ENVIRONMENT AGENCY

Chemical disinfecting agents in waters and effluents (2008)

Methods for the Examination of Waters and Associated Materials

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This booklet is an updated version of the previous document published in 1980. Major differences between this publication and the previous one appear in methods C and D. Differences include increasing the concentrations of diethyl-*p*-phenylenediamine (DPD) and disodium ethylenediaminetetraacetate (EDTA) and adjusting the buffer concentration to account for the increased use of EDTA, giving details of alternative analytical quality control procedures and specifying an alternative wavelength for the spectrophotometric DPD determination.

Whilst specific commercial products may be referred to in this document, this does not constitute an endorsement of these products but serves only as an illustrative example of the type of products available. Equivalent products are available and it should be understood that the performance of the method might differ when other materials are used and all should be confirmed by validation of the method.

Contents

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, soils (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 this booklet.

Publication of new or revised methods will be notified to the technical press. If users wish to receive copies or advanced notice of forthcoming publications or obtain details of the index of methods then contact the Secretary on the Agency's web-page (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
July 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 all regulations made under the 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.

Chemical disinfecting agents in waters and effluents

A1 Introduction

The following methods give details for the determination of the various disinfecting agents used in the treatment of water. These agents include chlorine, chlorine dioxide, chloramines, chloroisocyanurates, bromine, bromamines, iodine and ozone. Chemicals of these types are also used for the oxidation of organic matter and nitrogen compounds such as ammonia and cyanide in waters. The methods cover the determination of disinfecting agents in raw, drinking, sea and swimming-pool waters and effluents. Chlorine is by far the most generally used disinfecting agent for the treatment of such waters, and for its determination it is important to understand the chemistry of its reaction with water and certain dissolved constituents.

In pure waters, chlorine (Cl_2) hydrolyses to form hypochlorous acid (HOCl) which in turn partly dissociates to produce hydrogen ions and hypochlorite ($[OCl]^-$) ions. These three forms of chlorine exist in solution in equilibrium, their relative proportions being dependent on the pH value and temperature of the solution.

In the presence of ammonia and polluted waters, significant substitution reactions occur where the hydrogen atoms of the ammonia molecule are successively replaced by chlorine atoms forming chloramines, namely mono-chloramine, di-chloramine and nitrogen trichloride, i.e. NH_2Cl, $NHCl_2$ and NCl_3 respectively. These chloramines still possess disinfecting properties, but like those of the hypochlorite ion the disinfecting properties are much reduced compared with hypochlorous acid. Chloramines are, however, generally more stable than hypochlorous acid and the hypochlorite ion and are, therefore, more persistent in solution. In the presence of excess chlorine, mono- and di-chloramines can, over time, undergo degradation to produce nitrogen.

The so-called breakpoint is reached when all the ammoniacal nitrogen has been converted to nitrogen together with small amounts of nitrate and possibly nitrogen trichloride. In most natural waters, the breakpoint is produced when the ratio of added chlorine to ammoniacal nitrogen originally present in the water is about 10:1, although for heavily polluted waters the ratios may be considerably greater. Any residual chlorine after the production of a breakpoint is substantially in the form of hypochlorous acid and hypochlorite ion.

In situations where chlorine is present in solution in a form which releases free iodine from an acid solution of potassium iodide, this presence is known as "available chlorine". Chlorine that has been reduced to chloride represents a complete loss of available chlorine. It is normal practice to determine chlorine, chlorine dioxide, chloramines and other chlorine-containing disinfectants in terms of “available chlorine”. However, the “available chlorine” content of some disinfecting chlorine compounds is not a true measure of their disinfecting power. For example, the disinfecting power of chlorine dioxide (ClO_2) is only equivalent to about one-fifth of its “available chlorine” content. In the case of chlorine dioxide, chlorite (i.e. $[ClO_2]^-$) bromine and ozone, these substances are often expressed in terms of the substance itself.

From an analytical point of view, the forms of chlorine which are usually determined are separated into three types:

(i) Free available residual chlorine, defined as that residual chlorine existing in water as chlorine, hypochlorous acid and hypochlorite ion.

(ii) Combined available residual chlorine, defined as that residual chlorine existing in water in chemical combination with ammonia (i.e. mono-chloramine, di-chloramine and nitrogen trichloride) or organic nitrogen compounds.

