
	2,779	2,730
	2,872	2,903
	3,323	3,251
Crude sewage	207	208
	256	241
	338	330
	368	349
	467	454
	593	576
	605	593
	623	587
	660	664
	665	651
	864	892
Sewage works effluent	34	28
	35	31
	36	35
	42	35
	45	42
	45	43
	50	45
	51	52
	121	121

Methods B (open and closed tube versions) and C.

A large number of comparative tests have been made between these other variants and 1977 Flask Titrimetric Method, but most were made indirectly through the corresponding small-scale methods using mercury (see Ref. 10 for these methods). The results were similar to those in the above table and showed that the chief causes of variation arose (1) from small sample size if the sample contained suspended matter or was segregated, and (2) from very minor variations in procedure affecting the digestion temperature. With high COD values, sample dilution also caused loss of precision especially if the sample contained suspended matter. (See Refs 6 and 11).

The following laboratories contributed the test data and information which form the basis for the foregoing tables and the other relevant sections of the three methods.

Allied Colloids Ltd.
Anglian WA, Interlaboratory AQC Project
British Gas Board London Research Centre
British Steel Corp., Port Talbot
Forth R P B, Colinton Laboratory
ICI plc Blackley
Lothian RC, Edinburgh Laboratory
Mullards plc
Northumbrian WA, Pity Me Laboratory
SAC Scientific
Severn Trent WA, Finham Laboratory
Upper Tame Laboratory
Southern WA, Falmer Laboratory
Hampshire Laboratory
Strathclyde RC, Carbarns Laboratory
Cumnock Laboratory
Thames WA, Beckton Laboratory
Crossness Laboratory
Welsh WA, Caernarfon
Wessex WA, Saltford Laboratory
Wool Industries Research Assn.
WRC Stevenage Laboratory
Yorkshire WA, Bradford Laboratory
Leeds Laboratory
Olympia House Laboratory
Sheffield Laboratory
York Laboratory

D. Notes on tested Variants of the Preceding Methods

D1. Use of Potentiometric Titrators and Automation

D1.1 Potentiometric titrators with a shiny platinum electrode and a standard reference electrode such as the calomel electrode are often used for the titration of dichromate by iron II salts and give very good results. However, the equivalence potential (the inflection point on the titration curve) has been found to vary slightly with sample type.

If only one type of sample is titrated and experience shows that the potential does not vary, the usual practice of titrating to a fixed potential (which should be determined experimentally by the user) is satisfactory. Otherwise an instrument programmed to indicate the amount of titrant required to the inflection point of the titration curve, using the second differential of the titrant volume—potential plot, should be used. Most laboratories using this procedure find that the second differential technique is essential for accuracy.

D1.2 It is possible to automate the titration stage using a potentiometric titrator. In addition several laboratories have developed robot systems based on discrete sample analysers which use the methods in Parts B or C. Tubes are even sealed and unsealed automatically according to the programme.

D2. Use of Mixed Reagents

Method A

Reagent R7 is actually a combination of 5 ml of reagent R4 and 15 ml of reagent R11, the different volume taken compensating for a volume change on mixing. Section A7 gives recipes for combining reagent R8 into this mixture which avoids the necessity of keeping the reagent R8 stock bottle warm.

Method B

If a similar reagent were used with either version of method B, the recipe would need to be changed to 5.00 ± 0.05 ml of reagent R8 per 185.0 ± 0.2 ml of reagent R7 and 3.80 ml used. Any changes of this type need to be evaluated thoroughly by the users as the order of addition of the reagents does slightly affect the results obtained.

Method C

A combined dichromate, chromium III, sulphuric acid solution can be made up as follows: in about 500 ml of water dissolve 10.216 ± 0.0005 g of potassium dichromate and 16.7 ± 0.05 g potassium chromium sulphate (potassium chrome alum), carefully add 167 ± 2 ml of sulphuric acid d_{20} 1.84, cool and make up to 1 litre in a graduated flask.

At step C5.1.2 use 2.50 ± 0.02 ml of sample, 0.100 ± 0.005 ml of reagent [illegible] before, mix and allow to stand for at least 2 minutes, then add 1.50 ± 0.01 ml of the above mixed reagent followed by 3.5 ± 0.05 ml of reagent R10. Swirl to mix, then continue as before. (See also Tables 10 and 12).

