



ENVIRONMENT AGENCY

The determination of chemical oxygen demand
in waters and effluents (2007)

Methods for the Examination of Waters and Associated Materials

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Methods for the Examination of Waters and Associated Materials

This booklet contains guidance on methods for the determination of chemical oxygen demand using potassium dichromate solution, and notes for the disposal and recovery of selected reagents. This document revises the document published in 1986. Five methods are described and these include:

- A A reference large scale (10 ml) flask digestion procedure with mercury suppression.
- B A small scale (2 ml) flask digestion procedure with mercury suppression and spectrophotometric determination.
- C A mercury-free large scale (10 ml) flask digestion procedure using chromium(III) potassium sulphate and silver nitrate solutions.
- D A mercury-free small scale (2 ml) flask digestion procedure using chromium(III) potassium sulphate and silver nitrate solutions.
- E A mercury-free small scale (2.5 ml) flask digestion procedure using chromium(III) potassium sulphate and silver nitrate solutions.

Throughout the booklet, the term chemical oxygen demand (COD) is used to express the amount of oxygen consumed during oxidation of a sample with hot acid dichromate solution under defined conditions; the test provides an estimate of the oxidisable matter present in the sample. The result is usually expressed as milligrams of oxygen consumed per litre of sample (mg l^{-1}). All of the methods described in this booklet are empirical, and are based upon the oxidation of organic matter using acid dichromate solution followed by spectrophotometric determination or titrimetric determination of residual dichromate with iron(II) ammonium sulphate solution.

The following booklet in this series contains details on an inter-laboratory trial on COD determinations using some of the methods described in this booklet.

Whilst this booklet may report details of the materials actually used, this does not constitute an endorsement of these products but serves only as an illustrative example. Equivalent products are available and it should be understood that the performance characteristics of the method might differ when other materials are used. It is left to users to evaluate methods in their own laboratories.

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About this series

Introduction

This booklet is part of a series intended to provide authoritative guidance on recommended methods of sampling and analysis for determining the quality of drinking water, ground water, river water and sea water, waste water and effluents as well as sewage sludges, sediments, soil (including contaminated land) and biota. In addition, short reviews of the most important analytical techniques of interest to the water and sewage industries are included.

Performance of methods

Ideally, all methods should be fully evaluated with results from performance tests. These methods should be capable of establishing, within specified or pre-determined and acceptable limits of deviation and detection, whether or not any sample contains concentrations of parameters above those of interest.

For a method to be considered fully evaluated, individual results from at least three laboratories should be reported. The specifications of performance generally relate to maximum tolerable values for total error (random and systematic errors) systematic error (bias) total standard deviation and limit of detection. Often, full evaluation is not possible and only limited performance data may be available.

In addition, good laboratory practice and analytical quality control are essential if satisfactory results are to be achieved.

Standing Committee of Analysts

The preparation of booklets within the series "Methods for the Examination of Waters and Associated Materials"

and their continuing revision is the responsibility of the Standing Committee of Analysts. This committee was established in 1972 by the Department of the Environment and is now managed by the Environment Agency. At present, there are nine working groups, each responsible for one section or aspect of water quality analysis. They are

- 1 General principles of sampling and accuracy of results
- 2 Microbiological methods
- 3 Empirical and physical methods
- 4 Metals and metalloids
- 5 General non-metallic substances
- 6 Organic impurities
- 7 Biological methods
- 8 Biodegradability and inhibition methods
- 9 Radiochemical methods

The actual methods and reviews are produced by smaller panels of experts in the appropriate field, in co-operation with the working group and main committee. The names of those members principally associated with these methods are listed at the back of the booklet.

Publication of new or revised booklets will be notified to the technical press. If users wish to receive copies or advance notice of forthcoming publications, or obtain details of the index of methods then contact the Secretary on the Agency's internet web-site (www.environment-agency.gov.uk/nls) or by post.

Every effort is made to avoid errors appearing in the published text. If, however, any are found, please notify the Secretary.

Dr D Westwood
Secretary
August 2006

Warning to users

The analytical procedures described in this booklet should only be carried out under the proper supervision of competent, trained analysts in properly equipped laboratories.

All possible safety precautions should be followed and appropriate regulatory requirements complied with. This should include compliance with the Health and Safety at Work etc Act 1974 and regulations made under this Act, and the Control of Substances Hazardous to Health Regulations 2002 (SI 2002/2677). Where particular or exceptional hazards exist in carrying out the procedures described in this booklet, then specific attention is

noted. Numerous publications are available giving practical details on first aid and laboratory safety. These should be consulted and be readily accessible to all analysts. Amongst such publications are; "Safe Practices in Chemical Laboratories" and "Hazards in the Chemical Laboratory", 1992, produced by the Royal Society of Chemistry; "Guidelines for Microbiological Safety", 1986, Portland Press, Colchester, produced by Member Societies of the Microbiological Consultative Committee; and "Safety Precautions, Notes for Guidance" produced by the Public Health Laboratory Service. Another useful publication is "Good Laboratory Practice" produced by the Department of Health.

The determination of chemical oxygen demand in waters and effluents

1 Introduction

Methods for the determination of chemical oxygen demand have been previously published^(1, 2). These methods have been revised and other procedures developed and are included in this booklet.

Previously published methods	Equivalent method in this booklet
1977 method	A
	B (closed-tube)
	B (open-tube)
1986 method A	C
1986 method B (closed-tube)	D
1986 method C	E

Initially, methods C, D and E of this booklet were developed in 1986 as alternative methods to the use of method A, which, over a prolonged period of time, utilises significant quantities of mercury. Methods C and D were used for samples with chemical oxygen demand (COD) values of up to 400 mg l⁻¹. Method E was used where large numbers of samples were analysed and where it was considered appropriate to reduce the manipulative operations within the test, especially the dilution of samples. Consequently, method E was used where many samples with COD values of between 400 - 800 mg l⁻¹ were frequently analysed.

It has now been established that varying, biased results have been obtained when the mercury-free methods, i.e. methods C and E of this booklet, were used to determine COD values of certain sewage effluents possessing COD values of up to about 160 mg l⁻¹. Consequently, to address this issue but at the same time facilitate the reduction of mercury disposed to the environment, a small scale mercury COD method was developed; this is method B of this booklet and is effectively a scaled down version of method A. Method A is the original (and still remaining) reference method. The results obtained using method A have, in the past^(1, 2) been compared with the results obtained using methods C, D and E. Comparative data are also shown in this and the following booklet. Whilst COD values have been determined using procedures similar to those described in method B, these usually have involved test-kits, with the determination of residual dichromate using spectrophotometry. It is the laboratory's responsibility to ensure that the validation of methods, used in comparative exercises, is properly carried out to ensure equivalency of results on the samples analysed is demonstrated for the types of samples being analysed.

As stated, the determination of COD is empirical, and experiences have shown that departure from the concentration of reagents used, temperatures and other details specified in both the digestion, and titrimetric or spectrophotometric stages described in methods A - E can lead to significant differences being reported in the results determined. In addition, when the spectrophotometric determination is carried out, users should ensure that matrix effects (including turbidity) of individual samples are included in the validation of the test.

Where the expected COD is above 400 mg l⁻¹ (but see individual methods for range of application) the sample should be diluted accordingly, see Table 1.

Table 1 Example dilutions for expected COD values

Expected COD (mg l ⁻¹)	Dilution
0 - 400	none
400 - 800	2-fold
800 - 2000	5-fold
2000 - 4000	10-fold
2000 - 8000	20-fold
10000 - 20000	50-fold
10000 - 40000	100-fold
20000 - 80000	200-fold

Whilst all types of sewage effluents, trade wastes and other polluted waters can be analysed for COD, the test can also be applied to solutions of single organic compounds and inorganic substances. However, the rate and extent of oxidation of organic compounds and inorganic substances varies considerably. Some compounds are easily oxidised under the conditions of the test, while others are less so. For example, many heterocyclic compounds, for example sulphonic acid derivatives, are only partially oxidised under the test conditions. Furthermore, inorganic reducing compounds (such as nitrites, sulphites and iron(II) salts) usually react faster with dichromate than organic compounds, generally, and so contribute to the oxygen demand. If these inorganic compounds are present in relatively high concentrations, the concentration of dichromate can be reduced rapidly. This effect may affect the oxidisability of any organic compounds present in the same sample. Similarly, while certain organic compounds may be completely oxidised when present in solution, alone and in low concentrations, the oxidation may be hindered or inhibited when the same organic compound is present with other compounds that are oxidised faster. The presence of oxidising agents in samples reduces the COD values determined.

Interferences are known to occur with the oxidation, especially when chloride is present. For instance, chlorine may be formed, which although an oxidising agent, may be lost by volatilisation. Similarly, with many organic compounds and their partially oxidised intermediates. In the presence of large amounts of chloride, the presence of ammonia and certain amines may lead to falsely high COD values being determined. Chlorine reacts with these types of nitrogen compounds to form chloramines. Chloramines are then decomposed to give chloride, which is then re-oxidised to form chlorine. If not suppressed, chloride will cause positive bias, the magnitude of which depends on the concentration of chloride and the COD value of the sample. Using standard solutions of potassium hydrogen phthalate, the interference effects decrease as the true COD values increase. This is probably due to the reduction in the amount of residual dichromate in the refluxing mixture. In addition, the reaction temperature, which is dependent on many variables, including reaction mixture composition, apparatus design, the degree of immersion of the digest solution in the heater, etc, is important, as this and other factors affect the reaction rates, oxidation potential and volatilisation capability.

In methods A and B, mercury is used to suppress the effect of chloride. In methods C, D and E, silver is used as a catalyst, with chromium(III) and extra silver to suppress the effects of chloride. The effects of chloride may be reduced by treating the sample with silver nitrate solution, which precipitates silver chloride, which may then be removed from the sample mixture before the COD determination is carried out. Method C has been used in the past to determine the COD of samples with low values in the presence of

chloride, however, the use of methods A or B in this booklet may now be more appropriate, especially for the determination of COD values of final sewage effluents. It has also been shown that procedures involving closed tubes, as opposed to open-tube procedures, have resulted in the reporting of higher COD values. This is probably because closed tubes prevent the loss of volatile compounds, which may be lost when open-tube systems are used. Similar situations also arise when mixed reagents are employed instead of the addition of individual reagents. Falsely high COD values are obtained when pre-mixed reagents are added to the sample.

Whilst methods A and B can be adapted to a spectrophotometric end point determination, this is not usually the case with methods C, D and E. This is due to the high concentrations of chromium(III) and to the turbidity of resulting mixtures. In addition, when a spectrophotometric end point determination is employed, particular care needs to be taken to ensure a suitable solution is obtained which can be spectrophotometrically measured. Factors, such as turbidity, quality of (spectrophotometric) tubes, the matrix being analysed, etc are important considerations. Furthermore, extra work to investigate matrix and other interference effects due to the sample should be undertaken to ensure correct calibration is produced. There are several commercially available test-kits for determining COD values spectrophotometrically. Some of these test-kits involve mercury suppression, but others do not. Users should validate these test-kits with a range of sample types and standard solutions, taking into account known or suspected interferences.

The robustness and reliability of the test, especially for methods B, D and E where only 2 ml or 2.5 ml of sample are analysed, is dependent on the representative nature of the sample and any dilutions made on the sample. The use of a 10-ml aliquot of the sample may be more appropriate where the particulate matter of a sample is high. Where 2-ml or 2.5-ml aliquots are used, it should be ensured that the volume is representative of the bulk of the sample. This is particularly important where samples of an in-homogeneous nature are taken for analysis. Attempts to homogenise such samples, especially those containing volatile compounds, may result in the loss of volatile material, or the formation of films, which may adhere to the sampling equipment.

COD tests are required for compliance purposes for a number of EU directives. For substances that are soluble in water, solutions of known concentrations can be examined by any of the procedures described. Whilst this is generally not possible for insoluble and sparingly soluble substances the procedures can be modified to carry out meaningful COD determinations on such materials.

2 Sample collection, preservation and storage

It is as essential to follow agreed sampling procedures, as it is to follow agreed analytical procedures. A sample for analysis should be as representative as possible of the bulk sample from which it is taken. For in-homogeneous material, the initial sample should be sufficient to enable a representative sample to be taken and that a representative analysis can be made. If sampling is undertaken for investigatory purposes, consideration should be given as to whether or not any anomalous material should be included or excluded, or sampled and analysed separately. In addition, any air space above the sample should be kept to a minimum. More specific information on sampling and sampling techniques can be found elsewhere in this series⁽³⁾.

Care should be taken to ensure that sampling equipment does not react with or

contaminate the sample. Details of the procedures used should be recorded with the result for COD determinations on samples that have been filtered or allowed to settle. For example, the supernatant liquid (taken below any floating solids) or filtrate or centrifuged sample, with or without pH adjustment undertaken on the sample, may be used for the COD determination.

The failure to store samples correctly, or to have them analysed as soon as possible may lead to erroneous results being determined. Samples should be stored in suitable containers. Changes can be inhibited by refrigerating the sample at a temperature between 2 - 5 °C, or by reducing the pH to a value between 1 - 2 with sulphuric acid. The time for which preservation is effective should be established for each type of sample, as this may vary from a few hours to several days. Sample preservation procedures should be validated before being used routinely. The analyst should be aware of any preservative added before commencing the analysis.

In order to ensure that aliquots of the sample are representative, samples containing large amounts of suspended solid material should be homogenised before any portion is removed. Care should be taken to prevent the loss of volatile compounds, either by cooling the sample or by careful choice of the design of equipment used. If solid material is present, it should be separated from the sample and, if necessary, analysed separately.

Oily samples, especially emulsions, show a tendency to leave a surface film of grease on sample bottles and sampling equipment. Careful temperature control and the possibility of conditioning the glassware (by pre-rinsing) may sometimes avoid significant losses. If possible, oil should not be included in the sample and should be analysed separately, if required.

For samples requiring dissolved COD, the sample should be filtered before preservation of the sample is carried out. In addition, precautions should be taken to avoid contamination from the filter paper or from the atmosphere, and the use of membrane glass-fibre filters may be more appropriate. If volatile compounds are known or suspected of being present consideration should be given as to whether the sample should be filtered and if so, suction should not be applied. Where necessary, the filtration rate should be increased by applying inert gas pressure to the sample. Allowing the sample sufficient time to settle may be useful, but should only be considered if microbial action does not take place. Where a sample does not settle but which would settle if mixed with an inert material, filtration, dilution or pH-adjustment might be considered appropriate. Agreed procedures should, however, be followed and corrections made for any resultant volume changes.

Where samples are to be analysed by small-scale techniques, it is of paramount importance that a representative sample is taken for analysis. Homogenisation techniques may be used to pre-treat samples provided it is shown that the results produced are not unacceptably biased. Prolonged homogenisation has generally been shown to reduce the value of the COD determined.

3 Hazards

Poisonous gases may be evolved from samples which are acidified with sulphuric acid. The acidification of samples containing, for example, cyanide or sulphide should always be carried out in a fume cupboard. In addition, dangers of spillage arise if the sample contains carbonate. Acidification should, therefore, be conducted in a fume cupboard. Addition of concentrated sulphuric acid to water should always be carried out with care and with

gentle swirling of the contents of the flask. The methods described involve the handling of boiling, concentrated solutions of sulphuric acid and potassium dichromate. Protective equipment is essential. In the event of spillage, immediate rinsing with copious amounts of clean water is generally the most effective remedy. Adsorbents are also available which facilitate removal of the bulk of the spillage. Inhalation and ingestion of dichromate dust should be avoided. Care is required when preparing and handling concentrated solutions containing silver or dichromate as these salts are toxic.