(iii) Total available residual chlorine, defined as that residual chlorine being the sum of (i) and (ii).

The residual chlorine content of water changes after sampling and collection. Loss of free chlorine and combined chlorine is greater with rising temperatures and in the presence of organic matter, and is accelerated following exposure of the sample to sunlight. Reaction of freee chlorine with ammonia and chloramines to form more highly substituted chloramines and nitrogen trichloride can also occur. Residual chlorine tests should therefore be carried out as soon as possible following sampling and collection, preferably on-site at the time of sampling and collection. The results of on-site tests are likely to be more significant, since changes in the amount and nature of the residual chlorine, as might arise during transit to a laboratory, and which might be significant, are eliminated. For such on-site testing, commercial test kits are available and provide sufficient accuracy of measurement for most situations.

A2 Iodometric titration

The iodometric method should only be used for the determination of chlorine. It is used for the standardisation of chlorine solutions which may subsequently be required for the calibration of routine methods in day to day use. It can be used for routine work at chlorine concentrations greater than 1 milligram per litre (mg/l) provided there is no need to distinguish between free available residual chlorine and combined available residual chlorine, i.e. free and combined available chlorine. The iodometric method is a basic reference method for the determination of all oxidizing disinfecting agents, including chlorine, chlorine dioxide, bromine and ozone, but is rarely used.

A3 Diethyl-*p*-phenylenediamine method

In addition to the iodometric method used as a reference method for total disinfectant, this document also describes titrimetric and colourimetric procedures using diethyl-*p*-phenylenediamine (DPD) for the determination of various oxidizing disinfectants including free chlorine, chloramines, chloroisocyanurates, chlorine dioxide, bromine, bromamines, iodine and ozone in waters.

Methods for the separate determination of free available residual chlorine and combined available residual chlorine in chlorinated waters using DPD are well established. The use of DPD has been extensively tested. In particular, its ability to provide unambiguous determinations of free chlorine, the most potent species available for disinfection, without interference from nitrogen trichloride is considered important. The DPD titrimetric method is a very reliable method for measuring free chlorine, mono- and di-chloramine and even nitrogen trichloride provided care is taken during sampling to avoid any escape of nitrogen trichloride (which is a gas at room temperature).

Nitrogen trichloride, at concentrations up to at least 4 mg/l (as chlorine) produces no perceptible response in the free available residual chlorine fraction. In addition the accuracy of the supplementary DPD procedures for nitrogen trichloride has been confirmed against corresponding specific ultra violet absorption data. It has further been

established that the determination of free available residual chlorine by the DPD method is not affected by the presence of di-chloramine, and that mono-chloramine in concentrations of up to 4 mg/l (as chlorine) gives no perceptible colouration in the absence of iodide, in the titrimetric and spectrophotometric procedures. With a field test-kit using a visual comparison method, a faint positive response is observed giving an apparent free available residual chlorine reading of the order of two per cent of the mono-chloramine present.

A4 Analytical quality control

A4.1 Typical standards

Analytical quality control (AQC) procedures should be used regularly to check the suitability of reagents and the procedures carried out.

Calibration of comparator discs and direct reading instruments may be carried out using the procedures described. Checks on direct reading instruments may also be carried out using fixed certified standards traceable to national or international standards.

A choice of surrogate standards are available for use in AQC procedures. Potassium permanganate solution may be used for the method calibration and be appropriate for use in the laboratory to check calibration. The solutions are simple to prepare, and are more stable than chlorine solutions, thus it is more likely that better repeatable results are obtained. However, dilute potassium permanganate solutions deteriorate rapidly and should be used within an hour of preparation. Potassium iodate solutions, if stored correctly, should remain stable for up to 24 hours.

A4.2 Performance characteristics of the standards

Based on theoretical oxidising capacity, potassium permanganate and potassium iodate solutions should yield identical results. In the spectrophotometric procedure described in section D, no significant differences have been observed in their responses.

Commonly, commercial formulations of the DPD reagent are used. . These formulations provide stable, easy-to-use, pre-measured doses of the DPD indicators and buffers suitable for on-site testing. In tests using reagents from different suppliers, different responses have been observed with potassium permanganate and potassium iodate surrogate AQC solutions, the iodate solution response typically being up to 10 % higher at 0.25 - 1.00 mg/l (chlorine equivalent). Hence, for comparability of data obtained from a single site, a single surrogate solution should be selected for repeated routine monitoring.