D3. Adaptation to Insoluble Samples

D3.1 For the differentiation between COD on soluble and suspended matter in samples see Section S1.6.

D3.2 The determination of the COD/BOD_5 ratio of a chemical substance is one of the parameters required if the substance is submitted for notification under the 6th Amendment of the EEC Directive on Packaging and Labelling of Dangerous Substances [Directives (67/548/EEC) and (79/831/EEC)]. For soluble substances the COD value

can be determined on appropriate aqueous concentrations by the standard COD method **A**; but for materials insoluble at these concentration levels, modification of the COD procedure is necessary to allow addition of neat material. In this case, step A5.1.2 should be replaced by the following:

> Accurately weigh out not more than 1.0 mg of thoroughly homogenized sample to the nearest 0.01 mg on a glass slide. Transfer the sample and slide directly into the digestion flask and add 10 ± 0.1 ml of COD free water.

Appendix

The 1977 titrimetric Flask Digestion Method which follows is only given for information, as it is the ultimate standard with which the other methods were compared. It is no longer a recommended method because it uses mercury. If for any reason comparison requires its use, the mercury and silver must be recovered from the final solutions. It should not be used routinely.

Large-scale (10 ml sample) flask digestion with titrimetric determination of residual dichromate. (1977 Version, for reference purposes only) (4).

The method consists of a digestion procedure with a titrimetric final determination of residual dichromate.

Silver and mercury must be recovered from the final solutions and residues and not thrown away. For methods of recovery see Section W.

1. Performance Characteristics

(For further information on the determination and definition of performance characteristics see Ref. 15.)

1.1	Substances determined	Almost all types of organic compounds, and most inorganic reducing agents.
1.2	Types of sample	Sewages, trade wastes and other polluted waters.
1.3	Basis of the method	Oxidation in a standard, arbitrary manner with sulphuric acid and potassium dichromate; the residual dichromate is measured titrimetrically.
1.4	Range of application	Up to 400 mg/l COD; the range can be extended by pre-dilution of the sample with water.
1.5	Calibration curve	Linear
1.6	Standard deviation	

Sample	COD (mg/l)	Standard Deviation (mg/l)	Relative Standard Deviation (%)	Bias (%) (Where a range is given, the outside values are minimum and maximum, the central one is the mean)	Degrees of Freedom	Notes
Synthetic solution (b)	64	1.7–6.6				(a)
Synthetic solution (b)	400	1.4–6.2				(a)
Sewage effluent	64	2.3–5.2				(a)
Trade effluent	312	3.5–9.8				(a)
Synthetic solution (b)	250	3.3	1.3	−0.7	28	(c)
Synthetic solution (b)	250	2.4	1.0	−0.6	23	(c)
Synthetic solution (b)	250	3.3	1.3	−0.6	29	(c)
Synthetic solution (b)	250	3.7	1.5	−0.9	29	(c)
Synthetic solution (b)	80	1.7–6.6			5	(d)
Synthetic solution (b)	400	1.4–6.2			5	(d)
Effluent abt	80	2.3–5.2			4	(d)
Effluent abt	400	3.5–9.8			4	(d)
Synthetic solution (b)	400	4.22	1.055	1.0	large	
Synthetic solution (b)	350	7.03	2.05	−7.4, −1.8, −2.3	183	(e)
Synthetic solution (b)	64	S_x 3.162 S_y 5.114	8.00	−2.18	10	(f)
Synthetic solution (b)	400			−1.45	730	(f)
Deionized Water	—	1.59			64	(g)
Synthetic solution (b)	290	4.08	1.41	−6.7, −2.3, −0.9	89	(g)
Effluent mean	398	1.59	4.0	−3.4, −0.2, −5.2	51	(g)
Effluent mean	371	5.49	1.48	−5.7, −0.45, −3.8	89	(g)
Synthetic solution (b)	250	6.54	2.6	−5.93, −0.79, 5.47	33	(i)
Synthetic solution (b)	200	6.88	3.44	−6, 0.08, 2.4	32	(j)