In closed-tube methods, the tubes are under pressure during and immediately after the heating stage. Care should, therefore, be exercised when handling, sealing or unsealing tubes, the opening of which should always be directed away from staff. The closure, heating, removal from the heating block, and subsequent opening of closed tubes after cooling should be carried out behind a protective screen in a well ventilated hood. Care should be taken when opening the tubes so that any build-up of pressure is released gently and in a controlled manner.

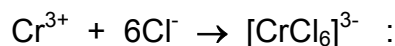
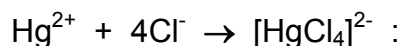
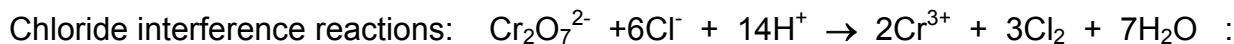
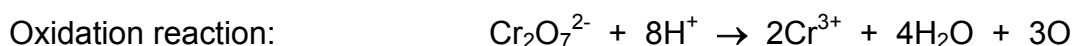
Sealed tubes that contain only water should not be placed in heating blocks as excessive pressures can be generated. In these circumstances, the contents of such tubes may boil explosively if the tubes are opened, or break. The resulting steam will be super-heated.

The disposal of silver and mercury are notifiable wastes and should be recovered from used solutions and not discarded down the drain. Alternatively, residues should be sent to authorised dealers for proper disposal.

4 Principle

The COD test is an empirical test and is applicable to almost any aqueous sample as an index of pollution. The test is not subject to inhibition by toxic components that would be affected by tests that are dependent upon biochemical oxidation. Samples are oxidised in a defined manner by refluxing with sulphuric acid and potassium dichromate. Silver is added to catalyse the oxidation of certain compounds, such as alcohols and low molecular weight acids. Mercury is added to suppress the effects of chloride and ammonia. In the mercury-free methods, chromium(III) is added, as chromium(III) potassium sulphate, which together with excess silver suppresses chloride interference and the effects due to the presence of ammonia. The resulting mixture is refluxed for two hours and residual dichromate is determined by titration with standardised iron(II) ammonium sulphate solution or spectrophotometrically. The amount of dichromate reduced is expressed as COD in the form of milligrams of oxygen consumed per litre of sample. Blank and analytical quality control determinations should always be undertaken with every batch of samples.

The reactions taking place during the oxidation can be expressed by the following series of equations.



5 Analytical quality control solutions

A variety of analytical quality control solutions may be used to challenge the oxidation procedure. Some of these solutions are more difficult to oxidise than others and may not achieve 100 % oxidation in the procedure. It may be that these solutions offer an alternative to the use of potassium hydrogen phthalate solution which may be more appropriate for use as a standard solution rather than as an AQC solution.

Analytical quality control solution	Concentration (mg l^{-1}) equivalent to 1000 mg l^{-1} COD
Sodium oxalate	8.376
Sodium acetate trihydrate	2.126
Succinic acid	1.054
Glucose	0.938

A variety of AQC solutions have been tested with two commercially available closed-tube systems in the COD ranges 0 - 150 mg l^{-1} and 0 - 1500 mg l^{-1} . Results are shown below and expressed as a percentage recovery of concentrations (in each range) of 50 mg l^{-1} and 500 mg l^{-1} respectively.

	Hach 0 - 150 mg l^{-1}	Hach 0 - 1500 mg l^{-1}	Palintest 0 - 150 mg l^{-1}	Palintest 0 - 1500 mg l^{-1}
Sodium oxalate	100	100	100	100
Sodium acetate trihydrate	94	98	90	100
Succinic acid	94	99	91	100
Glucose	100	100	100	100

Data provided by Palintest

A A reference large scale (10 ml) flask digestion procedure with mercury suppression

A1 Performance characteristics of the method

A1.1	Range of application	Up to a COD value of 400 mg l ⁻¹ . The range can be extended by dilution of the sample with water.
A1.2	Standard deviation	See Table A1.
A1.3	Limit of detection	Typically, 5 - 15 mg l ⁻¹ .
A1.4	Sensitivity	1 ml of 0.025 M iron(II) ammonium sulphate is equivalent to 20 mg l ⁻¹ COD.
A1.5	Bias	See Table A1.
A1.6	Interferences	See Table A2.
A1.7	Time required for analysis	Typically, the total analytical time for 1 - 10 samples is about 3 hours.

A2 Reagents

Except where otherwise stated, analytical reagent grade chemicals should be used. Reagents should be stored in glass bottles. All reagents, with the exception of iron(II) ammonium sulphate solution, may be stored at room temperature for up to one month. Commercially available mixtures are obtainable for many of the reagents described. Unacceptable blank values are usually caused by the oxygen demand of the water or sulphuric acid, or the use of dirty apparatus.

A2.1 Water. Water used for blank determinations and preparation of control standards should show negligible interference. Water with conductivity of less than 2 µS cm⁻¹ and total organic carbon content of less than 1 mg l⁻¹ has been shown to be satisfactory. Glassware used for the preparation and storage of water should be cleaned with chromic acid solution.

A2.2 Concentrated sulphuric acid (SG 1.84).

A2.3 Potassium dichromate solution (0.02083 M, i.e. M/48). To a 1000-ml volumetric flask, add 6.129 ± 0.001 g of potassium dichromate (previously dried for one hour at 140 - 150 °C). To the flask, add approximately 950 ml of water (A2.1) and mix the contents to dissolve. Make to 1000 ml with water, stopper and mix well.

A2.4 Silver sulphate in sulphuric acid (10 g l⁻¹). To a glass bottle, add 10.0 ± 0.1 g of silver sulphate and 1000 ± 10 ml of sulphuric acid (A2.2) and stopper. To obtain a satisfactory solution, swirl the initial mixture and allow it to stand overnight. Swirl the contents again until all the silver sulphate dissolves. This solution may be stored in the dark at room temperature for up to an indefinite period.

A2.5 1:10 phenanthroline iron(II) indicator solution ("Ferroin" indicator). Dissolve 3.5 ± 0.1 g of iron(II) sulphate heptahydrate in 500 ± 1 ml of water (A2.1). Add 7.4 ± 0.1 g of 1:10 phenanthroline monohydrate, and mix the contents to dissolve. This reagent may be obtained commercially. During the titration using 0.025 M iron(II) ammonium sulphate solution (A2.6) this indicator solution transfers a small amount of iron(II) to the titration flask. Thus, no more than 2 drops (i.e. 0.1 ml) of indicator solution should be used. Titrations should be made to the same colour end-point using equal amounts of indicator solution.

A2.6 Iron(II) ammonium sulphate solution (approximately 0.025 M). To a 1000-ml volumetric flask, add approximately 9.8 g of iron(II) ammonium sulphate hexahydrate to approximately 100 ml of water (A2.1). Add 20.0 ± 0.5 ml of sulphuric acid (A2.2) and swirl the mixture to dissolve the solid. Cool the solution and make to 1000 ml with water (A2.1). Stopper and mix the contents. This solution is not stable and should be prepared freshly on the day of use, and standardised prior to use.

Standardise the iron(II) ammonium sulphate solution against 0.02083 M potassium dichromate solution (A2.3) using the following procedure. To approximately 60 ml of water (A2.1) add 5.00 ± 0.05 ml of 0.02083 M potassium dichromate solution (A2.3). Carefully, add 15.0 ± 0.5 ml of sulphuric acid (A2.2) mix and cool the solution. Add no more than two drops of indicator solution (A2.5) and titrate to the end-point with the iron(II) ammonium sulphate solution to be standardised. Towards the end-point of the titration (see section A4.3.1, note f) the addition of the iron(II) ammonium sulphate solution (A2.6) from a narrow-bore burette, in quantities of 0.01 - 0.05 ml, facilitates the detection of the end-point. The titre should be approximately 25 ml.

The molarity, M, of the iron(II) ammonium sulphate solution (A2.6) is given by

$$M = 0.625 / V$$

where V is the volume (ml) of iron(II) ammonium sulphate solution.

Alternatively, $M = (0.020833 \times 30) / V$ or $M = 5 / (8 \times V)$.

A2.7 Mixed reagent. To a 2-litre flat bottomed borosilicate flask, add 250 ± 10 ml of water (A2.1). Carefully, add 1.53 ± 0.01 g of potassium dichromate and 7.5 ± 0.5 g of silver sulphate. Swirl the contents of the flask to mix. Cautiously, with frequent swirling of the flask, add 750 ± 25 ml of sulphuric acid (A2.2). The contents of the flask should be well mixed in order to dissolve the silver sulphate completely. Allow the solution to stand overnight in the dark. Swirl the flask before use. This mixed reagent may be stored at room temperature for up to 3 months in a stoppered bottle in the dark, but rapidly deteriorates in daylight. Owing to a volume reduction on pre-mixing, 18.5 ml of this solution is equivalent to the addition of separate volumes of 5 ml of potassium dichromate solution (A2.3) and 15 ml of silver sulphate solution (A2.4).

A2.8 Mercury(II) sulphate solution (20 %). Cautiously, add 50 ± 2 ml of sulphuric acid (A2.2) to 450 ± 5 ml of water (A2.1). To this solution, add 100 ± 1 g mercury(II) sulphate. Stir the mixture until the solid dissolves.

A2.9 Analytical quality control solution. For example, the following AQC solution of potassium hydrogen phthalate gives a theoretical COD value of 400 mg l^{-1} . To a 1000-ml volumetric flask, add 0.340 ± 0.001 g of potassium hydrogen phthalate (previously dried at 105°C for 2 hours) to approximately 950 ml of water (A2.1). Make to 1000 ml with water

(A2.1). This solution may be stored, without freezing, in a refrigerator for up to one month. An alternative solution may however be more appropriate, see section 5.

A2.10 Chromic acid used for cleaning. Alternatively, 50 % nitric acid may be used.

A3 Apparatus

High blank values may result from the presence of trace amounts of contaminants in the boiling flask, the reflux condenser or on the anti-bumping granules. Apparatus should be cleaned (on repeated occasions) by boiling with fresh dichromate/sulphuric acid/silver sulphate mixture until low and consistent blank values are obtained. Apparatus should be reserved solely for COD determinations. Glassware should have standard ground glass joints where appropriate and grease should not be used. When rinsed with water between use, the digestion apparatus should be drained and dried at 105 °C. The use of wet apparatus may cause loss of precision. To improve precision, volumetric glassware should be grade B or better.

A3.1 Boiling flask (150 ml). A distillation tray capable of holding all the contents of the boiling flask in the event of breakage during the digestion stage may also be useful.

A3.2 Pipettes and burette.

A3.3 Water-cooled condenser. For example, at least 150 mm, capable of being easily rinsed. A protective cap for the condenser helps to keep out dust when not in use. For example a small beaker may be satisfactory.

A3.4 Anti-bumping granules. All anti-bumping granules should be pre-cleaned by using the same digestion procedure.

A3.5 Uniform heating. It is essential to maintain gentle boiling under reflux. Point-sources of heating are unsatisfactory. No part of the flask should be heated to a temperature in excess of the temperature of the refluxing liquid as decomposition of dichromate commences at temperatures only slightly above this. This will lead to high results being determined.

A4 Analytical procedure

Step	Procedure	Notes
A4.1 Determination of chloride		
A4.1.1	Determine the chloride ⁽⁴⁾ content in the sample, see note a.	(a) If the chloride content of the sample is greater than 500 mg l ⁻¹ , continue as described in section A6.
A4.2 Digestion		
A4.2.1	See note b. Add several anti- bumping granules (A3.4) to the boiling flask (A3.1) and	(b) If the COD of the sample is known or expected to be above

add 10.0 ± 0.1 ml of sample or diluted sample, see note c.

400 mg l^{-1} the sample should be diluted with water. The dilution should be such that the titration of a 10-ml aliquot requires between approximately 5 - 20 ml of iron(II) ammonium sulphate solution (A2.6). If the amount of chloride in a 10-ml aliquot of diluted sample is more than 5 mg then go to section A6.2.1.

(c) At least two blank solutions (containing no sample) and an AQC sample (A2.9) should also be analysed.

A4.2.2 Add 1.0 ± 0.1 ml of mercury(II) sulphate solution (A2.8) and swirl the flask.

A4.2.3 To the flask, add 5.00 ± 0.01 ml of potassium dichromate solution (A2.3) followed by 15.0 ± 0.5 ml of silver sulphate-sulphuric acid solution (A2.4) see note d.

(d) Run the silver sulphate-sulphuric acid solution down the side of the flask whilst gently swirling and cooling the flask under running cold water. This procedure reduces loss of volatile compounds.

A4.2.4 Fit the condenser and gently boil under reflux for 120 ± 10 minutes (note e).

(e) Excessive reflux times will result in high blank values.

A4.2.5 Remove the flask and condenser from the source of heat and allow the contents to cool for approximately 10 minutes. Rinse the condenser with 25 ± 5 ml of water (A2.1) and allow the rinsings to collect in the flask. Disconnect the flask from the condenser and cool the flask and contents to below 20°C in running water.

A4.3 Determination of residual dichromate

A4.3.1 Add no more than two drops (0.1 ml) of indicator solution (A2.5) to the flask and titrate the residual dichromate with iron(II) ammonium sulphate solution (A2.6) (note f).

(f) After the first addition of iron(II) ammonium sulphate solution, the solution is blue-green in colour. During titration, the flask should be well mixed. The end-point of the titration occurs when the colour changes sharply from deep blue to pink. The blue colour may re-appear a few moments later but this should be ignored. This is especially common with samples high in chloride. See Figure A1.

A5 Calculation

The blank value should be the average of at least two determinations. If any blank value differs by more ± 0.5 ml from the average value it should be rejected. In these circumstances, it may be necessary to determine additional blank values.

An acceptable blank determination should require at least 23.5 ml of 0.025 M iron(II) ammonium sulphate solution (A2.6) in the titration. In addition, the difference between a refluxed blank value and an un-refluxed blank value should not exceed 1.5 ml of 0.025 M iron(II) ammonium sulphate solution (A2.6).

Standard chloride solutions may also need to be analysed to establish potential interference effects especially where samples are analysed and low COD values are obtained.

The analysis of AQC samples, for example solutions of potassium hydrogen phthalate (A2.9) or other appropriate solutions establishes that correct procedures are being followed.

The COD of the sample is given by

$$\text{COD} = 800 \times \text{DF} \times M (V_b - V_s) \quad \text{mg l}^{-1}$$

where

V_b is the average volume (ml) of iron(II) ammonium sulphate solution (A2.6) used in the titration of blank solutions (A4.3.1);

V_s is the volume (ml) of iron(II) ammonium sulphate solution (A2.6) used in the titration of the sample (A4.3.1);

DF is the dilution factor, if appropriate (note b, section A4.2.1);

M is the molarity of standardised iron(II) ammonium sulphate solution (A2.6).

A6 Chloride interference

The following procedure is applicable to samples for which the 10-ml aliquot taken for analysis contains more than 5 mg of chloride and employs additional mercury(II) sulphate such that the ratio of mercury(II) sulphate to chloride is 40 to 1.