A4.3 Reagents

All chemicals should be of analytical reagent grade quality unless otherwise specified. Store reagents in glass bottles.

A4.3.1 Water. Deionised or distilled free from oxidising agents and having negligible chlorine demand.

A4.3.2 Potassium permanganate stock solution (0.891 g/l). Add 0.8910 ± 0.0005 g of potassium permanganate to a 1000-ml volumetric flask, in approximately 200 ml of water (A4.3.1) and mix well. Make to 1000 ml with water (A4.3.1) and mix again. This solution

may be stored at room temperature for up to two months. (1 ml of this solution is equivalent to 1 milligram of chlorine, i.e. 1000 mg/l as chlorine.)

A4.3.3 Potassium permanganate solution (0.0891 g/l). Add 10.00 ml of potassium permanganate stock solution (A4.3.2) to a 100-ml volumetric flask. Make to 100 ml with water (A4.3.1) and mix. This solution should be prepared on the day of use. This solution is equivalent to 100 mg/l as chlorine.

A4.3.4 Potassium permanganate standard solution (0.00891 g/l). Add 10.00 ml of potassium permanganate solution (A4.3.3) to a 100-ml volumetric flask. Make to 100 ml with water (A4.3.1) and mix. This solution should be used within one hour of preparation. This solution is equivalent to 10 mg/l as chlorine.

A4.3.5 Potassium iodate stock solution (1.006 g/l). Add 1.006 ± 0.0006 g of potassium iodate to approximately 250 ml of water (A4.3.1) contained in a 1000-ml volumetric flask. Mix well. Make to 1000 ml with water (A4.3.1) and mix again.

A4.3.6 Potassium iodate-iodide solution (0.01006 g/l) Add 10.00 ml of potassium iodate stock solution (A4.3.5) to a 1000-ml volumetric flask. Add 0.10 ± 0.01 g of potassium iodide and mix. Make to 1000 ml with water (A4.3.1) and mix again. This solution should be prepared on the day of use. This solution is equivalent to 10 mg/l as chlorine.

A4.3.7 Sulphuric acid solution (1Molar). Slowly, add 54 ± 2 ml of concentrated sulphuric acid (SG 1.84) to about 800 ml of water (A4.3.1). Cool the solution and make to 1000 ± 1 ml with water (A4.3.1). This solution may be stored at room temperature for up to an indefinite period.

A4.3.8 Sodium hydroxide solution (0.2 Molar). Add 8.0 ± 0.1 g of sodium hydroxide to about 800 ml of water and mix carefully. Cool the solution and make to 1000 ± 1 ml with water (A4.3.1) and mix again. Transfer to a plastic container and cap. This solution may be stored at room temperature for up to an indefinite period.

A4.3.9 Sodium hydroxide solution (0.02 Molar). Add 10.00 ml of sodium hydroxide solution (A4.3.8) to a 100-ml volumetric flask and mix. Make to 100 ml with water (A4.3.1) and mix again.

A4.4 Analytical procedure

A4.4.1 Using potassium permanganate solutions

A4.4.1.1 Add the appropriate volumes (see table below) of potassium permanganate solution (A4.3.4) to separate100-ml volumetric flasks and mix. Make each flask to 100 ml with water (A4.3.1) and mix again, see section A4.4.1.2.

Volume of potassium permanganate solution (A4.3.4) (ml)	Chlorine equivalent (mg/l)
10.00 ± 0.05	1.0
8.00 ± 0.05	0.8
6.00 ± 0.05	0.6
4.00 ± 0.05	0.4
2.00 ± 0.05	0.2

A4.4.1.2 Prepare each solution and use immediately before proceeding to the next concentration. Using the AQC solution (see table above) in place of the sample, carry out the procedure described in the method, for example see section D8.2.

A4.4.2 Using potassium iodate solutions

A4.4.2.1 Add the appropriate volumes (see table below) of potassium iodate solution (A4.3.6) to separate100-ml volumetric flasks and mix. Add 1 ml of sulphuric acid (A4.3.7) to each flask, and after 1.0 ± 0.1 minute, add 10 ml of sodium hydroxide solution (A4.3.8). Mix and make to 100 ml with water (A4.3.1). Mix again, see section A4.4.2.3.