1.6 *continued*

Sample	COD (mg/l)	Standard Deviation (mg/l)	Relative Standard Deviation (%)	Bias (%) (Where a range is given, the outside values are minimum and maximum, the central one is the mean)			Degrees of Freedom	Notes
Synthetic solution (b)	210	5.11	2.43	−7,	−1.2,	4.7	46	(j)
Synthetic solution (b)	240	6.12	2.55	−6,	−0.19,	4.6	21	(j)
Synthetic solution (b)	252	8.26	3.30	−6,	−1.44,	8	49	(j)
Synthetic solution (b)	200	5.42	2.71	−6.3,	−2.79,	5.5	254	(k)

1.7	Limit of detection	4.6 to 7.8 mg/l (with 4 degrees of freedom) (h) 6 to 15 mg/l (9 degrees of freedom)
1.8	Sensitivity	1 ml of 0.025M ferrous ammonium sulphate is equivalent to 20 mg/l COD.
1.9	Bias	Although some laboratories on certain types of sample do get a slight positive bias, the general concensus of tests indicates a slight negative (−1 to −2%) bias using potassium hydrogen phthalate; this bias is dependent on laboratory. See data under 1.6 above.
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.
1.11	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; each estimate has approximately 4–9 degrees of freedom.
(b) A solution of potassium hydrogen phthalate in distilled water.
(c) North West Water Authority interlaboratory AQC programme data.
(d) Yorkshire Water Authority comparative study data.
(e) Welsh Water Authority, two different laboratories, within laboratory AQC programme data.
(f) South West Water Authority data.
(g) Anglian Water Authority interlaboratory AQC.
(h) Anglian Water Authority interlaboratory AQC programme data from 6 acceptable laboratories.
(i) Laboratory of the Government Chemist.
(j) Southern Water Authority interlaboratory AQC programme data from 17 laboratories.
(k) Severn–Trent Water Authority Finham Laboratory within laboratory AQC programme data.
(l) Severn–Trent Water Authority—a range of estimates from 8 laboratories is given.

For further information on the testing of this and related mercury containing methods see Refs 5 and 6.

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 by titration with standardized ferrous ammonium sulphate solution.

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

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

2.6.3 Chloride interference reactions

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

2.6.4 Chloride interference is suppressed by complexion with mercury II

$$Hg^{++} + 4Cl^- \rightarrow Hg\ Cl_4^{2-}$$

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 unless chloride is present in sufficient amount to cause interference. Some ammonium ion is then oxidized. 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 salts etc. will contribute to the COD. Oxidizing agents can give negative false results and (low) results.

3.5 If not suppressed, chloride would cause positive interference the magnitude of which would depend 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. The minimum and maximum effects are shown in the table below. The results were obtained with the amount of mercuric sulphate specified in Section 5.1.3 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

	Deviation in mg/l COD			
COD mg/l	5 mg Cl^- in 10 ml aliquot	10 mg Cl^- in 10 ml aliquot	15 mg Cl^- in 10 ml aliquot	20 mg Cl^- in 10 ml 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

*Measurement 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 6.

4. Apparatus

High blank values may result from 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 R10 in

the apparatus until low and consistent blank values are obtained. Apparatus should be reserved solely for COD determinations.

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

Digestion Apparatus

4.2 150 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.

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

4.4 Water-cooled condenser, at least 150 mm long, capable of being easily rinsed as required in step A5.1.5.

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

A4.6 Predigested anti-bumping granules All anti-bumping granules and aids should be precleaned by digestion for 2 hours as described in Section 5.

4.6.1 Use of 90 ± 5 mm diameter PTFE rod has been suggested by North West Water Authority, Ribble division. Rods must be cleaned by boiling with the test reagents (without a sample) prior to use.

4.7 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 inside 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.

4.8 25 ml burette

5. Analytical Procedure

5.0.1 READ THE SECTION 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.

5.0.2 Determine the chloride content in the sample (see the appropriate publications in this series (8)) and, if greater than 2 g/l, see Section 6.