Step	Procedure	Notes
A6.1	Determination of chloride	
A6.1.1	Following the determination of chloride in the sample, calculate the amount of chloride in 10 ml of sample, note g.	(g) If the amount is less than 5 mg continue as described in section A4.2.
A6.2.1	Add several anti-bumping granules (A3.4) to the boiling flask (A3.1) and add 10.0 ± 0.1 ml of sample or diluted sample, see	(h) Ensure that the blank and AQC solutions (A2.9) contain the same amount of mercury(II) sulphate as

note c. To the flask, add solid mercury(II) sulphate equal to forty times the mass of chloride in the 10-ml aliquot (note h). Swirl the flask vigorously for approximately 2 minutes. Continue as described in section A4.2.3.

used for the 10-ml aliquot of sample or diluted sample.

A7 Modified procedure using mixed reagents

For laboratories where very large numbers of samples, or where samples containing volatile compounds, are analysed for COD, the following procedure, using a mixed reagent, reduces the manipulative work per sample. However, the possibility that higher COD values may be obtained should be recognised.

Step	Procedure	Notes
A7.1	Digestion	
A7.1.1	Add several anti-bumping granules (A3.4) into the boiling flask (A3.1). Add 10.0 ± 0.1 ml of sample or diluted sample (note i). Add 1.0 ± 0.1 ml of mercury(II) sulphate solution (A2.8) and swirl the flask. Carefully add 18.5 ± 0.2 ml of mixed reagent (A2.7) swirling the flask gently. Continue as described in A4.2.4.	(i) The effects due to chloride and any dilution should be taken into account.

Figure A1 Colour of solutions before and after digestion and titration



Before digestion



Following digestion



Immediately before
titration end-point



Immediately following
titration end-point

Table A1 Performance data

Sample type	COD (mg l ⁻¹)	S _t (mg l ⁻¹)	RSD (%)	Bias (%)	DOF
synthetic solution	64	1.7-6.6			
synthetic solution	400	1.4-6.2			
sewage effluent	64	2.3-5.2			
trade effluent	312	3.5-9.8			
synthetic solution	250	3.3	1.3	-0.7	28
synthetic solution	250	2.4	1	-0.6	23
synthetic solution	250	3.3	1.3	-0.6	29
synthetic solution	250	3.7	1.5	-0.9	29
synthetic solution	80	1.7-6.6			5
synthetic solution	400	1.4-6.2			5
effluent	80	2.3-5.2			4
effluent	400	3.5-9.8			4
synthetic solution	400	4.2	1.1		
synthetic solution	350	7.0	2.1	-1.8	183
synthetic solution	64	5.1	8	-2.2	10
synthetic solution	400			-1.5	730
distilled water	-	1.6			64
synthetic solution	290	4.1	1.4	-2.3	89
effluent	398	1.6	4	0.2	51
effluent	371	5.5	1.5	0.5	89
synthetic solution	250	6.5	2.6	-0.8	33
synthetic solution	250	6.9	3.4	0.1	32
synthetic solution	210	5.1	2.4	-1.2	46
synthetic solution	240	6.1	2.6	-0.2	21
synthetic solution	252	8.3	3.3	-1.4	49
synthetic solution	200	5.4	2.7	-2.8	254

Synthetic solutions comprised standard solutions of potassium hydrogen phthalate in distilled water.

S_t is total standard deviation: RSD is relative standard deviation: DOF is degrees of freedom.

Data provided by various effluent water authority laboratories.

Table A2 Chloride interference using procedures described in section A4.2.2

COD (mg l ⁻¹)	Deviation on COD value (mg l ⁻¹) Amount of chloride in 10 ml aliquot (mg)			
	5	10	15	20
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.

B A small scale (2 ml) closed-tube digestion procedure with mercury suppression and spectrophotometric determination

In order to reduce the amount of mercury disposed to the environment, it may be more appropriate to use methods C, D or E for samples with COD values above 300 mg l⁻¹.

B1 Performance characteristics of the method

B1.1	Ranges of application	Two ranges of up to 160 mg l ⁻¹ COD and 1600 mg l ⁻¹ COD. The range can be extended up to 3200 mg l ⁻¹ by dilution of the sample with water.
B1.2	Standard deviation	See Table B1.
B1.3	Limit of detection	Typically, 10 mg l ⁻¹ .
B1.4	Sensitivity	0.01 absorbance units is equivalent to 3 mg l ⁻¹ COD in the 160 mg l ⁻¹ range and 20 mg l ⁻¹ COD in the 1600 mg l ⁻¹ range.
B1.5	Bias	See Table B1.
B1.6	Interferences	Chloride interferes above 500 mg l ⁻¹ , see Table B2.
B1.7	Time required for analysis	Typical total analytical time for 1 - 20 samples is about 3 hours.

B2 Reagents

Except where otherwise stated, analytical reagent grade chemicals should be used. Reagents should be stored in glass bottles. All reagents may be stored at room temperature for up to one month, except where specified. Commercially available mixtures are obtainable for many of the reagents described. Unacceptable blank values are usually caused by the COD of the water or sulphuric acid, or the use of dirty apparatus.

B2.1 Water. Water used for blank determinations and preparation of control standards should show negligible interference. Water with conductivity of less than 2 µS cm⁻¹ and total organic carbon content of less than 1 mg l⁻¹ has been shown to be satisfactory. Glassware used for the preparation and storage of water should be cleaned with chromic acid solution.

B2.2 Concentrated sulphuric acid (SG 1.84).

B2.3 Potassium dichromate solution (0.00833 M, i.e. M/120) for 160 mg l⁻¹ range. To a 1000-ml volumetric flask, add 2.451 ± 0.001 g of potassium dichromate (previously dried for one hour at 140 - 150 °C). To the flask, add approximately 950 ml of water (B2.1) and mix the contents to dissolve. Make to 1000 ml with water, stopper and mix well.

B2.4 Potassium dichromate solution (0.0833 M , i.e. $\text{M}/12$) for 1600 mg l^{-1} range. To a 1000-ml volumetric flask, add $24.51 \pm 0.01\text{ g}$ of potassium dichromate (previously dried for one hour at $140 - 150\text{ }^{\circ}\text{C}$). To the flask, add approximately 950 ml of water (B2.1) and mix the contents to dissolve. Make to 1000 ml with water, stopper and mix well.

B2.5 Silver sulphate in sulphuric acid (10 g l^{-1}). To a glass bottle, add $10.0 \pm 0.1\text{ g}$ of silver sulphate and $1000 \pm 10\text{ ml}$ of sulphuric acid (B2.2) and stopper. To obtain a satisfactory solution, swirl the initial mixture and allow it to stand overnight. Swirl the contents again until all the silver sulphate dissolves. This reagent may be stored in the dark at room temperature for up to an indefinite period.

B2.6 Mixed reagent for 160 mg l^{-1} range. To a 2-litre flat-bottomed borosilicate flask, add $250 \pm 10\text{ ml}$ of water (B2.1). Carefully, add $0.612 \pm 0.001\text{ g}$ of potassium dichromate and $7.5 \pm 0.5\text{ g}$ of silver sulphate. Swirl the contents of the flask to mix. Cautiously, with frequent swirling, add $750 \pm 25\text{ ml}$ of sulphuric acid (B2.2). The contents of the flask should be well swirled, in order to dissolve the silver sulphate completely. Allow the solution to stand overnight in the dark. Swirl the solution again before use. This mixed reagent may be stored in the dark in a glass bottle, with a polytetrafluoroethylene-lined or glass stopper at room temperature for up to 3 months, but rapidly deteriorates in daylight. Owing to a volume reduction on pre-mixing, 3.7 ml of this solution is equivalent to the addition of separate volumes of 1 ml of potassium dichromate solution (B2.3) and 3 ml of silver sulphate solution (B2.5).

B2.7 Mixed reagent for 1600 mg l^{-1} range. To a 2-litre flat-bottomed borosilicate flask, add $250 \pm 10\text{ ml}$ of water (B2.1). Carefully, add $6.12 \pm 0.01\text{ g}$ of potassium dichromate and $7.5 \pm 0.5\text{ g}$ of silver sulphate. Swirl the contents of the flask to mix. Cautiously, with frequent swirling of the solution, add $750 \pm 25\text{ ml}$ of sulphuric acid (B2.2). The contents of the flask should be well swirled, in order to dissolve the silver sulphate completely. Allow the solution to stand overnight in the dark. Swirl the solution again before use. This mixed reagent may be stored in the dark in a glass bottle, with a polytetrafluoroethylene-lined or glass stopper at room temperature for up to 3 months, but rapidly deteriorates in daylight. Owing to a volume reduction on pre-mixing, 3.7 ml of this solution is equivalent to the addition of separate volumes of 1 ml of potassium dichromate solution (B2.4) and 3 ml of silver sulphate solution (B2.5).

B2.8 Mercury(II) sulphate solution (20%). Cautiously, add $50 \pm 2\text{ ml}$ of sulphuric acid (B2.2) to $450 \pm 5\text{ ml}$ of water (B2.1). To this solution, add $100 \pm 1\text{ g}$ mercury(II) sulphate. Stir the solution until the solid dissolves.

B2.9 Standard solution (theoretical equivalent to 4000 mg l^{-1} COD). To a 1000-ml volumetric flask, add $3.40 \pm 0.01\text{ g}$ of potassium hydrogen phthalate (previously dried at $105\text{ }^{\circ}\text{C}$ for 2 hours) to approximately 950 ml of water (B2.1). Make to 1000 ml with water (B2.1). This solution may be stored, without freezing, in a refrigerator for up to one month.

B2.10 Standard solution (theoretical equivalent to 400 mg l^{-1} COD). To a 1000-ml volumetric flask, add $0.340 \pm 0.001\text{ g}$ of potassium hydrogen phthalate (previously dried at $105\text{ }^{\circ}\text{C}$ for 2 hours) to approximately 950 ml of water (B2.1). Make to 1000 ml with water (B2.1). This solution may be stored, without freezing, in a refrigerator for up to one month. An alternative solution may be more appropriate as an AQC sample, see section 5.

B2.11 Chromic acid used for cleaning. Alternatively, 50% nitric acid may be used.

B3 Apparatus

High blank values may result from the presence of trace amounts of contaminants in the boiling tube. Apparatus should be cleaned by boiling with fresh dichromate, sulphuric acid and silver sulphate mixture (on repeated occasions) until low and constant blank values are obtained. Apparatus should be reserved solely for COD determinations. Between use the digestion tubes should be rinsed with water, drained and dried at 105 °C. The use of wet apparatus may cause loss of precision. To improve precision volumetric glassware should be grade B or better.

B3.1 Pipettes and burette. Graduated pipettes capable of dispensing 1.00 ± 0.01 ml, 2.00 ± 0.02 ml, 0.20 ± 0.02 ml and up to 4.00 ± 0.05 ml, and burette graduated in 0.10 ml divisions.

B3.2 Heating source. Thermostatically controlled heating block capable of accommodating the digestion tubes such that the level of the liquid in the tube is coincident with or below the surface of the block. The block should be controlled to give a digest temperature sufficient to gently reflux the oxidation mixture. A temperature of 150 ± 3 °C is suitable. Care should be taken to ensure that the temperature within the block does not rise above this temperature. An alternative heating source for the closed-tube procedure is a suitably controlled air oven.

B3.3 Tubes for closed-tube digestion. Many types of tubes have been shown to be suitable. The main criteria are that the tubes can be heated, cooled, and removed from the heater without risk of bursting or spillage of contents. The test data in the tables were obtained using borosilicate-glass culture vials 125 x 16 mm with plastic screw cap and polytetrafluoroethylene liner. Tubes with any noticeable defect should be discarded. Many commercial systems are available where the tube is used only once and then discarded or recycled according to documented procedures, or returned to the manufacturer.

B3.4 Spectrophotometer or colourimeter. Capable of operating at wavelengths of 420 - 450 nm, and 600 - 620 nm and with cell holder capable of accepting appropriate tubes or glass vials.

B4 Analytical procedure

The digestion procedure described in this method is based on a 1:5 scaled-down version of the flask procedure described in method A. Residual dichromate is determined spectrophotometrically.

Step	Procedure	Notes
B4.1	Determination of chloride	
B4.1.1	Determine the chloride ⁽⁴⁾ content in the sample, see note a.	(a) If the chloride content of the sample is greater than 500 mg l ⁻¹ , dilute accordingly so that 2 ml of diluted sample contains no more than 1 mg of chloride. See section B6. Dilution of the sample to eliminate chloride interference may need to be balanced against reducing the expected COD value to too low a value.

B4.2 Standard solutions

Depending on the expected COD value carry out the appropriate procedure described in B4.2.1 or B4.2.2.

B4.2.1 Into separate 100-ml volumetric flasks, add (to ± 0.01 ml) 0.0, 5.0, 10.0, 15.0, 20.0, 25.0, 30.0, 35.0 or 40.0 ml of potassium hydrogen phthalate solution (B2.10). Make each flask to 100 ml with water (B2.1). These solutions are equivalent to 0, 20, 40, 60, 80, 100, 120, 140 and 160 mg l⁻¹ COD respectively when used as described as below.

B4.2.2 Into separate 100-ml volumetric flasks, add (to ± 0.1 ml) 0.0, 5.0, 10.0, 15.0, 20.0, 25.0, 30.0, 35.0 or 40.0 ml of potassium hydrogen phthalate solution (B2.9). Make each flask to 100 ml with water (B2.1). These solutions are equivalent to 0, 200, 400, 600, 800, 1000, 1200, 1400 and 1600 mg l⁻¹ COD respectively when used as described as below.

B4.2.3 Add 2.00 ± 0.02 ml of each standard solution (B4.2.1 or B4.2.2 as appropriate depending on range) to a boiling tube and carry out the closed-tube digestion procedure (B4.3) and determination of dichromate (B4.4).

B4.2.4 Prepare a calibration curve of absorbance (at the appropriate wavelength, see note g) against equivalent COD concentration.

B4.3 Closed-tube digestion

B4.3.1 See note b. Add 2.00 ± 0.02 ml of sample or diluted sample to the boiling tube (B3.3). See note c

(b) If the COD value of the sample is known or expected to be above the range identified in B4.2.1 or B4.2.2 the sample should be diluted with water (B2.1).

(c) At least three reagent blanks containing 2.00 ± 0.01 ml water (B2.1)

in place of sample should also be analysed and an AQC sample (B2.10).

B4.3.2 Add 0.20 ± 0.02 ml of mercury(II) sulphate solution (B2.8) and swirl the tube to mix the contents.

B4.3.3 To the tube, add 1.00 ± 0.01 ml of potassium dichromate solution (B2.3 or B2.4 depending on range) followed by 3.00 ± 0.05 ml of silver sulphate-sulphuric acid solution (B2.5) see note d.

(d) Run the silver sulphate - sulphuric acid solution down the side of the tube whilst gently swirling the contents and cooling the tube under running cold water. This procedure reduces loss of volatile compounds.

B4.3.4 Close the tube securely, swirl the tube to mix the contents. and place in the heating source (B3.4). Reflux for 120 ± 10 minutes (note e). Remove the tubes and allow the contents to cool to below 20°C for approximately 5 minutes under running water or allow to cool in a test tube rack.

(e) Excessive reflux times will result in high blank values

B4.3.5 Wipe the outside of each tube, for example with a damp cloth, to remove all extraneous matter from the optical surface of the tube, see note f. Dry with a lint-free cloth.

(f) This should eliminate interference to ensure a correct absorbance reading can be measured.

B4.4 Determination of residual dichromate

B4.4.1 Using a spectrophotometer or colorimeter (B3.4) select the appropriate wavelength for the measurement (see note g).