A4.4.2.2 The optimum pH value of each solution should be between 6 and 7. For more accurate work, pH adjustment may be achieved by adding 9.5 ml of sodium hydroxide (A4.3.8) and diluting to about 80 ml with water (A4.3.1) and then adding up to 5 ml of sodium hydroxide solution (A4.3.9) until the correct pH is achieved.

Volume of potassium iodate solution (A4.3.6) (ml)	Chlorine equivalent (mg/l)
10.00 ± 0.05	1.0
8.00 ± 0.05	0.8
6.00 ± 0.05	0.6
4.00 ± 0.05	0.4
2.00 ± 0.05	0.2

A4.4.2.3 Prepare each solution and use immediately before proceeding to the next concentration. Using the AQC solution (see table above) in place of the sample, carry out the procedure described in the method, for example see section D8.2.

Further information can be founding in “Guidance on calibration and analytical quality control for residual chlorine measurements” produced by the Drinking Water Inspectorate.

In the procedures described in this booklet any reference to quality of glassware and the tolerances to be adopted with respect to the amount or volume of reagents to be used is left to the discretion of the laboratory. These tolerances should be as appropriate in order to satisfy any performance criteria that may be prescribed.

A5 Expression of results

Throughout this document results are expressed as chlorine (Cl_2) or its equivalent unless otherwise stated.

B Determination of total available residual chlorine in waters by iodometric titration

B1 Performance characteristics of the method

B1.1	Substance determined	Total available residual chlorine.
B1.2	Types of sample	Raw, drinking and swimming pool waters, but see section A1.
B1.3	Basis of method	Quantitative liberation of iodine from an acid solution of potassium iodide followed by iodometric titration with sodium thiosulphate.
B1.4	Range of application	1 - 20 mg/l. The range may be extended by diltiuon of the sample.
B1.5	Standard deviation	See Table B1.
B1.6	Limit of detection	Approximately 0.15 mg/l (as Cl_2).
B1.7	Sensitivity	1 ml of 0.0125M sodium thiosulphate solution is equivalent to 0.89 mg/l (as Cl_2).
B1.8	Bias	Potential negative bias due to loss of chlorine and iodine, and a tendency to under titrate slightly to the end point.
B1.9	Time required for analysis	Total analytical and operator time is approximately five minutes per sample. A further five minutes is required for reagent standardisation.

B2 Principle

Free available residual chlorine and combined available residual chlorine liberate iodine quantitatively from an acid solution of potassium iodide. The free iodine is determined by titration with sodium thiosulphate solution using starch indicator.

B3 Interferences

Oxidising agents other than those being determined, which liberate iodine from iodide will interfere. Substances such as nitrite, manganese(III) and higher oxidation states of manganese, chromate, iron(III), copper(II) or, rarely, cerium(IV) if present in the sample may interfere. The extent of the interference will depend on the overall composition of the sample. If any of these substances are present at a concentration which could cause significant interference a modified method is advised as described in section B8.2.

B4 Hazards

Glacial acetic acid is corrosive and an eye irritant, and should be handled with care.

B5 Reagents

All chemicals should be of analytical reagent quality unless otherwise specified. Store reagents in glass bottles.

B5.1 Water. Deionised or distilled, free from oxidising agents and having negligible chlorine demand.

B5.2 Potassium iodide, crystals.

B5.3 Sodium acetate, trihydrate.

B5.4 Acetic acid, glacial.

B5.5 Starch solution. Grind 0.5 ± 0.1 g of soluble starch into a smooth paste with a little cold water and pour, with constant stirring, into 100 ± 10 ml of boiling water. Boil for one minute and allow the mixture to cool before use. The reagent may be stored in a refrigerator for up to one week. Solid indicators are available commercially and may be used in accordance with manufacturer's instructions.

B5.6 Sodium thiosulphate solution. Either of two concentrations may be used. The performance data shown in Table B1 were obtained using 0.0125M sodium thiosulphate solution. Alternatively, 0.014M sodium thiosulphate solution may be used, which gives a simple relationship between volume of titrant used and chlorine concentration of the sample. The difference in performance between the two concentrations is negligible.