5.0.3 For a modified procedure for large numbers of samples, see Section 7.

Step	Procedure	Notes
5.1	**Digestion**	
5.1.1	Insert the anti-bumping aid or granules into the boiling flask (note (a)).	(a) Once in a position they need not be removed between determinations.
5.1.2	Measure 10.0 ± 0.1 ml of sample into the flask (notes (b) and (c)).	(b) If the chemical oxygen demand exceeds 400 mg/l oxygen, the sample should be quantitatively diluted by a suitable factor and a 10 ml aliquot of the diluted sample taken for oxidation. This diluted sample should consume dichromate equivalent to between 5 and 20 ml of 0.025M ferrous ammonium

Step	Procedure	Notes
		sulphate (R6.3). This dilution factor must be taken into account when making the final calculation.
		(c) If the sample (after any necessary dilution) contains more than 5 mg of chloride ion, see Section 6.
5.1.3	Add 1.0 ± 0.2 ml of 20% m/v mercuric sulphate solution and swirl to mix; add 5.00 ± 0.03 ml of 0.02083M potassium dichromate (R4). Using an automatic dispensing pipette or burette add 15.0 ± 0.5 ml of 1% m/v silver sulphate in sulphuric acid (R11) (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 6).
5.1.4	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.
5.1.5	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 as to rinse residual dichromate from the condenser. Disconnect the flask from the condenser and cool the flask to room temperature in running water. Proceed to Section 5.2.	
5.2	**Determination of Residual Dichromate** (see also 5.0.2 and D1).	
5.2.1	Add not more than two drops of 'Ferroin' indicator (R5) to the flask and titrate the residual dichromate with standardized 0.025M ferrous ammonium sulphate (R6) (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.
5.2.2	**Blank determination** 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.	
5.2.3	The blank test is carried out as described in steps 5.1.1 to 5.2.1 inclusive, replacing the 10 ml of sample by the same amount of water (R2) (notes (h) and (i)).	(h) When more than 5 mg of chloride ion is found in 10 ml of test sample, see Section 6.
		(i) An acceptable blank test should require at least 23.5 ml of 0.025 M ferrous ammonium sulphate, or its equivalent, in the titration. (See Sections R1 and R2).
5.2.4	**Calculation of results** If it was necessary to pre-dilute the sample, the appropriate factor must be included in the calculation.	(j) Ferrous ammonium sulphate solutions do not retain their titre. If not freshly prepared and standardized that day, they should be restandardized (see Section R6).
	$COD = 800M\ (V - V_s)$ mg/l	

Step	Procedure	Notes
	Where V = average number of ml ferrous ammonium sulphate (R6) used in titrating the blank (steps 5.2.2); V_s = number of ml ferrous ammonium sulphate (R6) used in titrating the sample; M = molarity of standard ferrous ammonium sulphate solution, as determined in Section R6 (note (j)).	

6. Procedure for Suppressing Chloride Interference

(see also 7.3)

(aliquots containing in excess of 5 mg of chloride per 10 ml) It is recommended that, where possible, the chloride ion concentration of the sample aliquot taken for the test be limited to a maximum of 3 g/l 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 ON HAZARDS BEFORE STARTING THIS PROCEDURE.

Step	Procedure	Notes
6.1	Determine the chloride concentration in the sample by a suitable procedure (Ref. 8).	
6.2	Carry out steps A5.1.1 and A5.1.2.	
6.3	Add to the flask a weight of solid 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.	
6.4	Continue with step 5.1.3 onward beginning at the potassium dichromate addition.	
6.5	**Blank determinations** Blank determinations are carried out as described in steps 5.2.2 and 5.2.3 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.

7. 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. Premixed reagents (R7) are commercially available.

READ SECTION ON HAZARDS BEFORE STARTING THIS PROCEDURE.

Step	Procedure	Notes
7.1	Add 10 ml of sample and the required amount of 20% m/v mercuric sulphate solution to the oxidation flask as described in steps 5.1.2 and 5.1.3.	

Step	Procedure	Notes
7.2	Measure 18.5 ± 0.2 ml of oxidizing mixture (R7) into the flask using an automatic dispensing pipette or burette (note (o)).	(o) Automatic dispensing pipettes require periodic checks on their calibration for accurate dispensing of reagents.
7.3	Continue onward with step 5.1.4.	

W. Waste disposal and reagent recovery

Silver and mercury compounds are notifiable wastes requiring prior consultation before disposal to land or water. These compounds are also expensive and recovery may be more economical than disposal.