(g) For the 160 mg l^{-1} range greater sensitivity is achieved by measuring reduction in yellow colour at 420 - 450 nm, and determining remaining Cr^{6+} . For the 1600 mg l^{-1} range, the increase in blue colour at 600 - 620 nm determines the amount of Cr^{3+} produced.

B 4.4.2 Zero the instrument with water, and measure the absorbance of the three blanks. Determine the average value. (note h).

(h) Use any light cap or cover provided to exclude light during the measurement.

B 4.4.3 Insert the tube containing the sample or diluted sample into the cell holder and measure the absorbance (note h).

B5 Calculation

The blank tubes are most important, as all other tubes are compared with these. Three blanks are prepared and the average value absorbance determined. If any blank value differs by more ± 0.01 absorbance units from the average value it should be rejected. In these circumstances, it may be necessary to determine additional blank values.

Standard chloride solutions may also need to be analysed to establish potential interference effects especially where samples are analysed and low COD values are determined.

The analysis of AQC samples, for example standard solutions of potassium hydrogen phthalate (B2.10) or other appropriate solutions establishes that correct procedures are being followed.

B6 Chloride interference

The following procedure is applicable to samples for which the 2-ml aliquot taken for analysis contains more than 1 mg of chloride and employs additional mercury(II) sulphate such that the ratio of mercury(II) sulphate to chloride is 40 to 1.

Step	Procedure	Notes
B6.1	Closed-tube digestion	
B6.1.1	Add 2.00 ± 0.02 ml of sample or diluted sample to the boiling tube (B3.3) see note c. To the tube, add solid mercury(II) sulphate equal to forty times the mass of chloride in the 2-ml aliquot (note j). Cap the tube and shake vigorously for approximately 2 minutes. Continue as described in section B4.3.3.	(j) Ensure that the blank and AQC solutions (B2.10) contain the same amount of mercury(II) sulphate used for the 2-ml aliquot of sample or diluted sample.

B7 Modified procedure using mixed reagents

For laboratories where very large numbers of samples, or where samples containing volatile compounds, are analysed for COD, the following procedure, using a mixed reagent, reduces the manipulative work per sample. However, the possibility that higher COD values may be determined should be recognised.

Step	Procedure	Notes
B7.1	Closed-tube digestion	
B7.1.2	Add 2.00 ± 0.02 ml of sample or diluted sample (see note k) into the boiling tube (B3.3). Add 0.20 ± 0.02 ml of mercury(II) sulphate solution (B2.8) and swirl the tube. Carefully, add 3.70 ± 0.05 ml of mixed reagent (B2.6 or B2.7 as appropriate depending on the range). Continue as described in B4.3.4.	(k) The effects due to chloride and any dilution should be taken into account.

B8 Open-tube procedure

Alternatively, an open-tube procedure can be used based on the procedures described in sections B4 - B7, but utilising a colourimetric determination. Reagents and apparatus required in addition to those given in sections B2 and E3 include the following.

B8.1 1:10 phenanthroline iron(II) indicator solution. ("Ferroin" indicator). Dissolve 3.5 ± 0.1 g of iron(II) sulphate heptahydrate in 500 ± 1 ml of water (B2.1). Add 7.4 ± 0.1 g of 1:10 phenanthroline monohydrate, and mix to dissolve. This reagent may be obtained commercially. During the titration using iron(II) ammonium sulphate solution (B8.2) this indicator solution transfers a small amount of iron(II) to the titration flask. Thus, no more than 2 drops (i.e. 0.1 ml) of indicator solution should be used. Titrations should be made to the same colour end point using equal amounts of indicator solution.

B8.2 Iron(II) ammonium sulphate solution (approximately 0.008 M). To a 1000-ml volumetric flask, add approximately 3.2 g of iron(II) ammonium sulphate hexahydrate to approximately 100 ml of water (B2.1). Add 20.0 ± 0.5 ml of sulphuric acid (B2.2) and swirl the mixture to dissolve the solid. Cool and make to 1000 ml with water (B2.1). Stopper and mix well. This solution is not stable and should be prepared freshly on the day of use, and standardised prior to use.

Standardise the iron(II) ammonium sulphate solution against 0.00833 M potassium dichromate solution (B2.3) using the following procedure. To approximately 60 ml of water (B2.1) add 5.00 ± 0.05 ml of 0.00833 M potassium dichromate solution (B2.3). Carefully, add 15.0 ± 0.5 ml of sulphuric acid (B2.2) mix and cool the solution. Add no more than two drops of indicator solution (B8.1) and titrate to the end point with the iron(II) ammonium sulphate solution to be standardised. Towards the end point of the titration (see section B9.3.1, note f) the addition of the iron(II) ammonium sulphate solution (B8.2) from a narrow-bore burette, in quantities of 0.01 - 0.05 ml, facilitates the detection of the end point. The expected titre should be approximately 30 ml.

The molarity, M, of the iron(II) ammonium sulphate solution (B8.2) is given by

$$M = 0.25 / V$$

where V is the volume (ml) of iron(II) ammonium sulphate solution.

Alternatively, $M = (0.00833 \times 30) / V$ or $M = 30 / (120 \times V)$.

1 ml of 0.00833 M iron(II) ammonium sulphate is equivalent to 32 mg l⁻¹ COD.

B8.3 Tubes for open-tube digestion. Borosilicate glass tubes, for example 16 mm diameter with a 14/23 ground glass socket and a total volume of not less than 15 ml. Tubes with any noticeable defect should be discarded.

B8.4 Air condenser. For example, 13 mm diameter and not less than 150 mm long.

B8.5 Anti-bumping granules. All anti-bumping granules should be pre-cleaned by using the same digestion procedure.

B9 Analytical procedure

The digestion procedure described is based on a 1:5 scaled-down version of the flask procedure described in method A. Residual dichromate is determined colourimetrically.

Step	Procedure	Notes
B9.1	Determination of chloride	
B9.1.1	Determine the chloride ⁽⁴⁾ content in the sample, see note a.	(a) If the chloride content of the sample is greater than 500 mg l ⁻¹ , continue as described in section B11.
B9.2	Open-tube digestion	
B9.2.1	See note b. Add several anti-bumping granules (B8.5) to the boiling tube (B8.3) and add 2.00 ± 0.01 ml of sample or diluted sample, see note c.	(b) If the COD of the sample is known or expected to be above 160 mg l ⁻¹ the sample should be diluted with water. The dilution should be such that the titration of a 2-ml aliquot requires between approximately 1.2 - 5 ml of iron(II) ammonium sulphate solution (B8.2). If the amount of chloride in a 2-ml aliquot of sample or diluted sample is more than 1 mg, continue as described in section B11. (c) At least two blank solutions (containing no sample) and an AQC sample (B2.10) should also be analysed.
B9.2.2	Add 0.20 ± 0.02 ml of mercury(II) sulphate solution (B2.8) and swirl the tube to mix the contents.	

B9.2.3 To the tube, add 1.000 ± 0.005 ml of potassium dichromate solution (B2.3) followed by 3.00 ± 0.05 ml of silver sulphate-sulphuric acid solution (B2.5) see note d. Swirl the tube to mix the contents.

B9.2.4 Fit the condenser to the tube and gently boil under reflux for 120 ± 10 minutes (note e).

B9.2.5 Remove the tube and condenser from the source of heat and allow the flask and contents to cool to below 20°C in running water. Remove the condenser from the tube, rinse the condenser with approximately 2 ml of water (B2.1) and allow the rinsings to collect in a titration flask. Quantitatively transfer the contents of the tube to the titration flask, rinsing the tube as appropriate with a small amount of water.

(d) Run the silver sulphate-sulphuric acid solution down the side of the tube whilst gently swirling and cooling the tube under running cold water. This procedure reduces loss of volatile compounds.

(e) Excessive reflux times will result in high blank values.

B9.3 Determination of residual dichromate

B9.3.1 Add no more than two drops (0.1 ml) of indicator solution (B8.1) to the flask and titrate the residual dichromate with iron(II) ammonium sulphate solution (B8.2) (note f).

(f) After the first addition of iron(II) ammonium sulphate solution, the solution is blue-green in colour. During titration, the flask should be well mixed. The end point of the titration occurs when the colour changes sharply from deep blue to pink. The blue colour may reappear a few moments later but this should be ignored. This is especially common with samples high in chloride. See Figure A1.

B10 Calculation

The blank value should be the average of at least two determinations. If any blank value differs by more ± 0.1 ml from the average value it should be rejected. In these circumstances, it may be necessary to determine additional blank values. An acceptable blank determination should require at least 28.5 ml of 0.00833 M iron(II) ammonium sulphate solution (B8.2) in the titration. In addition, the difference between a refluxed blank value and an un-refluxed blank value should not exceed 1.5 ml of 0.00833 M iron(II) ammonium sulphate solution (B8.2).

Standard chloride solutions may also need to be analysed to establish potential interference effects especially where samples are analysed and low COD values are determined.

The analysis of AQC samples, for example standard solutions of potassium hydrogen phthalate (B2.10) or other appropriate solutions establishes that correct procedures are being followed. The COD of the sample is given by

$$\text{COD} = 4000 \times \text{DF} \times M (V_b - V_s) \quad \text{mg l}^{-1}$$

where

V_b is the average volume (ml) of iron(II) ammonium sulphate solution (B8.2) used in the titration of blank solutions (B9.3.1);

V_s is the volume (ml) of iron(II) ammonium sulphate solution (B8.2) used in the titration of the sample (B9.3.1);

DF is the dilution factor, if appropriate (note b, section B9.2.1);

M is the molarity of standardised iron(II) ammonium sulphate solution (B8.2)

B11 Chloride interference

The following procedure is applicable to samples for which the 2-ml aliquot taken for analysis contains more than 1 mg of chloride and employs additional mercury(II) sulphate such that the ratio of mercury(II) sulphate to chloride is 40 to 1.

Step	Procedure	Notes
B11.1 Determination of chloride		
B11.1.1	Following the determination of chloride in the sample, calculate the amount of chloride in 2 ml of sample, note g.	(g) If the amount is less than 1 mg continue as described in section B9.2.
B11.2 Open-tube digestion		
B11.2.1	Add several anti-bumping granules (B8.5) to the boiling tube (B8.3) and add 2.00 ± 0.01 ml of sample or diluted sample, see note c. To the tube, add solid mercury(II) sulphate equal to forty times the mass of chloride in the 2-ml aliquot (note h). Swirl the flask vigorously for approximately 2 minutes. Continue as described in section B9.2.3.	(h) Ensure that the blank and AQC solutions (B2.10) contain the same amount of mercury(II) sulphate as used for the 2-ml aliquot of sample or diluted sample.

B12 Modified procedure using mixed reagents

For laboratories where very large numbers of samples, or where samples containing volatile compounds, are analysed for COD, the following procedure, using a mixed reagent, reduces the manipulative work per sample. However, the possibility that higher COD values may be determined should be recognised.

Step	Procedure	Notes
B12.1	Open-tube digestion	
B12.1.1	Add several anti-bumping granules (B8.5) into the boiling tube (B8.3) and add 2.00 ± 0.01 ml of sample or diluted sample (see note i). Add 0.20 ± 0.02 ml of mercury(II) sulphate solution (B2.8) and swirl the tube. Carefully, add 3.70 ± 0.01 ml of mixed reagent (B2.6) swirling the tube gently. Continue as described in B9.2.4.	(i) The effects due to chloride and any dilution should be taken into account.

Table B1 Comparison of COD results

Method	Laboratory*	COD (mean mg l ⁻¹)	NOR	S _w
B (closed-tube)	1	108.1	10	5.2
B (closed-tube)	4	122.4	10	3.9
B (closed-tube)	5	134.2	10	4.2
B (closed-tube)	7	131.3	6	1.7
B (closed-tube)	8	123.2	10	6.7
B (open-tube)	7	122.0	10	1.7
D (closed-tube)	2	124.4	2	
D (closed-tube)	6	120.0	4	2.1
A	11	125.9	10	2.8

Standard solution of potassium hydrogen phthalate (125 mg l⁻¹ COD).

NOR is the number of results: S_w is within-batch standard deviation.

* See also the following booklet in this series.

Data provided in DOE funded report produced by Yorkshire LabServices.

Table B2 Comparison of COD results in the presence of chloride

See also Table 12B in the following booklet in this series.

Method	Laboratory	COD (mean mg l ⁻¹)	NOR	S _w
B (closed-tube)	1	109.7	9	1.5
B (closed-tube)	4	115.6	10	1.6
B (closed-tube)	5	138.5	10	4.2
B (closed-tube)	6	126.5	8	4.2
B (closed-tube)	7	126.7	6	
B (closed-tube)	8	123.9	9	3.5
B (open-tube)	7	122.7	9	1.1
D (closed-tube)	2	155.1	8	15.7
D (closed-tube)	5	126.6	2	
D (closed-tube)	6	128.7	3	
A	11	124.2	10	3.6

Standard solution of potassium hydrogen phthalate (125 mg l⁻¹ COD) in the presence of 500 mg l⁻¹ chloride
NOR is the number of results: S_w is within-batch standard deviation.

Data provided in DOE funded report produced by Yorkshire LabServices.

C A mercury-free large scale (10 ml) flask digestion using chromium(III) potassium sulphate and silver nitrate solutions

C1 Performance characteristics of the method

C1.1	Range of application	Up to 400 mg l ⁻¹ COD. The range can be extended by dilution of the sample with water.
C1.2	Standard deviation	See Tables C1 and C2. See also Table C3 for a comparison of results obtained using methods A and C.
C1.3	Limit of detection	Typically, 5 mg l ⁻¹ .
C1.4	Sensitivity	1 ml of 0.025 M iron(II) ammonium sulphate corresponds to 20 mg l ⁻¹ COD.
C1.5	Bias	See Tables C1 and C2.
C1.6	Interferences	Ammonium ion is not oxidised unless chloride is present in sufficient quantities. See Table C4.
C1.7	Time required for analysis	Typical total analytical time for 1 - 10 samples is about 3 hours.

C2 Reagents

Except where otherwise stated, analytical reagent grade chemicals should be used. Reagents should be stored in glass bottles. All reagents, with the exception of iron(II) ammonium sulphate solution, may be stored at room temperature for up to one month. Commercially available mixtures are obtainable for many of the reagents described. Unacceptable blank values are usually caused by the oxygen demand of the water or sulphuric acid, or the use of dirty apparatus.

C2.1 Water. Water used for blank determinations and preparation of control standards should show negligible interference. Water with conductivity of less than 2 µS cm⁻¹ and total organic carbon content of less than 1 mg l⁻¹ has been shown to be satisfactory. Glassware used for the preparation and storage of water should be cleaned with chromic acid solution.

C2.2 Concentrated sulphuric acid (SG 1.84).

C2.3 Potassium dichromate solution (0.02083 M, i.e. M/48). To a 1000-ml volumetric flask, add 6.129 ± 0.001 g of potassium dichromate (previously dried for one hour at 140 - 150 °C). To the flask, add approximately 950 ml of water (C2.1) and mix to dissolve. Make to 1000 ml with water, stopper and mix well.

C2.4 Silver sulphate in sulphuric acid (10 g l⁻¹). To a glass bottle, add 10.0 ± 0.1 g of silver sulphate and 1000 ± 10 ml of sulphuric acid (C2.2) and stopper. To obtain a satisfactory solution, swirl the initial mixture and allow it to stand overnight. Swirl the

contents again until all the silver sulphate dissolves. This solution may be stored in the dark at room temperature for up to an indefinite period.