B5.6.1 Sodium thiosulphate (0.125M). Dissolve 31.2 ± 0.05 g of sodium thiosulphate pentahydrate in approximately 200 ml of water (B5.1) in a 1000-ml volumetric flask. Make to 1000 ml with water (B5.1) and mix well. Store in an amber glass bottle. The expiry date of this reagent is variable and limited. Turbid solutions should be discarded. This solution may be stored at room temperature for up to one month.

B5.6.2 Sodium thiosulphate (0.0125M). Add 50.00 ± 0.05 ml of sodium thiosulphate solution (B5.6.1) into a 500-ml volumetric flask. Make to 500 ml with water (B5.1) and mix well. Prepare fresh on the day of use.

B5.6.3 Sodium thiosulphate (0.014M). Add 56.00 ± 0.05 ml of sodium thiosulphate solution (B5.6.1) to a 500-ml volumetric flask and make to 500 ml with water (B5.1). Prepare fresh on the day of use. When used as described, 1 ml of this solution is equivalent to 1 mg/l of chlorine in the sample.

B5.6.4 Standardisation of the sodium thiosulphate solution. This should be carried out immediately before use for the analysis of samples. Pipette 10.00 ml of 0.00208M potassium iodate solution (B5.8) into 500 ± 5 ml of water (B5.1) in a 1000 ml conical flask. Add 0.5 ± 0.1 g of potassium iodide crystals (B5.2) and 5 ± 1 ml of acetic acid (B5.4) and mix and allow the solution to stand for 60 ± 5 seconds. Titrate the solution with the sodium thiosulphate solution to be standardised (B5.6.2 or B5.6.3) until the colour of the liberated iodine is nearly discharged. Add 2.0 ± 0.5 ml of starch solution (B5.5) and titrate rapidly until the blue colour disappears for 30 seconds, and then re-appears. Note the titration volume, V_1 ml.

B5.7 Potassium iodate solution (0.0208M, i.e. M/48). Dissolve 4.460 ± 0.005 g of potassium iodate (previously dried at 110 ± 5 °C for 1 hour) in approximately 200 ml of water (B5.1) in a 1000-ml volumetric flask. Make to 1000 ml with water (B5.1) and mix well. This solution may be stored at room temperature for up to one week.

B5.8 Potassium iodate solution (0.00208M, i.e. M/480). Add 50.00 ml of potassium iodate solution (B5.7) into a 500-ml volumetric flask and make to 500 ml with water (B5.1). Mix well. This solution may be stored at room temperature for up to one week.

B6 Apparatus

B6.1 Common laboratory glassware, including pipettes, conical flasks, measuring cylinders and beakers.

B6.2 Microburette. Measuring up to 5 ml and graduated to 0.02 ml divisions for concentrations up to 4 mg/l. For higher concentrations up to 20 mg/l, a 25 ml burette graduated to 0.1 ml may be more appropriate.

B7 Sample collection and preservation

In aqueous solutions, chlorine is not stable and the chlorine content of samples tends to decrease over time. Exposure to sunlight or other strong light or agitation accelerates the rate of this decrease.

The determination of chlorine should be carried out immediately after sampling and collection. If this is not possible, chlorinated final drinking waters may be stored for up to three hours without significant loss of disinfectant occurring provided the sample is taken in an amber glass bottle where no air-gap or head-space volume is allowed to be left in the fully filled bottle, and stored in a refrigerator.

When determinations are not carried out immediately after sampling and collection, the time between sampling and analysis, and the conditions of storage and transport should be recorded. This is so that such factors may be taken into account in assessing the reported result.

B8 Analytical procedure

Step	Procedure	Notes
B8.1	Samples in the absence of interferences	
B8.1.1	Add 500 ± 5 ml of sample (note a) to a 1000-ml conical flask. Add 5 ± 1 ml of acetic acid (B5.4) and 0.5 ± 0.1 g of potassium iodide crystals (B5.2). Gentle swirl the flask to mix the contents, note b.	(a) Care should be taken to minimize losses of volatile disinfectants. (b) It is essential that all the chlorine reacts with the iodine before titration begins.