W1. Silver

W1.1 Removal of silver

Place 40 ml of hydrochloric acid (d_{20}1.84) in a Winchester bottle and add the spent test solutions including precipitates to the acid. When the Winchester is full, allow the silver chloride precipitate to settle overnight. Decant the supernatant liquid into a beaker. If mercury is also present, subject this liquid to procedure W2. If mercury is absent it may be discarded. Wash the settled precipitate with water, by decantation, until the washings are no longer strongly acid.

W1.2 Silver recovery

Silver chloride can be dried, and stored until sufficient has accumulated to make it worth selling to precious metal refiners. The minimum amounts purchased are not excessive. Precious metal dealers are listed in trade directories such as the latest edition of Kompass (12). Alternatively, see reference 8 Section H1.

W2. Mercury

If silver and mercury are both present carry out step W1.1 first, then treat the supernatant liquor from that procedure by the following process.

W2.1 Removal of mercury (see also the notes which follow). Add between 1 and 3 g of ferrous sulphide to the collected waste samples in a large beaker. 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. Wash the settled precipitate with water by decantation until free of hydrogen sulphide.

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

(b) The supernatant liquid contains a relatively high concentration of sulphide. This liquid should be oxidized or diluted 500 to 1 before disposal.

(c) Some laboratories precipitate mercury by addition of the stoichiometric amount of potassium iodide instead of using ferrous sulphide.

W2.2 Mercury recovery

Metal refiners and recoverers may accept mercury sulphide for recovery. For further information see a trade directory such as the appropriate section of Kompass (12). See also Refs 8 Section H2 and 14.

N. Use of Block Digesters

N1. Introduction

Block digesters are finding increasing use in the analytical laboratory to digest samples and convert determinands of interest to a more determinable form. The most common reasons for the increase are that traditional digestion techniques tend (i) to consume much operator time, (ii) to use a large area of bench space for multiple digestions and (iii) to be hazardous. A block digester approach tends to reduce these three aspects of a digestion procedure. Also, it is claimed that experimental conditions are more controlled with the use of block digesters, resulting in an increase in precision and accuracy of data.

There are numerous factors relating to the use of block digesters; for further information see Refs 20 and 23.

N2. Selection of Digestion Tubes

The following points are considered important for the selection of the glass tube used for digestion.

(a) The glass itself must be durable, resistant to high temperatures, have a low coefficient of expansion and be of a thickness which allows a rapid transfer of heat to the solution contained within.

(b) Tubes must be straight-sided, cylindrical and round-bottomed. They should fit snugly into the drilled hole yet must be easily removable.

(c) Invariably, the digested sample is subsequently analysed as a solution. Calibrated digestion tubes are an advantage in the preparation of this solution.

(d) The overall height of the tube is also important. The level of the liquid in the digestion tube should not protrude above the top of the heating block and the remaining height should be such that the air space above the level of the liquid is sufficient for satisfactory reflux of the liquid without loss.

Enquiries to suppliers of digestion tubes regarding guarantees of tolerances of manufacture have revealed a reluctance to supply such a guarantee. To some extent this attitude is understandable but naturally it makes the user's life more difficult. However, a few glass-blowing companies will guarantee tolerance for their manufacture, but it is emphasised that the potential user of the tubes should produce the specification of dimensions and liaise closely with the manufacturer. An increased precision of manufacture is usually associated with increased costs.

Screw-capped culture tubes, bought in bulk, have been used for small-scale block digestion. Experience has shown that as high as 20% rejection can occur due to inappropriate dimensions.

N3. Safety Precautions

N3.1 Removal of toxic fumes

The digestion procedures may result in the generation of toxic fumes. The need for an efficient extraction system to remove the fumes cannot be over emphasised. The operator should consider a custom-built extraction hood which is conveniently seated on top of a collection of digestion tubes in the block. The extraction hood may then be connected to a suitable fume removal unit. Advice on extraction systems of this type is usually available from manufacturers.