C2.5 1:10 phenanthroline iron(II) indicator solution ("Ferroin" indicator). Dissolve 3.5 ± 0.1 g of iron(II) sulphate heptahydrate in 500 ± 1 ml of water (C2.1). Add 7.4 ± 0.1 g of 1:10 phenanthroline monohydrate, and mix to dissolve. This reagent may be obtained commercially. During the titration using 0.025 M iron(II) ammonium sulphate solution (C2.6) this indicator solution transfers a small amount of iron(II) to the titration flask. Thus, no more than 2 drops (i.e. 0.1 ml) of indicator solution should be used. Titrations should be made to the same colour end point using equal amounts of indicator solution.

C2.6 Iron(II) ammonium sulphate solution (approximately 0.025 M). To a 1000-ml volumetric flask, add approximately 9.8 g of iron(II) ammonium sulphate hexahydrate to approximately 100 ml of water (C2.1). Add 20.0 ± 0.5 ml of sulphuric acid (C2.2) and swirl the mixture to dissolve the solid. Cool and make to 1000 ml with water (C2.1). Stopper and mix well. This solution is not stable and should be prepared freshly on the day of use, and standardised prior to use.

Standardise the iron(II) ammonium sulphate solution against 0.02083 M potassium dichromate solution (C2.3) using the following procedure. To approximately 60 ml of water (C2.1) add 5.00 ± 0.05 ml of 0.02083 M potassium dichromate solution (C2.3). Carefully, add 15.0 ± 0.5 ml of sulphuric acid (C2.2) mix and cool the solution. Add no more than two drops of indicator solution (C2.5) and titrate to the end point with the iron(II) ammonium sulphate solution to be standardised. Towards the end point of the titration (see section C4.3.1, note g) the addition of the iron(II) ammonium sulphate solution (C2.6) from a narrow-bore burette, in quantities of 0.01 - 0.05 ml, facilitates the detection of the end point. The titre should be approximately 25 ml.

The molarity, M, of the iron(II) ammonium sulphate solution (C2.6) is given by

$$M = 0.625 / V$$

where V is the volume (ml) of iron(II) ammonium sulphate solution.

Alternatively, $M = (0.020833 \times 30) / V$ or $M = 5 / (8 \times V)$.

C2.7 Mixed reagent. To a 2-litre flat bottomed borosilicate flask, add 250 ± 10 ml of water (C2.1). Carefully, add 1.53 ± 0.01 g of potassium dichromate and 7.5 ± 0.5 g of silver sulphate. Swirl the contents of the flask to mix. Cautiously, with frequent swirling of the flask, add 750 ± 25 ml of sulphuric acid (C2.2). The contents of the flask should be well swirled in order to dissolve the silver sulphate completely. Allow the solution to stand overnight in the dark. Swirl the contents again before use. This mixed reagent may be stored at room temperature for up to 3 months in a stoppered bottle in the dark, but rapidly deteriorates in daylight. Owing to a volume reduction on pre-mixing, 18.5 ml of this solution is equivalent to the addition of separate volumes of 5 ml of potassium dichromate solution (C2.3) and 15 ml of silver sulphate solution (C2.4).

C2.8 Chromium(III) potassium sulphate solution (250 g l^{-1}). Dissolve 25.00 ± 0.01 g of chromium(III) potassium sulphate dodecahydrate ($\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$) in 100 ± 1 ml of hot water (C2.1) i.e. water above 50°C . This solution is saturated at 30°C . This solution may be stored at room temperature in a glass bottle with a polytetrafluoroethylene

stopper, for up to an indefinite period. When required for use, warm to 50 °C and stir before use, to re-dissolve any solids.

C2.9 Silver nitrate (1000 g l^{-1}). Dissolve $100 \pm 1 \text{ g}$ of silver nitrate in approximately 80 ml of water (C2.1). Warm the solution if necessary. Cool and make to $100 \pm 1 \text{ ml}$ with water (C2.1). Do not store below 10 °C as this solution is saturated at 0 °C. Stored in the dark in a stoppered glass bottle, this solution should keep indefinitely.

C2.10 Combined mixed reagent. To $185.0 \pm 0.2 \text{ ml}$ of mixed reagent (C2.7) add $4.00 \pm 0.05 \text{ ml}$ of chromium(III) potassium sulphate solution (C2.8) and mix well before use.

C2.11 Analytical quality control solution. For example, the following AQC solution of potassium hydrogen phthalate gives a theoretical COD value of 400 mg l^{-1} . To a 1000-ml volumetric flask, add $0.340 \pm 0.001 \text{ g}$ of potassium hydrogen phthalate (previously dried at 105 °C for 2 hours) to approximately 950 ml of water (C2.1). Make to 1000 ml with water (C2.1). This solution may be stored, without freezing, in a refrigerator for up to one month. An alternative solution may however be more appropriate, see section 5.

C2.10 Chromic acid used for cleaning. Alternatively, 50 % nitric acid may be used.

C3 Apparatus

High blank values may result from the presence of trace amounts of contaminants in the boiling flask, the reflux condenser or on the anti-bumping granules. Apparatus should be cleaned (on repeated occasions) by boiling with fresh dichromate/sulphuric acid/silver sulphate mixture until low and consistent blank values are obtained. Apparatus should be reserved solely for COD determinations. Glassware should have standard ground glass joints where appropriate and grease should not be used. When rinsed with water between use, the digestion apparatus should be drained and dried at 105 °C. The use of wet apparatus may cause loss of precision. To improve precision, volumetric glassware should be grade B or better.

C3.1 Boiling flask (150 ml). A distillation tray capable of holding all the contents of the boiling flask in the event of breakage during the digestion stage may also be useful.

C3.2 Pipettes and burette.

C3.3 Water-cooled condenser. For example, at least 150 mm, capable of being easily rinsed. A protective cap for the condenser helps to keep out dust when not in use. For example a small beaker may be satisfactory.

C3.4 Anti-bumping granules. All anti-bumping granules should be pre-cleaned by using the same digestion procedure.

C3.5 Uniform heating. It is essential to maintain gentle boiling under reflux. Point-sources of heating are unsatisfactory. No part of the flask should be heated to a temperature in excess of the temperature of the refluxing liquid as decomposition of dichromate commences at temperatures only slightly above this. This will lead to high results being determined.

C4 Analytical procedure

Step	Procedure	Notes
C4.1	Determination of chloride	
A4.1.1	Determine the chloride ⁽⁴⁾ content in the sample, see note a.	(a) If the chloride content of the sample is greater than 2000 mg l ⁻¹ , continue as described in section C6.
C4.2	Digestion	
C4.2.1	See note b. Add several anti- bumping granules (C3.4) to the boiling flask (C3.1) and add 0.60 ± 0.02 ml of silver nitrate solution (C2.9) and 10.0 ± 0.1 ml of sample or diluted sample, see note c. Swirl the flask to mix the contents.	(b) If the COD of the sample is known or expected to be above 400 mg l ⁻¹ the sample should be diluted with water. The dilution should be such that the titration of a 10-ml aliquot requires between approximately 5 - 20 ml of iron(II) ammonium sulphate solution (C2.6). If the amount of chloride in a 10-ml aliquot of sample or diluted sample is more than 20 mg, continue as described in section C6.2. (c) At least two blank solutions (containing no sample) and an AQC sample (C2.11) should also be analysed.
C4.2.2	Add 0.40 ± 0.05 ml of chromium(III) potassium sulphate solution (C2.8) and swirl the flask to mix the contents. To the flask, add 5.00 ± 0.03 ml of potassium dichromate solution (C2.3) followed by 15.0 ± 0.5 ml of silver sulphate-sulphuric acid solution (C2.4) see note d. Swirl the flask to mix the contents.	(d) Run the silver sulphate-sulphuric acid solution down the side of the flask whilst gently swirling and cooling the flask under running cold water. This procedure reduces loss of volatile compounds.
C4.2.3	Fit the condenser and gently boil under reflux for 120 ± 10 minutes (note e).	(e) Excessive reflux times will result in high blank values.
C4.2.4	Remove the flask and condenser from the source of heat and allow the contents to cool for approximately 10 minutes. Rinse the condenser with 25 ± 5 ml of water (C2.1) and allow the rinsings to collect in the flask. Disconnect the flask from the condenser and cool the flask to below 20 °C in running water, note f.	(f) The titrimetric end point fades unless the digest solution is titrated between 15 - 20 °C.

C4.3 Determination of residual dichromate

C4.3.1 Add no more than two drops (0.1 ml) of indicator solution (C2.5) to the flask and titrate the residual dichromate with iron(II) ammonium sulphate solution (C2.6) (note g).

(g) After the first addition of iron(II) ammonium sulphate solution, the solution is blue-green in colour. During titration of the contents, the flask should be well mixed. The end point of the titration occurs when the colour changes sharply from deep blue to pink. The blue colour may reappear a few moments later but this should be ignored. This is especially common with samples high in chloride.

C5 Calculation

The blank value should be the average of at least two determinations. If any blank value differs by more ± 0.5 ml from the average value it should be rejected. In these circumstances, it may be necessary to determine additional blank values.

An acceptable blank determination should require at least 23.5 ml of 0.025 M iron(II) ammonium sulphate solution (C2.6) in the titration. In addition, the difference between a refluxed blank value and an un-refluxed blank value should not exceed 1.5 ml of 0.025 M iron(II) ammonium sulphate solution.

Standard chloride solutions may also need to be analysed to establish potential interference effects especially where samples are analysed and low COD values are obtained.

The analysis of AQC samples, for example standard solutions of potassium hydrogen phthalate (C2.11) or other appropriate solutions establishes that correct procedures are being followed.

The COD of the sample is given by

$$\text{COD} = 800 \times \text{DF} \times M (V_b - V_s) \quad \text{mg l}^{-1}$$

where

V_b is the average volume (ml) of iron(II) ammonium sulphate solution (C2.6) used in the titration of blank solutions (C4.3.1);

V_s is the volume (ml) of iron(II) ammonium sulphate solution (C2.6) used in the titration of the sample (C4.3.1);

DF is the dilution factor, if appropriate (note b, section C4.2.1);

M is the molarity of standardised iron(II) ammonium sulphate solution (C2.6).

C6 Chloride interference

The following procedure is applicable to samples for which the 10-ml aliquot taken for analysis contains more than 20 mg of chloride.

Step	Procedure	Notes
C6.1	Determination of chloride	
C6.1.1	Following the determination of chloride in the sample, calculate the amount of chloride in 10 ml of sample, note g.	(g) If the amount is less than 20 mg continue as described in section C4.2.
C6.2	Digestion	
C6.2.1	Add several anti-bumping granules (C3.4) to the boiling flask (C3.1) and add 1.20 ± 0.05 ml of silver nitrate solution (C2.9) and 10.0 ± 0.1 ml of sample or diluted sample (note h). Swirl the flask vigorously for approximately 2 minutes.	(h) Ensure that the blank and AQC solutions contain the same amount of silver nitrate as used for the 10-ml aliquot of sample or diluted sample.
C6.2.2	Add 0.80 ± 0.05 ml of chromium(III) potassium sulphate solution (C2.8). Swirl the flask again to mix the contents. To the flask, add 5.00 ± 0.03 ml of potassium dichromate solution (C2.3) followed by 15.0 ± 0.5 ml of silver sulphate-sulphuric acid solution (C2.4) see note d. Swirl the flask to mix the contents. Continue as described in section C4.2.3, note i.	(i) If the colour change at the end point to the titration is now less easy to observe, use of a potentiometric titrator may be more appropriate.

C7 Modified procedure using mixed reagents

For laboratories where very large numbers of samples, or where samples containing volatile compounds, are analysed for COD, the following procedure, using a mixed reagent, reduces the manipulative work per sample. However, the possibility that higher COD values may be determined should be recognised.

Step	Procedure	Notes
C7.1	Digestion	
C7.1.1	Add several anti-bumping granules (C3.4) into the boiling flask (C3.1). Add 0.60 ± 0.02 ml of silver nitrate solution (C2.9) and 10.0 ± 0.1 ml of sample or diluted sample (note j). Swirl the flask and leave for approximately 2 minutes. Add 0.40 ± 0.05 ml of chromium(III) potassium sulphate solution (C2.8) and swirl the contents to mix. Carefully, add 18.50 ± 0.05 ml of mixed reagent (C2.7) swirling the flask gently. Continue as described in C4.2.3.	(j) The effects due to chloride and dilution should be taken into account.
C7.1.2	Alternatively, add several anti-bumping granules (C3.4) into the boiling flask (C3.1). Add 0.60 ± 0.02 ml of silver nitrate solution (C2.9) and 10.0 ± 0.1 ml of sample or diluted sample (note j). Swirl the flask and leave for approximately 2 minutes. Carefully, add 18.90 ± 0.05 ml of combined mixed reagent (C2.10) swirling the flask gently. Continue as described in C4.2.3.	

Table C1 Performance data

COD (mg l ⁻¹)	S _w		Bias		Number of laboratories	Batch size
	(range (mg l ⁻¹))	(mean) (mg l ⁻¹)	(range (mg l ⁻¹))	(mean) (mg l ⁻¹)		
0	0.1 to 3.3	0.9	-1.6 to 1.6	0.9	5	5-10
100	0 to 3.4	1.5	-13.4 to 4.8	-2.2	6	5-10
200	1.4 to 3.3	2.4	-12.2 to 0.6	-3.9	6	5-10
300	1.4 to 5.0	3.0	-14.6 to 5.0	-9.6	6	4-10
400	0 to 7.2	3.1	-23.4 to 0.6	-8.5	7	2-10

Based on standard solutions of potassium hydrogen phthalate.

The average mean bias is approximately -2 %.

S_w is within-batch standard deviation.

Table C2 Relative standard deviations on samples

Sample type	Mean COD (mg l ⁻¹)	Relative standard deviation (%)	Degrees of freedom
Crude sewage	47.6	3.6	4
	48	0	4
	206	0.7	4
	269	2.9	4
	346	1.7	4
	388	1.9	4
	480	3.1	4
	611	1.5	4
	617	2.2	4
	656	0.1	4
	679	1	4
Industrial effluents	9.8	9.2	4
	71.5	1.4	4
	74.4	3	4
	95.4	9.0	4
	146	1.4	4
	187	1.4	4
	216	1.1	4
	311	0.5	4
	420	2.5	4
	567	2.1	4
	1018	7.1	4
	1041	1.2	4
	2828	2.7	4
	2840	0.5	4
Sewage works effluents	36.7	8.2	4
	39.0	4.6	4
	41.9	4.8	4
	47.6	3.6	4
	50	1.8	4
	55.3	1.5	4
	121	1.4	4

Table C3 Comparison of COD results determined using methods A and C

Sample type	Method C (mg l ⁻¹)	Method A (mg l ⁻¹)
Industrial effluent	8	6
	63	55
	63	60
	94	92
	137	128
	174	162
	258	308
	310	309
	403	387
	557	547
	1003	988
	1011	982
	2779	2730
	2872	2903
	3323	3251
Crude sewage	207	208
	256	241
	338	330
	368	349
	467	454
	593	576
	605	593
	623	587
	660	664
	665	651
Sewage works effluent	864	892
	34	28
	35	31
	36	35
	42	35
	45	42
	45	43
	50	45
	51	52
	121	121

Whilst the agreement is good for some matrices others show significant differences, illustrating agreement might be sample dependent.