B8.1.2 Immediately titrate with standardised 0.0125M sodium thiosulphate solution (B5.6.2) until the colour of the liberated iodine is nearly discharged. Add 2.0 ± 0.5 ml of starch solution (B5.5) and titrate rapidly until the blue colour disappears and re-appears within 30 seconds (note c). Note the titration volume, V_2 ml.

(c) Titrate to the first end point only, since problems may occur due to recurring end points caused by slow oxidation by air and other substances.

B8.2 Samples in the presence of interferences (notes d and e)

(d) These procedures should be used where the following concentrations are exceeded;
nitrite (as N) - 0.5 mg/l;
manganese(III) and higher valency states (as Mn) - 0.03 mg/l;
iron(III) (as Fe) - 2 mg/l;
or where other oxidizing agents are present and there is reason to suspect this might cause interference.

(e) For samples containing di-chloramine and related forms of available residual chlorine, the neutral titration described in this section may give low results, due to incomplete reaction of some forms of combined available residual chlorine. Such circumstances are uncommon with raw and drinking waters. In such cases, one of the DPD methods (method C or D) may be more appropriate.

B8.2.1 In a 1000-ml conical flask, adjust 500 ± 5 ml of sample (note a) to a pH value between 4.5 - 8.0 by addition of acetic acid (B5.4) or sodium acetate (B5.3) as necessary.

B8.2.2 To the 1000-ml conical flask, add 0.5 ± 0.1 g of potassium iodide crystals (B5.2). Gentle swirl the flask to mix the contents. See note b.

B8.2.3 Immediately titrate with standardised 0.0125M sodium thiosulphate solution (B5.6.2) until the colour of the liberated iodine is nearly discharged. Add 2.0 ± 0.5 ml of starch solution (B5.5) and titrate rapidly until the blue disappears and

re-appears within 30 seconds (note c).
Note the titration volume, V_2 ml.

B9 Calculation of results

Using 0.0125M sodium thiosulphate solution (B5.6.2):

Total available chlorine = (V_2 x 10 x 0.89) / V_1 mg/l as chlorine

Using 0.014M sodium thiosulphate solution (B5.6.3):

Total available chlorine = (V_2 x 10) / V_1 mg/l as chlorine

Table B1 Performance data

Equivalent chlorine concentration* (mg/l)	Standard deviation (mg/l)	Degrees of freedom
2	0.044 - 0.074	11
20	0.077 - 0.13	11

* Data obtained using standard potassium iodate solutions equivalent to the listed concentrations.
Data provided by Southern Water Authority and Wallace & Tiernan Ltd, Tonbridge, Kent.

C Titrimetric determination of free available residual chlorine and total available residual chlorine using diethyl-*p*-phenylenediamine

C1 Performance characteristics of the method

C1.1	Substance determined	Total available residual chlorine, or if separately determined, the amount of free available residual chlorine and combined available residual chlorine.
C1.2	Type of sample	Raw and drinking waters, swimming pool waters, waste waters and effluents.
C1.3	Basis of method	Development of a red colour with diethyl-*p*-phenylenediamine (DPD) followed by titration with ferrous ammonium sulphate solution to a colourless end point.
C1.4	Range of application	Typically, 0.02 - 5 mg/l (without dilution of the sample).
C1.5	Standard deviation	See Table C1.
C1.6	Limit of detection	Typically, 0.011 mg/l with 10 degrees of freedom
C1.7	Sensitivity	1 ml of 0.00282M ferrous ammonium sulphate is equivalent to 0.1 mg of chlorine.
C1.8	Interferences	Manganese(III) and its higher oxidation valency states may interfere and cause high results.
C1.9	Time required for analysis	Typically, 3 - 5 minutes per sample for free available residual chlorine and combined available residual chlorine, and 5 - 10 minutes for differential procedure.

C2 Principle

Free available residual chlorine reacts with diethyl-*p*-phenylenediamine (DPD) to produce a red colour. The addition of a small amount of potassium iodide causes mono-chloramine to produce a colour with the same reagent. Further addition of an excess of iodide causes di-chloramine and any nitrogen trichloride present to produce a colour. However, a change in the order of addition of reagents causes the nitrogen trichloride to react and produce a colour in the first free available residual chlorine fraction. Using this, an estimation of the concentration of nitrogen trichloride can be made. The individual fractions can be determined by titration with standard ferrous ammonium sulphate solution to colourless end points.