N3.2 Safety screens

A safety screen should be placed between block digester and operator. Digestion tubes may crack, or the control mechanism may malfunction and the temperature of the block

increase unexpectedly. There is great danger to the operator if digestion reagents come into contact with a heated block. Consideration must also be given to containment of liquid. After such an event, the electronics should be thoroughly inspected by a qualified electrician for damage. The drilled holes should be thoroughly cleaned with copious amounts of water or very dilute alkali solution using pads of tissue paper soaked in water or dilute alkali.

N3.3 Rejection of unsuitable block positions

These analyses require very reproducible temperature control for comparative results. If tests show any block positions that are outside the specification for the analysis, they should be filled by dummy samples. These should be the same as reagent blank samples except that they are suitably marked and never analysed. Never use tubes filled only with water as dummy samples. To check block positions use tubes containing blank samples and a suitable thermometer (see Part B5.1.6 note (b)).

Estimation of the Accuracy of Analytical Results using the Methods in this Booklet

Experience has shown that the accurate determination of COD (dichromate value), needs careful quality control.

It is recommended that the quality of analytical results is checked by making special tests with each batch of samples. A standard solution containing 400 mg/l COD for methods A and B or 800 mg/l COD for method C (Reagents R15 and R16, prepared from potassium hydrogen phthalate) should be analysed with each batch, together with triplicate blanks and a duplicate of one of the samples analysed. Although this will not necessarily expose errors (e.g. the absence of silver sulphate, or failure to reach 150°C will not necessarily result in a low value for the potassium hydrogen phthalate solution) the plotting of results on quality control charts as described in Ref. 9 will provide a useful check on day-to-day performance of the method. If experience shows that the COD of one type of regularly submitted sample does not change on storage, intermittent reanalysis of old samples is another useful control. Other good standard solutions are oxalates, with a COD of one gram atom of oxygen per mole of oxalate ion; while, as tests for the ability to digest other substances, acetic acid with four gram atoms of oxygen per mole, 2-propanol with nine gram atoms of oxygen per mole and isonicotinic acid with eleven gram atoms per mole have been used.

It is desirable to know the accuracy achievable in all laboratories concerned with a particular analysis. It would, therefore, be of great value for any laboratory using or considering the use of any of these methods to estimate the accuracy of its own analytical results.

The precision achieved is of particular interest. The value of this information would be greatly enhanced if it were obtained at the same determined concentrations as those for which some information has already been gained, as set out in the Performance Characteristics sections of these methods. Similar information at other determined concentrations, and in sample types other than those already studied, would also be of great assistance. Detailed specifications for the tests to be carried out are beyond the scope of this booklet, but standard texts—such as those published by the Water Research Centre (9) and by the DOE Standing Committee of Analysts (15)—provide guidelines from which precision tests may be designed. The same texts also provide guidelines for interference and recovery tests and any information on these matters would be gratefully received.

As mentioned earlier, factors required special attention are reagent strengths and quantities used, digestion temperature and conditions (which can vary even across a thermostatically controlled heater), sample volatility, sample homogenity and representativeness, sample oxidizability and the effects of catalysts, interferents and other oxidizable matter present, loss of dichromate by absorption into precipitates and above all general carefulness and alertness.

Particular attention needs to be paid to the reproductibility of sampling, especially if oxidizable suspended matter is present. It is suggested that tests also be included to control the representativeness of the sample. Tests using samples to which different coloured particles of similar consistency to those found in the sample have been added, may often be used to reduce the number of full analyses required in such an investigation as visual examination may indicate inadequate mixing. Such tests using additives should not be made on analytical samples.

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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 booklet are requested to write to:

The Secretary
The Standing Committee of Analysts
The Department of the Environment
Romney House, 43 Marsham Street
LONDON SW1P 3PY
England

Standing Committee of Analysts

At one time or another a considerable number of people have worked on the drafting and testing of these methods, some co-opted for only a few meetings. The list that follows is as accurate as records allow. Except for the Silver and Mercury Recovery Panel who were actually part of the Chloride Methods Panel, dates of service have been shown.