Table C4 Chloride interference

Sample type	COD (mg l ⁻¹)	Chloride (mg l ⁻¹)	Mean deviation due to chloride (mg l ⁻¹)	Degrees of freedom
Phthalate standards	0	500	4.7	4
	100	500	6.2	4
	200	500	- 0.5	4
	300	500	- 0.6	4
	400	500	0.5	4
	0	1000	13.5	6
	100	1000	5.7	4
	200	1000	- 0.8	4
	300	1000	5.5	4
	400	1000	0.6	6
	0	2000	11.5	6
	100	2000	6.4	4
	200	2000	1.6	4
	300	2000	4.7	4
	400	2000	1.6	5
	0	5000	42.5	6
	100	5000	14.5	4
	200	5000	8.8	4
	300	5000	12.3	4
	400	5000	11.9	6
	0	10000	94.1	8
	100	10000	62.6	5
	200	10000	34.7	5
	300	10000	23.8	5
	400	10000	24.7	6
Industrial effluent	187*	3500	3.2	4
	567*	3480	10	4
Ammonia	0	5000	45.4	2

Ammonia present as 100 mg l⁻¹ NH₃.

*These samples initially contained negligible chloride, were analysed, spiked with chloride and then re-analysed.

D A mercury-free small scale (2 ml) flask digestion procedure using chromium(III) potassium sulphate and silver nitrate solutions

D1 Performance characteristics of the methods

D1.1	Range of application	Up to 400 mg l ⁻¹ COD. The range can be extended by pre-dilution of the sample with water.
D1.2	Standard deviation	See Tables D1 - D4.
D1.3	Limit of detection	Open-tube method - typically 10 mg l ⁻¹ (17 degrees of freedom). Closed-tube method - typically 9 mg l ⁻¹ (15 degrees of freedom).
D1.4	Sensitivity	1 ml of 0.025 M iron(II) ammonium sulphate solution corresponds to 100 mg l ⁻¹ COD.
D1.5	Bias	Open-tube digestion - see Tables D1 and D2. Closed-tube digestion - see Tables D3 and D4.
D1.6	Interferences	See Tables D5 and D6.
D1.7	Time required for analysis	Typical total analytical time for from 1 - 36 samples is about 3.5 hours.

D2 Reagents

Except where otherwise stated, analytical reagent grade chemicals should be used. Reagents should be stored in glass bottles. All reagents, with the exception of iron(II) ammonium sulphate solution, may be stored at room temperature for up to one month. Commercially available mixtures are obtainable for many of the reagents described. Unacceptable blank values are usually caused by the oxygen demand of the water or sulphuric acid, or the use of dirty apparatus.

D2.1 Water. Water used for blank determinations and preparation of control standards should show negligible interference. Water with conductivity of less than 2 µS cm⁻¹ and total organic carbon content of less than 1 mg l⁻¹ has been shown to be satisfactory. Glassware used for the preparation and storage of water should be cleaned with chromic acid solution.

D2.2 Concentrated sulphuric acid (SG 1.84).

D2.3 Silver nitrate solution (1200 g l⁻¹). Dissolve 120 ± 1 g of silver nitrate in approximately 80 ml of water (D2.1). Warm the solution if necessary. Cool and make to 100 ± 1 ml with water (D2.1). Do not cool below about 10 °C as this solution is saturated at 0 °C. Stored in the dark in a stoppered glass bottle, this solution may be stored at room temperature for up to an indefinite period.

D2.4 Chromium(III) potassium sulphate (250 g l^{-1}). Dissolve $25.00 \pm 0.01 \text{ g}$ of chromium(III) potassium sulphate dodecahydrate ($\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$) in $100 \pm 1 \text{ ml}$ of hot water (D2.1) i.e. water above 50°C . This solution is saturated at 30°C . Stored in a glass bottle with a polytetrafluoroethylene stopper, this solution may be stored for up to an indefinite period. When required for use, warm the contents to 50°C and stir before use, to re-dissolve any solids.

D2.5 Mixed reagent. Add $250 \pm 10 \text{ ml}$ of water (D2.1) into a 2 litre flat-bottomed borosilicate flask. Carefully, add $1.53 \pm 0.01 \text{ g}$ of potassium dichromate and $7.5 \pm 0.5 \text{ g}$ of silver sulphate. Swirl the contents of the flask to mix. Cautiously, with frequent swirling of the flask, add $750 \pm 25 \text{ ml}$ of sulphuric acid (D2.2). The contents of the flask should be well swirled in order to dissolve the silver sulphate completely. Allow the solution to stand overnight in the dark. Swirl the flask before use. This mixed reagent may be stored for up to 3 months in a stoppered bottle in the dark, but rapidly deteriorates in daylight. Because of a volume reduction on pre-mixing, 3.7 ml of this solution is equivalent to separate volumes of 1 ml of potassium dichromate solution (D2.8) and 3 ml of silver sulphate solution (D2.9).

D2.6 1:10 phenanthroline iron(II) indicator solution ("Ferroin" indicator). Dissolve $3.5 \pm 0.1 \text{ g}$ of iron(II) sulphate heptahydrate in $500 \pm 1 \text{ ml}$ of water (D2.1). Add $7.4 \pm 0.1 \text{ g}$ of 1:10 phenanthroline monohydrate, and mix to dissolve. This reagent may be obtained commercially. During the titration using iron(II) ammonium sulphate (D2.7) the use of this indicator solution transfers a small amount of iron(II) to the titration flask. Hence, not more than 2 drops (i.e. 0.1 ml) of indicator solution should be used. Titrations should be made to the same colour end point using equal amounts of indicator solution.

D2.7 Iron(II) ammonium sulphate solution (approximately 0.025 M). To a 1000-ml volumetric flask, add approximately 9.8 g of iron(II) ammonium sulphate hexahydrate to approximately 100 ml of water (D2.1). Add $20.0 \pm 0.5 \text{ ml}$ of sulphuric acid (D2.2) and swirl to dissolve the solid. Cool and make to 1000 ml with water (D2.1). Stopper and mix well. This solution is not very stable and should be prepared freshly on the day of use, and standardised before use.

Standardise the iron(II) ammonium sulphate solution against 0.02083 M potassium dichromate solution (D2.8) using the following procedure. To approximately 60 ml of water (D2.1) add $5.00 \pm 0.05 \text{ ml}$ of 0.02083 M potassium dichromate solution (D2.8). Carefully add $15.0 \pm 0.5 \text{ ml}$ of sulphuric acid (D2.2) and cool the solution. Add no more than two drops of indicator solution (D2.6) and titrate to the end point with the iron(II) ammonium sulphate solution to be standardised. Towards the end point of the titration, addition of the iron(II) ammonium sulphate solution (D2.7) from a narrow-bore burette, in quantities of $0.01 - 0.05 \text{ ml}$, facilitates the detection of the end point. The titre should be approximately 25 ml .

The molarity, M , of the iron(II) ammonium sulphate solution (D2.7) is given by:-

$$M = 0.625 / V$$

where V is the volume (ml) of iron(II) ammonium sulphate solution (D2.7).

Alternatively, $M = (0.020833 \times 30) / V$ or $M = 5 / (8 \times V)$

D2.8 Potassium dichromate solution (0.02083 M, ie M/48). To a 1000-ml volumetric flask, add 6.129 ± 0.001 g of potassium dichromate (previously dried for one hour at $140 - 150\text{ }^{\circ}\text{C}$) in approximately 800 ml of water (D2.1) in. Make to 1000 ml with water, stopper and mix well.

D2.9 Silver sulphate in sulphuric acid (10 g l^{-1}). To a glass bottle, add 10.0 ± 0.1 g of silver sulphate in a 1000 ± 10 ml of sulphuric acid (D2.2) and stopper. To obtain a satisfactory solution, swirl the initial mixture and allow it to stand overnight, Swirl again until all the silver sulphate dissolves. Store in the dark at room temperature. This solution may be stored for up to an indefinite period.

D2.10 Analytical quality control solution. For example, the following AQC solution of potassium hydrogen phthalate gives a theoretical COD value of 400 mg l^{-1} . To a 1000-ml volumetric flask, add 0.340 ± 0.001 g of potassium hydrogen phthalate (previously dried at $105\text{ }^{\circ}\text{C}$ for 2 hours) to approximately 950 ml of water (D2.1). Make to 1000 ml with water (D2.1). This solution may be stored, without freezing, in a refrigerator for up to one month. An alternative solution may however be more appropriate, see section 5.

D3 Apparatus

High blank values may result from the presence of trace amounts of contaminants in the digestion tube, the reflux condenser or on the anti-bumping granules. Apparatus should be cleaned (on repeated occasions) by boiling with fresh dichromate/sulphuric acid/silver sulphate mixture until low and consistent blank values are obtained. Apparatus should be reserved solely for COD determinations. Glassware should have standard ground glass joints where appropriate and grease should not be used. When rinsed with water between use, the digestion apparatus should be drained and dried at $105\text{ }^{\circ}\text{C}$. The use of wet apparatus may cause loss of precision. To improve precision, volumetric glassware should be grade B or better.

D3.1 Tubes for open-tube digestion. Borosilicate glass tubes, for example 16 mm diameter with a 14/23 ground glass socket and a total volume of not less than 15 ml. Tubes with any apparent defects should be discarded.

D3.2 Air condenser. For example, 13 mm diameter and not less than 150 mm long.

D3.3 Tubes for closed-tube digestion. Many types of tubes have been shown to be suitable. The main criteria are that the tubes can be heated, cooled, removed from the heater and opened without risk of bursting or spillage. The test data in the tables were obtained using borosilicate-glass culture vials, 125 x 16 mm with plastic screw-cap and polytetrafluoroethylene liner. Tubes with any apparent defect should be discarded. Many commercial systems are available where the tube is used once, and discarded or sent for disposal.

D3.4 Heating source. Thermostatically controlled heating block capable of accommodating the digestion tubes such that the level of the liquid in the tubes is coincident with the surface of the block. The block should be controlled to give a digest temperature of $150 \pm 3\text{ }^{\circ}\text{C}$. Care should be taken to ensure that the temperature within the block does not rise above $153\text{ }^{\circ}\text{C}$. An alternative heating source is a suitable air oven, controlled so as to give a digest temperature of $150 \pm 3\text{ }^{\circ}\text{C}$.

D3.5 Pipettes and burette. Graduated pipettes capable of dispensing

0.100 ± 0.005 ml and 0.20 ± 0.01 ml, and burette graduated in 0.02 ml divisions.

D3.6 Anti-bumping granules. All anti-bumping granules should be pre-cleaned by using the same digestion procedure.

D4 Analytical procedure

The digestion procedure described is based on a 1:5 scaled-down version of the flask procedure described in method C.

Step	Procedure	Notes
D4.1	Determination of chloride	
D4.1.1	Determine the chloride ⁽⁴⁾ content in the sample, see note a.	(a) If the chloride content of the sample is greater than 2000 mg l ⁻¹ , continue as described in section D6.
D4.2	Open-tube digestion	
D4.2.1	See note b. Add several anti- bumping granules (B3.6) to the boiling tube (D3.1) and add 0.100 ± 0.002 ml of silver nitrate solution (D2.3) add 2.00 ± 0.02 ml of sample or diluted sample, see note c. Swirl the tube and allow the tube and contents to stand for approximately 2 minutes.	(b) If the COD of the sample is known or expected to be above 160 mg l ⁻¹ the sample should be diluted with water. The dilution should be such that the titration of a 2-ml aliquot requires between approximately 5 - 20 ml of iron(II) ammonium sulphate solution (D2.7). If the amount of chloride in a 2-ml aliquot of diluted sample is more than 4 mg, continue as described in section B6.2 or B6.3. (c) At least two blank solutions (containing no sample) and an AQC sample (D2.10) should also be analysed.
D4.2.2	To the tube, add 0.100 ± 0.005 ml of chromium(III) potassium sulphate solution (D2.4) and swirl the tube to mix the contents.	
D4.2.3	Add 1.00 ± 0.01 ml of potassium dichromate solution (D2.8) and 3.00 ± 0.05 ml of silver sulphate-sulphuric acid solution (D2.9) see note d. Swirl the tube to mix the contents.	(d) Run the silver sulphate-sulphuric acid solution down the side of the tube whilst gently swirling and cooling the tube under running cold water. This procedure reduces loss of volatile compounds.
D4.2.4	Fit the condenser to the tube and	(e) Excessive reflux times will result

gently boil under reflux for 120 ± 10 minutes (note e).

D4.2.5 Remove the tube and condenser from the source of heat and allow the contents to cool to below $20\text{ }^{\circ}\text{C}$ in running water, note f. Remove the condenser from the tube, rinse the condenser with approximately 2 ml of water (D2.1) and allow the rinsings to collect in a titration flask. Quantitatively transfer the contents of the tube to the titration flask, rinsing the tube as appropriate with a small amount of water. Continue as described in section D4.4.

D4.3 Closed-tube digestion

D4.3.1 See note b. Add several anti-bumping granules (D3.6) to the boiling tube (D3.3) and add 0.100 ± 0.005 ml of silver nitrate solution (D2.3) and add 2.00 ± 0.01 ml of sample or diluted sample, see note c. Swirl the tube to mix the contents.

D4.3.2 To the tube, add 0.100 ± 0.005 ml of chromium(III) potassium sulphate solution (D2.4) and swirl the tube to mix the contents.

D4.3.3 Add 1.00 ± 0.01 ml of potassium dichromate solution (D2.8) and 3.00 ± 0.05 ml of silver sulphate-sulphuric acid solution (D2.9) see note d.

D4.3.4 Close the tube and ensure it is secure. Swirl the tube to mix the contents. Place the tubes in the heating source and reflux for 120 ± 10 minutes (note e) Remove the tubes and allow the contents to cool for approximately 5 minutes under running water to below $20\text{ }^{\circ}\text{C}$, note f. Cautiously unseal the digestion tube.

D4.3.5 Quantitatively transfer the contents of the tube to a titration flask, rinsing the tube as appropriate with a small amount of water.

D4.4 Determination of residual dichromate

D4.4.1 Add no more than two drops (0.1 ml) of indicator solution (D2.6) to the flask and titrate the residual dichromate with iron(II) ammonium sulphate solution (D2.7) (note g).

in high blank values.

(f) The titrimetric end point fades unless the digest solution is titrated between $15 - 20\text{ }^{\circ}\text{C}$.

(g) After the first addition of iron(II) ammonium sulphate solution, the solution is blue-green in colour. During titration, the flask should be well mixed. The end point of the titration occurs when the colour

changes sharply from deep blue to pink. The blue colour may reappear a few moments later but this should be ignored. This is especially common with samples high in chloride.

D5 Calculation

The blank value should be the average of at least two determinations. If any blank value differs by more ± 0.5 ml from the average value it should be rejected. In these circumstances, it may be necessary to determine additional blank values.

An acceptable blank determination should require at least 23.5 ml of 0.025 M iron(II) ammonium sulphate solution (D2.7) in the titration. In addition, the difference between a refluxed blank value and an un-refluxed blank value should not exceed 1.5 ml of 0.025 M iron(II) ammonium sulphate solution (D2.7).

Standard chloride solutions may also need to be analysed to establish potential interference effects especially where samples are analysed and low COD values are determined.

The analysis of AQC samples, for example standard solutions of potassium hydrogen phthalate (D2.10) or other appropriate solutions establishes that correct procedures are being followed.