C3 Interferences

Oxidising agents, other than those being determined which are capable of reacting with DPD under the experimental conditions, can interfere. Ethylenediaminetetraacetic acid (EDTA) added to the mixture avoids interference in some cases, for example from copper. Section C8.7 describes a modified procedure to avoid interference from oxidised manganese. Other oxidising disinfecting agents, if present, may also react,. In these cases, it may be more appropriate to use the procedures described in section E.

C4 Hazards

Mercuric chloride and sodium arsenite are toxic compounds, and care should be taken in their handling. Diethyl-*p*-phenylenediamine may cause dermatitis; the low concentrations used in the procedures may, however, not be a cause for concern. Thioacetamide is a carcinogen.

C5 Reagents

All chemicals should be of analytical reagent grade quality unless otherwise specified. Store reagents in glass bottles.

C5.1 Water. Deionised or distilled free from oxidising agents and having negligible chlorine demand.

C5.2 Sulphuric acid (10 % v/v). Slowly add 10.0 ± 0.1 ml of concentrated sulphuric acid (SG 1.84) to about 80 ml of water. Cool the solution and make to 100 ± 1 ml with water (C5.1). This solution may be stored at room temperature for up to one year.

C5.3 Disodium ethylenediaminetetraacetate dihydrate (8 g/l). Add 8.0 ± 0.1 g of disodium ethylenediaminetetraacetate dihydrate to approximately 200 ml of water (C5.1). Mix well. Make to 1000 ± 20 ml with water. Mix well. This solution may be stored at room temperature for up to 3 months.

C5.4 Mercuric chloride solution (2 % m/v). Add 2.0 ± 0.1 g of mercuric chloride to 100 ± 10 ml of water (C5.1). Warm to dissolve and mix well. Cool the solution. This solution may be stored at room temperature for up to three months.

C5.5 Buffer solution. Add 2.40 ± 0.05 g of disodium hydrogen phosphate and 4.6 ± 0.5 g of potassium dihydrogen phosphate to approximately 50 ml of water (C5.1). Add 10 ± 1 ml of disodium ethylenediaminetetraacetate dihydrate solution (C5.3) and make to 100.0 ± 0.5 ml with water (C5.1). Add two drops (0.1 ml) of 2 % m/v mercuric chloride solution (C5.4) to prevent mould growth and to prevent interference in the free available residual chlorine test caused by trace amounts of iodide. This solution may be stored at room temperature for up to one month.

C5.6 Diethyl-*p*-phenylenediamine (DPD) solution. Add 0.300 ± 0.005 g of DPD sulphate pentahydrate (or 0.220 ± 0.005 g of anhydrous DPD sulphate) to approximately 50 ml of water (C5.1) containing 2.0 ± 0.1 ml of 10 % v/v sulphuric acid (C5.2) and 2.5 ± 0.1 ml of disodium ethylenediaminetetraacetate dihydrate (C5.3). Mix well. Make to 100.0 ± 0.5 ml with water (C5.1). The solution may be stored in an amber glass bottle at room temperature for up to one week. Discard the solution if it becomes discoloured.

C5.6.1 A combined DPD-buffer reagent is commercially available in powder or tablet form.

C5.7 Sodium arsenite solution (0.5 % m/v). Dissolve 0.50 ± 0.05 g of sodium arsenite in 100.0 ± 0.5 ml of water (C5.1). Alternatively, 0.25 % m/v thioacetamide solution may be used. Add 0.25 ± 0.02 g of thioacetamide to 100.0 ± 0.5 ml of water (C5.1) and mix well. These solutions may be stored at room temperature for up to one month.

C5.8 Potassium iodide crystals.

C5.8.1 Potassium iodide solution (0.5 % m/v). This solution may be used in some situations as an alternative to the potassium iodide crystals, i.e. 0.1 ml of potassium iodide solution is equivalent to 0.5 mg of potassium iodide crystals. Weigh out 0.50 ± 0.05 g of potassium iodide and dissolve in 100 ± 2 ml of water (C5.1). Prepare fresh on the day of use as this solution soon becomes discoloured.