	Main Committee	Working ø Group 3	COD ø Panels
Mr JB Allcroft		1975–81	1978–81
Mr MA Allen		1975–81	1975–81
Dr GI Barrow	1976 on		
Mr FB Basketter	1982 on		
Mr D Best		1981 on	
Dr GA Best	1980 on		
Miss N Bland			1978–81
Mr DE Bond	1973–74		
Mr J Borland	1975–78		
Dr JM Carter	1975–82		
Dr PA Chave	1982 on		
Mr RV Cheeseman	1985 on*		1975–77
Mr EI Clarke		1980–84	
Dr JRP Clarke		1985 on	
Dr GW Clayfield	1973–85	1973–85	1973–85
Mr BEP Clement	1978 on		
Dr V Collins	1975–77		
Dr RL Cooper	1975–83	1973–74	1973–74
Dr J Cope		(1973–75	
		(1985 on	
Mr M Croall		1985 on	
Dr BT Croll	1975 on		
Mr SJ Davis		1985 on	occasional
Mr C Deakin		1985 on	
Mr EK de Casseres		1983 on	
Mr TA Dick	1975–84		1977
Dr JWR Dutton	1978–82		
Mr GE Eden	1973–75		
Mr MC Finniear	1982 on		
Dr J Gardiner	1980–83		
Dr R Gardiner	1982–85		
Dr M Gardner		1985 on	
Mr GI Goodfellow	1979 on	1985	
Dr K Goodhead	1978–80		
Mr TR Graham	1977 on		
Mr LA Green		1985 on	
Mr BJ Harland		occasional	
Dr N Harkness	1973–75		
Dr I Harper	1980–82		
Mr PJ Hewitt		1978–81	1978–81
Mr AE Hey		1973 on	1973 on
Mr E Hodges	1975–85		
Mr GJ Holland	1973–82		
Dr AJ Howard	1975–77		
Dr DTE Hunt	1980 on		
Dr G Jones	1985 on		
Mr JS Leahy	1982 on		

	Main Committee	Working ø Group 3	COD ø Panels
Mr WM Lewis	1973–80	1973–74	1973–74
Mr R Lisle		1978 on	1983 on
Mr A Lloyd		1985 on	1983 on
Mr DJ Lloyd		1975–81	1975–78
Mr PJ Long	1975 on		
Mr GF Lowden		1973–80	1973–81
Dr GH Mansfield		occasional	
Mr JC McCullins	1976 on		
Mr D Mercer	1973–74		
Mr P Morries	1975–82		1977
Mr CC Musselwhite		1978 on	1978–80
Mr D Myles	1975–84*	1975–83	1975–78
Mr AH Nield	1976–85	1975–78	1975–78
Dr JD Norris		1974–78	1974–78
Dr DI Packham	1980–83		
Mr V Page		1978–81	1978–81
Dr HA Painter	1975–80		
Mr JF Palframan		1973–75	1973–75
Dr AT Palin	1973–75		
Dr SJ Patterson	1973–80		
Mr AS Pearce		1976–83	1977–81
Mr B Pettman		1974–75	1974–75
Dr KW Petts		1985 on	
Mr LR Pittwell	1973 on	(1974–6	1977
		(1983 on	
Dr JE Portmann	1975 on		
Mr LD Purdie	1975 on		
Mr BD Ravenscroft	1975 on	1975 on	1977
Mr TD Rees		1973–75	1973–75
Mr B Rhodes	1977–82		
Mr LA Richards	1982 on	1975–78	
		1985 on	
Dr M Riley		1985 on	
Professor JP Riley	1975 on		
Mr DT Scofield			1978–81
Mr CC Scott		1978–81	
Mr R Sinar	1973–79*		
Mr PAH Sperring	1975–76		
Mr JR Street		1984 on	
Dr D Taylor	1984 on		
Mr A Tetlow	1980–85		
Mr A Thompson		1973–75*	1973–75*
Dr KC Thompson	1982 on	1986	
Dr AM Ure	1979 on		
Mr RJ Vincent	1985 on		
Mr PJ Walker		1985 on	
Mr AR Watkins		1978–81	1978–81
Mr JP Weiner		1985 on	
Dr KC Wheatstone		1973–75	1973–75
Mr FJ Whitby		1975–81	
Mr BT Whitham	1975–83		
Dr DA Williams	1984 on		
Mr AL Wilson	1973–80		1977
Dr R Wood (LGC)+	1975–78		
Dr R Wood (MAFF)+	1983 on		

ø at times these were almost identical
* died while still a member
+ not the same person

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