The COD of the sample is given by

$$\text{COD} = 4000 \times \text{DF} \times M (V_b - V_s) \quad \text{mg l}^{-1}$$

where

V_b is the average volume (ml) of iron(II) ammonium sulphate solution (D2.7) used in the titration of blank solutions (D4.4.1);

V_s is the volume (ml) of iron(II) ammonium sulphate solution (D2.7) used in the titration of the sample (D4.4.1);

DF is the dilution factor, if appropriate (note b, section D4.2.1);

M is the molarity of standardised iron(II) ammonium sulphate solution (D2.7).

D6 Chloride interference

The following procedure is applicable to samples for which the 2-ml aliquot taken for analysis contains more than 4 mg of chloride.

Step	Procedure	Notes
D6.1 Determination of chloride		
D6.1.1	Following the determination of chloride	(g) If the amount is less than 4 mg

in the sample, calculate the amount of chloride in 2 ml of sample, note g.

continue as described in section D4.2 or D4.3.

D6.2 Open-tube digestion

D6.2.1 Add several anti-bumping granules (D3.6) to the boiling tube (D3.1) and add 0.20 ± 0.01 ml of silver nitrate solution (D2.3) add 2.00 ± 0.02 ml of sample or diluted sample, see note c. Swirl the tube to mix the contents. Allow the tube and contents to stand approximately 2 minutes. To the tube, add 0.20 ± 0.01 ml of chromium potassium sulphate (D2.4) and swirl the tube to mix the contents. Continue as described in section D4.2.3, note i.

(h) Ensure that the blank and AQC solutions (D2.10) contain the same amount of silver nitrate and chromium potassium sulphate as used for the 2-ml aliquot of sample or diluted sample.

(i) If the colour change at the end point to the titration is less easy to observe, the use of a potentiometric titrator may be more appropriate.

D6.3 Closed-tube digestion

D6.3.1 Add several anti-bumping granules (D3.6) to the boiling tube (D3.3) and add 0.20 ± 0.01 ml of silver nitrate solution (D2.3) and 2.00 ± 0.02 ml of sample or diluted sample. Swirl the tube to mix the contents. Allow the tube and contents to stand approximately 2 minutes. To the tube add 0.20 ± 0.01 ml of chromium(III) potassium sulphate (D2.4) and swirl the tube to mix the contents. Continue as described in section D4.3.3, note i.

D7 Modified procedure using mixed reagents

For laboratories where very large numbers of samples, or where samples containing volatile compounds, are analysed for COD, the following procedure, using a mixed reagent, reduces the manipulative work per sample. However, the possibility that higher COD values may be obtained should be recognised.

Step	Procedure	Notes
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D7.1 Open-tube digestion

D7.1.1 Add several anti-bumping granules (D3.6) into the boiling tube (D3.1) and add 0.100 ± 0.001 ml of silver nitrate solution (D2.3) and 2.00 ± 0.02 ml of sample or diluted sample (see note i). Swirl the tube to mix the contents. To the tube, add 0.100 ± 0.005 ml of chromium(III) potassium sulphate solution (D2.4) and swirl to mix the contents. Carefully, add

(i) The effects due to chloride and any dilution should be taken into account.

3.70 ± 0.02 ml of mixed reagent (D2.5) swirling the tube gently. Continue as described in D4.2.4.

D7.2 Closed-tube digestion

D7.2.1 Add several anti-bumping granules (D3.6) into the boiling tube (D3.3) add 0.100 ± 0.005 ml of silver nitrate solution (D2.3) and 2.00 ± 0.02 ml of sample or diluted sample (see note i). Swirl the tube to mix the contents. To the tube, add 0.100 ± 0.005 ml of chromium(III) potassium sulphate solution (D2.4) and swirl to mix the contents. Carefully, add 3.70 ± 0.01 ml of mixed reagent (D2.5). Continue as described in D4.3.4.

Table D1 Standard deviation and bias (open-tube method)

COD (mg l ⁻¹)	S _w (mg l ⁻¹)	Bias of the mean (mg l ⁻¹)	Number of (laboratories)	Batch size
0	4.3	-2		5
100	3.0	-2		5
200	4.5	-2	1	5
300	4.1	-3	1	5
400	4.5	-4	1	5

S_w is within-batch standard deviation.

Based on standard solutions of potassium hydrogen phthalate.

Table D2 Relative standard deviation (open-tube method)

Sample type	COD (mg l ⁻¹)	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 D3 Standard deviation and (closed-tube method)

COD (mg l ⁻¹)	S _w (mg l ⁻¹)		Bias of the mean (mg l ⁻¹)		Number of laboratories	Batch size
	Range	Mean	Range	Mean		
0	1.9 to 5	3.2	-5 to 12.5	3.2	3	5
100	1.2 to 3.9	2.7	-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

S_w is within-batch standard deviation.

Table D4 Relative standard deviations on samples (closed-tube method)

Sample type	COD (mg l ⁻¹)	Relative standard deviation (%)	Degrees of freedom
Crude sewage	38.0	8.0	4
	66.5	2.1	4
	169	2.2	4
	208	1.5	4
	209	1.8	4
	903	1.8	4
Industrial effluent	39.3	7.1	4
	44	5.9	4
	95.4	9.0	4
	142	3.2	4
	184	3.6	4
	188	5.4	4
	212	1.8	5
	272	0.8	5
	279	1.4	5
	293	1.8	4
Sewage works effluent	60	8.5	4
	62	6.8	4
	79	3.7	4

Table D5 Chloride interference (open-tube method)

Sample type	COD (mg l ⁻¹)	Chloride (mg l ⁻¹)	Mean deviation due to chloride (mg l ⁻¹ COD)	Degrees 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	1000	7	4
	100	1000	9	4
	200	1000	10	4
	300	1000	4	4
	400	1000	-3	4
	0	2000	9	4
	100	2000	16	4
	200	2000	9	4
	300	2000	3	4
	400	2000	2	4
Industrial effluent	164*	3500	10	4
Ammonia	0	5000	97	1

Ammonia present as 100 mg l⁻¹ NH₃

* This sample initially contained negligible chloride, was analysed, spiked with chloride and then re-analysed.

Table D6 Chloride interference (closed-tube method)

Sample type	COD (mg l ⁻¹)	Chloride (mg l ⁻¹)	Mean deviation due to chloride (mg l ⁻¹ 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	1000	2.6	4
	100	1000	19.6	4
	200	1000	8	4
	300	1000	33	4
	400	1000	-5	4
	0	2000	8	4
	100	2000	19	4
	200	2,000	16	4
	300	2000	12	4
	400	2000	-2	4
	0	5000	86	4
	100	5000	25	4
	200	5000	7	4
	300	5000	7	4
	400	5000	-5	4
	0	10000	86	4
	100	10000	92	4
	200	10000	81	4
	300	10000	12	4
	400	10000	19	4
Industrial effluents	168*	3370	-16.2	4
Ammonia	0	5000	20	1

Ammonia present as 100 mg l⁻¹ NH₃

* This sample initially contained negligible chloride, was analysed, spiked with chloride and then re-analysed.

E A mercury-free small scale (2.5 ml) flask digestion procedure using chromium(III) potassium sulphate and silver nitrate solutions

E1 Performance characteristics of the method

E1.1	Range of application	Up to 800 mg l ⁻¹ COD. The range can be extended by dilution of the sample with water.
E1.2	Standard deviation	See Tables E2 and E3.
E1.3	Limit of detection	Typically, 10 mg l ⁻¹ (17 degrees of freedom).
E1.4	Sensitivity	1 ml of 0.025 M iron(II) ammonium sulphate solution is equivalent to 80 mg l ⁻¹ COD.
E1.5	Bias	See Tables E1 - E4.
E1.6	Interferences	See tables E5 - E7.
E1.7	Time required for analysis	Typical total analytical time for from 1 - 36 samples is about 3.5 hours.

E2 Reagents

Except where otherwise stated, analytical reagent grade chemicals should be used. Reagents should be stored in glass bottles. All reagents, with the exception of iron(II) ammonium sulphate solution, may be stored at room temperature for up to one month. Commercially available mixtures are obtainable for many of the reagents described. Unacceptable blank values are usually caused by the oxygen demand of the water or the sulphuric acid, and dirty apparatus.

E2.1 Water. Water used for blank determinations and preparation of control standards should show negligible interference. Water with conductivity of less than 2 µS cm⁻¹ and total organic carbon content of less than 1 mg l⁻¹ has been shown to be satisfactory. Glassware used for the preparation and storage of water should be cleaned with chromic acid solution.

E2.2 Concentrated sulphuric acid (SG 1.84).

E2.3 Silver nitrate solution (500 g l⁻¹). Dissolve 50.0 ± 0.5 g of silver nitrate in approximately 80 ml of water (E2.1). Warm the solution if necessary. Cool and make to 100 ± 1 ml with water (E2.1). Do not cool below about 10 °C as this solution is saturated at 0 °C. Stored in the dark in a stoppered glass bottle, this solution may be stored at room temperature for up to an indefinite period.

E2.4 Chromium(III) potassium sulphate (250 g l⁻¹). Dissolve 25.0 ± 0.1 g of chromium(III) potassium sulphate dodecahydrate (KCr(SO₄)₂·12H₂O) in 100 ± 1 ml of hot water (E2.1) i.e. water above 50 °C. This solution is saturated at 30 °C. Stored in a glass bottle with a polytetrafluoroethylene stopper, this solution should keep indefinitely. When required for use, warm to 50 °C and stir before use, to re-dissolve any solids.

E2.5 Potassium dichromate solution (0.03473 M). To a 1000-ml volumetric flask, add 10.216 ± 0.001 g of potassium dichromate (previously dried for one hour at $140 - 150^\circ\text{C}$) in approximately 800 ml of water (E2.1). To the flask, add, with external cooling and stirring, 167 ± 1 ml of sulphuric acid (E2.2). Cool and make to 1000 ml with water (E2.1). Mix thoroughly. This reagent may be stored at room temperature for up to 3 months in a stoppered bottle in the dark.

E2.6 Silver sulphate in sulphuric acid (50 g l^{-1}). To a glass bottle, add 50.0 ± 0.1 g of silver sulphate and 1000 ± 10 ml of sulphuric acid (E2.2). To obtain a satisfactory solution, swirl the initial mixture and allow it to stand overnight. Swirl again until all the silver sulphate dissolves. Store in the dark at room temperature. This solution may be stored for up to an indefinite period.

E2.7 1:10 phenanthroline iron(II) indicator solution ("Ferroin" indicator). Dissolve 3.5 ± 0.1 g of iron(II) sulphate heptahydrate in 500 ± 1 ml of water (E2.1). Add 7.4 ± 0.1 g of 1:10 phenanthroline monohydrate, and mix to dissolve. This reagent can be obtained commercially. During the titration using iron(II) ammonium sulphate, the use of this indicator solution transfers a small amount of iron(II) to the titration flask. Hence, no more than 2 drops (i.e. 0.1 ml) of indicator solution should be used. Titrations should be made to the same colour end point using equal amounts of indicator solution.

E2.8 Iron(II) ammonium sulphate solution (approximately 0.025 M). To a 1000-ml volumetric flask, add approximately 9.8 g of iron(II) ammonium sulphate hexahydrate to approximately 100 ml of water (E2.1). Add 20.0 ± 0.5 ml of sulphuric acid (E2.2) and swirl to dissolve the solid. Cool and make to 1000 ml with water (E2.1). Stopper and mix well. This solution is not stable and should be prepared freshly on the day of use, and standardised prior to use.

To standardise the iron(II) ammonium sulphate solution against 0.02083 M potassium dichromate solution (E2.9) add 5.00 ± 0.05 ml of 0.02083 M potassium dichromate solution (E2.9) and dilute with water (E2.1) to approximately 60 ml. Carefully, add 15.0 ± 0.5 ml of sulphuric acid (E2.2) and cool. Add no more than two drops of indicator solution (E2.5) and titrate to the end point with the iron(II) ammonium sulphate solution to be standardised. Towards the end point of the titration, addition of the iron(II) ammonium sulphate solution (from a narrow-bore burette) in quantities of 0.01 - 0.05 ml, facilitates the detection of the end point. The titre normally expected is approximately 25 ml. The molarity, M, of the iron(II) ammonium sulphate solution is given by:-

$$M = 0.625 / V$$

where V is the volume (ml) of iron(II) ammonium sulphate solution.

Alternatively, $M = (0.020833 \times 30) / V$ or $M = 5 / (8 \times V)$

E2.9 Potassium dichromate solution (0.02083 M, i.e. M/48). To a 1000-ml volumetric flask, add 6.129 ± 0.001 g of potassium dichromate (previously dried for one hour at $140 - 150^\circ\text{C}$). To the flask add approximately 950 ml of water (E2.1) and mix to dissolve. Make to 1000 ml with water, stopper and mix well.

E2.10 Combined mixed reagent. To a 1000 ml volumetric flask, add 10.216 ± 0.001 g of potassium dichromate, 16.70 ± 0.01 g of chromium(III) potassium sulphate and

approximately 600 ml of water (E2.1). Cautiously, add 167 ± 1 ml of sulphuric acid (E2.2). Cool and make to 1000 with water (E2.1).

E2.11 Analytical quality control solution. For example, the following AQC solution of potassium hydrogen phthalate gives a theoretical COD value of 800 mg l^{-1} . To a 1000-ml volumetric flask, add 0.680 ± 0.001 g of potassium hydrogen phthalate (previously dried at 105°C for 2 hours) to approximately 950 ml of water (E2.1). Make to 1000 ml with water (E2.1). This solution may be stored, without freezing, in a refrigerator for up to one month. An alternative solution may however be more appropriate, see section 5.

E3 Apparatus

High blank values may result from the presence of trace amounts of contaminants in the digestion tube, the reflux condenser or on the anti-bumping granules. Apparatus should be cleaned (on repeated occasions) by boiling with fresh dichromate/sulphuric acid/silver sulphate mixture 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 and grease should not be used. When rinsed with water between use, the digestion apparatus should be drained and dried at 105°C . The use of wet apparatus causes loss of precision. To improved precision, volumetric glassware should be grade B or better.

E3.1 Tubes for open-tube digestion. Borosilicate glass tubes, for example 16 mm diameter with a 14/23 ground glass socket and a total volume of not less than 15 ml. Tubes with any apparent defects should be discarded.

E3.2 Air condenser. For example, 13 mm diameter and not less than 150 mm long.

E3.3 Heating source. Thermostatically controlled heating block capable of accommodating the digestion tubes such that the level of liquid in the tube is coincident with the surface of the block. The block should be controlled to give a digest temperature of $150 \pm 3^\circ\text{C}$. Care should be taken to ensure that the temperature within the block does not rise above 153°C . An alternative heating source is a suitable air oven, controlled so as to give a digest temperature of $150 \pm 3^\circ\text{C}$.

E3.4 Pipettes and burette. Graduated pipettes capable of dispensing 0.100 ± 0.005 ml and 0.20 ± 0.01 ml, and burette graduated in 0.02 ml divisions.

E3.6 Anti-bumping granules. All anti-bumping granules should be pre-cleaned by using the same digestion procedure.

E4 Analytical procedure

The digestion procedure is based on the open-tube procedure in method D using a more concentrated solution of the oxidising reagent, potassium dichromate.

Step	Procedure	Notes
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E4.1 Determination of chloride

E4.1.1 Determine the chloride⁽⁴⁾ content in the (a) If the chloride content of the

sample, see note a.

sample is greater than 2000 mg l⁻¹, continue as described in section E6.

E4.2 Open-tube digestion

E4.2.1 See note b. Add several anti-bumping granules (E3.6) to a digestion tube (E3.1) and add 0.100 ± 0.001 ml of silver nitrate solution (E2.3) and 2.50 ± 0.02 ml of sample (note c). Swirl the tube to mix the contents.

(b) If the COD of the sample is known or expected to be above 800 mg l⁻¹ the sample should be diluted with water. The dilution should be such that the titration of a 2.5-ml aliquot requires between approximately 5 - 20 ml of iron(II) ammonium sulphate solution (E2.8). If the amount of chloride in a 2.5-ml aliquot of diluted sample is more than 5 mg, continue as described in section E6.2.

(c) At least two blank solutions (containing no sample) and an AQC sample (E2.11) should also be analysed.

E4.2.2 To the tube, add 0.100 ± 0.001 ml of chromium(III) potassium sulphate solution (E2.4). Mix well and stand for at least 2 minutes.

E4.2.3 Add 1.50 ± 0.01 ml of potassium dichromate solution (E2.5).

E4.2.4 To the tube, add 3.50 ± 0.01 ml of silver sulphate-sulphuric acid solution (E2.6) note d. Swirl the tube to mix the contents. Allow any evolved gas to escape.

(d) Run the silver sulphate-sulphuric acid solution down the side of the tube whilst gently swirling and cooling the tube under running cold water. This procedure reduces loss of volatile compounds.

E4.2.5 Place the condenser on top of the tube. Place the tube in the heating source and allow the solution to digest at 150 ± 3 °C for 120 ± 10 minutes, note e. Remove the tubes and allow the solution to cool for 5 minutes, then cool under running to below 20 °C (note f). Remove the condenser from the digestion tube. Rinse the condenser with 2.0 ± 0.1 ml of water (E2.1) and allow the rinsings to run into a titration flask. Quantitatively transfer the contents of the tube into the flask using 10 ± 1 ml of water as appropriate.

(e) Excessive reflux times will result in high blank values.

(f) The titrimetric end point fades unless tubes are kept at between 15 - 20 °C.

E4.3 Determination of residual dichromate

E4.3.1 Add no more than two drops of indicator solution (E2.7) to the flask and titrate the residual dichromate with standardised iron(II) ammonium sulphate (E2.8) note g).

(g) After the first addition of iron(II) ammonium sulphate solution, the solution is blue-green in colour. During titration the flask should be well mixed. The end point of the titration occurs when the colour changes sharply from deep blue to pink. The blue colour may reappear a few moments later but this should be ignored. This is especially true for samples high in chloride.

E5 Calculation

The blank value should be the average of at least two determinations. If any blank value differs by more ± 0.5 ml from the average value it should be rejected. In these circumstances, it may be necessary to determine additional blank values.

An acceptable blank determination should require at least 23.5 ml of 0.025 M iron(II) ammonium sulphate solution (E2.8) in the titration. In addition, the difference between a refluxed blank value and an un-refluxed blank value should not exceed 1.5 ml of 0.025 M iron(II) ammonium sulphate solution (E2.8).

Standard chloride solutions may also need to be analysed to establish potential interference effects especially where samples are analysed and low COD values are obtained.

The analysis of AQC samples for example standard solutions of potassium hydrogen phthalate (E2.11) establishes that correct procedures are being followed. The COD of the sample is given by

$$\text{COD} = 3200 \times \text{DF} \times M (V_b - V_s) \quad \text{mg l}^{-1}$$

where

V_b is the average volume (ml) of iron(II) ammonium sulphate solution (E2.8) used in the titration of blank solutions (E4.3.1);

V_s is the volume (ml) of iron(II) ammonium sulphate solution (E2.8) used in the titration of the sample (E4.3.1);

DF is the dilution factor, if appropriate (note b, section E4.2.1);

M is the molarity of standardised iron(II) ammonium sulphate solution (E2.8).

E6 Chloride interference

The following procedure is applicable to samples for which the 2.5-ml aliquot taken for analysis contains more than 5 mg of chloride.

Step	Procedure	Notes
E6.1	Determination of chloride	
E6.1.1	Following the determination of chloride in the sample, calculate the amount of chloride in 2 ml of sample, note h.	(h) If the amount is less than 5 mg continue as described in section E4.2.
E6.2	Open-tube digestion	
E6.2.1	Add several anti-bumping granules (E3.6) to the boiling tube (E3.1) and add 0.20 ± 0.01 ml of silver nitrate solution (E2.3) and 2.50 ± 0.02 ml of sample or diluted sample, see note c. Swirl the tube to mix the contents. Allow the tube and contents to stand approximately 2 minutes. To the tube add 0.20 ± 0.01 ml of chromium(III) potassium sulphate (E2.4) note i. Swirl the tube to mix the contents. Continue as described in section E4.2.3, note j.	(i) Ensure that the blank and AQC solutions contain the same amount of silver nitrate and chromium(III) potassium sulphate as used for the 2.5-ml aliquot of sample or diluted sample. (j) If the colour change at the end point to the titration is less easy to observe, the use of a potentiometric titrator may be more appropriate.

E7 Modified procedure using mixed reagents

For laboratories where very large numbers of samples or where samples containing volatile compounds are analysed for COD, the following procedure, using a mixed reagent, reduces the manipulative work per sample. However, the possibility that higher COD values may be obtained should be recognised.

Step	Procedure	Notes
E7.1	Open-tube digestion	
E7.1.1	Add several anti-bumping granules (E3.6) into the boiling tube (E3.1) and add 0.100 ± 0.001 ml of silver nitrate solution (E2.3) and 2.50 ± 0.02 ml of sample or diluted sample (see note k). Swirl the tube to mix the contents. Carefully, add 1.50 ± 0.01 ml of combined mixed reagent (E2.10) swirling the tube gently. Continue as described in E4.2.4.	(k) The effects due to chloride and any dilution should be taken into account.

Table E1 Recovery tests

Substance	Concentration (mg l ⁻¹)	Theoretical COD (mg l ⁻¹)	Actual COD (mg l ⁻¹)	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	97.1	3

* Data obtained using mercury under similar conditions but in a closed tube.

Table E2 Standard deviation and bias (based on procedures described in E4)

COD (mg l ⁻¹)	S _w Range (mg l ⁻¹)	Mean (mg l ⁻¹)	Bias of the mean Range (mg l ⁻¹)	Mean (mg l ⁻¹)	Number of laboratories	Batch size
0	0.9 to 4.1	2.5	0 to 6.6	2.6	6	5-10
100	2.8 to 11	4.8	-5.4 to 13	1.7	7	5-10
200	2.4 to 4.1	4	-7 to +6	0.4	6	5-10
300	3.3 to 10	4.9	-10 to +3	-3.1	6	5-9
400	2.8 to 6.5	4.1	-6 to +7.2	1	6	5-14
800	2.7 to 8.3	4.9	-19 to +1	-6.9	5	5-17

S_w is within batch standard deviation.

Based on standard solutions of potassium hydrogen phthalate.

Table E3 Standard deviation and bias (based on procedures described in E6)

COD (mg l ⁻¹)	S _w Mean (mg l ⁻¹)	Bias of the mean Mean (mg l ⁻¹)	Number of laboratories	Batch size
100	4.0	-1	1	5
200	2.5	6	1	5
200	3.4	2	1	5
400	0	-9	1	5
400	4	-4	1	5
800	0.3	-17	1	5

S_w is within batch standard deviation.

Based on standard solutions of potassium hydrogen phthalate.

Table E4 Relative standard deviation on samples

Sample type	COD (mg l ⁻¹)	Relative standard deviation (%)	Degrees of freedom
Crude sewage	214	1.7	4
	272	3.5	4
	367	1.6	4
	394	1.4	4
	409	1.1	4
	415	0.7	4
	448	7.0	4
	516	0.5	4
	563	1.0	4
	728	1.0	4
	1124	8.0	4
	1526	1.4	4
Industrial effluent	114	1.9	4
	136	4.3	4
	251	1.5	4
	342	2.7	4
	438	1.8	4
	479	1.1	4
	3686	0.5	4
	3780	1.0	4
	3896	0	4
	3954	0.9	4
	4300	0.4	4
	4465	1.4	4
	6213	0.9	4
	8322	0.9	4
Sewage works effluent	432	7.7	4
	60	6.2	4
	66	5.1	4
	73	3.0	4
	77	4.2	4
	78	4.6	4
	82	5.1	4
	96	3.3	4
	159	3.1	4
	167	5.3	8
	241	2.7	4
	339	4.3	4

Table E5 Chloride interference (based on procedures described in E4)

Sample type	COD (mg l ⁻¹)	Chloride (mg l ⁻¹)	Mean deviation due to chloride (mg l ⁻¹ 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	1000	-14.1	5
	100	1000	9.9	4
	200	1000	8.4	4
	300	1000	9.5	5
	400	1000	3.8	4
	800	1000	-0.1	3
	0	2000	16.6	5
	100	2000	9.8	5
	200	2000	9.2	4
	300	2000	5.5	4
	400	2000	8.9	4
	800	2000	-6.2	3
	0	3500	16.8	17
	0	3500	20.4	4
	0	5000	34.7	5
	100	5000	24.2	5
	200	5000	18.3	5
	300	5000	17.9	4
	400	5000	12.5	5
	800	5000	-5.8	3
	0	10000	104.6 (41)	5
	100	10000	65.2 (52)	5
	200	10000	63.2 (21)	5
	300	10000	55.3 (25)	5
	400	10000	27.2 (12)	5
	800	10000	-5.8 (7)	5
industrial effluent	42.2*	3500	-1.6	
	476	3500	-4.3	
	147*	3500	11.2	
	233*	3685	18	
	335*	3570	-4	

Figures in brackets were obtained with twice the amount of silver nitrate and chromium(III) potassium sulphate.

*These samples initially contained negligible chloride, were analysed, spiked with chloride and then re-analysed.

Table E6 Chloride interference (based on procedures described in E6)

Sample type	COD (mg l ⁻¹)	Chloride (mg l ⁻¹)	Mean deviation due to chloride (mg l ⁻¹ COD)	Degrees of freedom
Phthalate standards	0	2000	12.3	4
	0	3500	15.7	4
	100	3500	10	4
	200	3500	10	4
	0	10000	96 (28)	4 (4)
	100	10000	96 (30)	4
	200	10000	96 (29)	4

Figures in brackets were obtained with twice the amount of silver nitrate and chromium(III) potassium sulphate.

Table E7 Ammonia and chloride interferences

Sample type	COD (mg l ⁻¹)	Ammonia (mg l ⁻¹)	Chloride (mg l ⁻¹)	Mean deviation (mg l ⁻¹ COD)	Degrees of freedom
Phthalate standard	0	100	5000	34	2
	0	100	5000	48.9 (9)	4
Glutamic acid at 500 mg l ⁻¹ COD	490	-	0	15	3
	490	-	2000	31	3
	490	-	3500	30	3
	490	-	5000	41	3

The figure in brackets was obtained using twice the amount of silver nitrate and chromium(III) potassium sulphate.

F References

- 1 Standing Committee of Analysts, Chemical Oxygen Demand (Dichromate Value) of Polluted and Waste Waters 1977, *Methods for the Examination of Waters and Associated Materials*, ISBN 0117512494, in this series.
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- 3 Standing Committee of Analysts, General Principles of Sampling Water and Associated Materials (second edition) 1996, Estimation of Flow and Load 1996, *Methods for the Examination of Waters and Associated Materials*, ISBN 011752364X, in this series.
- 4 Standing Committee of Analysts, Chloride in Water, Sewage and Effluents 1981, *Methods for the Examination of Waters and Associated Materials*, ISBN 0117516260, in this series

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G Waste disposal and recovery of mercury and silver

Wastes containing mercury and silver are notifiable wastes requiring authorisation before disposal. Procedures described below can be used to recovery mercury and silver from the test solutions used in methods A - E.

G1 Recovery of silver

Place approximately 50 ml of concentrated hydrochloric acid (SG 1.18) into a 2.5 litre glass bottle. After each determination, add the spent test solutions (including any precipitates) to the bottle. When the bottle is full allow any silver chloride to settle. Decant the supernatant liquid into a large beaker.

Add water to the settled precipitate of silver chloride in the bottle and mix well. Allow the precipitate to settle. Decant the supernatant liquid to waste. Repeat this process until the washings are no longer strongly acid. The silver chloride can be dried, and stored until a sufficient quantity has been accumulated for refining or for disposal.

If mercury is present in the supernatant liquid in the large beaker, see above paragraph, treat as described in section G2.

If mercury is absent in the supernatant liquid in the large beaker, dilute the liquid with copious amounts of water and discard.

G2 Recovery of mercury

Add 1 - 3 g of iron(II) sulphide to the large beaker containing the supernatant liquid, see section G1 and mix the contents gently. Allow the mixture to stand at least 24 hours, occasionally swirling or stirring the solution to disperse any hydrogen sulphide that may be evolved. This procedure should be carried out in a fume cupboard.

Add water to the beaker and mix the contents. Allow the precipitate of mercury sulphide to settle. Decant the supernatant liquid to waste diluting with copious amounts of water (in the ratio of about 500:1). Repeat this process until the washings are free of hydrogen sulphide. The precipitated mercury can be dried and stored until a sufficient quantity has been accumulated for refining or for disposal.

Alternatively, mercury may be precipitated the by addition of a stoichiometric amount of potassium iodide instead of iron(II) sulphide. The precipitated mercury can be dried and stored until a sufficient quantity has been accumulated for refining or for disposal.

Address for correspondence

However well procedures may be tested, there is always the possibility of discovering hitherto unknown problems. Analysts with such information are requested to contact the Secretary of the Standing Committee of Analysts at the address given below. In addition, if users would like to receive advanced notice of forthcoming publications please contact the Secretary on the Agency's web-page.

Standing Committee of Analysts
Environment Agency (National Laboratory Service)
56 Town Green Street
Rothley
Leicestershire, LE7 7NW
<http://www.environment-agency.gov.uk/nls>

Standing Committee of Analysts

Members assisting with this booklet (in addition to members listed in the previously published document)

V Argent
S Davis
G Harper
D Morris
H A Painter
K C Thompson
P Walker
P Whittle

Grateful acknowledgement is made to Paul Wright of Leicestershire Scientific Services for providing colour photographs.

CONTACTS:

ENVIRONMENT AGENCY HEAD OFFICE

Rio House, Waterside Drive, Aztec West, Almondsbury, Bristol BS32 4UD

www.environment-agency.gov.uk

www.environment-agency.wales.gov.uk

ENVIRONMENT AGENCY REGIONAL OFFICES

ANGLIAN

Kingfisher House
Goldhay Way
Orton Goldhay
Peterborough PE2 5ZR

SOUTHERN

Guildbourne House
Chatsworth Road
Worthing
West Sussex BN11 1LD

MIDLANDS

Sapphire East
550 Streetsbrook Road
Solihull B91 1QT

SOUTHWEST

Manley House
Kestrel Way
Exeter EX2 7LQ

NORTH EAST

Rivers House
21 Park Square South
Leeds LS1 2QG

THAMES

Kings Meadow House
Kings Meadow Road
Reading RG1 8DQ

NORTH WEST

PO Box 12
Richard Fairclough House
Knutsford Road
Warrington WA4 1HG

WALES

Cambria House
29 Newport Road
Cardiff CF24 0TP



ENVIRONMENT AGENCY
GENERAL ENQUIRY LINE

08708 506 506

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