C5.9 Ferrous ammonium sulphate solution (0.00282M). Boil approximately 200 ml of water (C5.1). Cool. Add 2.5 ± 0.1 ml of 10 % v/v sulphuric acid (C5.2). Add 1.106 ± 0.005 g of ferrous ammonium sulphate hexahydrate. Mix well. Quantitatively transfer the solution to a 1000-ml volumetric flask and make to 1000 ml with water (C5.1). Transfer the solution to a stoppered amber glass bottle. The stability of this solution varies with storage conditions and with the amount of free air-space above the solution in the bottle. This solution may be stored at room temperature for up to one week. Before use, the solution should be checked against standard potassium dichromate. (1 ml of 0.00282M ferrous ammonium sulphate solution is equivalent to 100 µg of chlorine).

To 100.0 ml of 0.00282M ferrous ammonium sulphate solution, add 20.0 ± 0.5 ml of 10 % v/v sulphuric acid (C5.2) and 5 ml of phosphoric acid (C5.11) and 2 ml of barium diphenylaminesulphonate solution (C5.12). Titrate with the potassium dichromate solution to a violet end point that persists for 30 seconds. Repeat this procedure two more times and calculate the average titre, T ml.

If the ferrous ammonium sulphate solution is made accurately, 100.0 ml of 0.00282M ferrous ammonium sulphate solution is equivalent to 28.2 ml of 0.01N potassium dichromate solution (C5.10). If the ferrous ammonium sulphate solution requires significantly less than 28.2 ml of potassium dichromate solution, discard the ferrous ammonium sulphate solution and prepare a fresh ferrous ammonium sulphate solution. For ferrous ammonium sulphate solutions which are slightly under the required concentration then a standardisation factor can be used. For 0.01N potassium dichromate solution, the factor is T/28.2, where T is the volume (ml) of standard potassium dichromate solution.

C5.10 Potassium dichromate solution (0.01N, i.e. M/600). Dry just over 0.5 g of potassium dichromate at 105 - 120 °C to constant weight. Add 0.4903 ± 0.0005 g of this potassium dichromate to a 1000 ml volumetric flask and add approximately 800 ml of water (C5.1). Mix well. Make to 1000 ml with water. Mix well. This solution may be stored at room temperature for up to one month.

C5.11 Phosphoric acid (SG 1.83).

C5.12 Barium diphenylaminesulphonate solution (0.1 % m/v). Dissolve 0.10 ± 0.02 g of barium diphenylaminesulphonate in 100 ml of water (C5.1). It may be necessary to

warm the water to dissolve the reagent. This solution may be stored in a glass stoppered bottle at room temperature for up to one week.

C6 Apparatus

C6.1 Common laboratory glassware, including pipettes, conical and volumetric flasks and measuring cylinders.

C6.2 Microburette. Measuring up to 5 ml, graduated to 0.02 ml

C7 Sample collection and preservation

In aqueous solutions, chlorine is not stable and the chlorine content of samples tends to decrease over time. Exposure to sunlight or other strong light or agitation accelerates the rate of this decrease.

The determination of chlorine should be carried out immediately after sampling and collection. If this is not possible, chlorinated final drinking waters may be stored for up to three hours without significant loss of disinfectant occurring provided the sample is taken in an amber glass bottle where no air-gap or head-space volume is allowed to be left in the fully filled bottle, and stored in a refrigerator.

When determinations are not carried out immediately after sampling and collection, the time between sampling and analysis, and the conditions of storage and transport should be recorded. This is so that such factors may be taken into account in assessing the reported result.

C8 Analytical procedure

The quantities of reagents given are suitable for concentrations of total available residual chlorine of up to 5 mg/l. When the concentration exceeds this figure, dilution of the sample with water (C5.1) is required. However, care should be taken to ensure no losses of residual chlorine levels occur. For very high concentrations, it is important to dilute the sample, as bleaching of the colour can occur leading to erroneous and mis-leading results. This is usually indicated by the appearance of a transient red colour followed by rapid fading.

Glassware should be rinsed thoroughly between determinations. Any carry-over of traces of iodide can lead to mono-chloramine break-through into the free chlorine fraction of the subsequent determination.

Step	Procedure	Notes
C8.1	Free available residual chlorine	
C8.1.1	Add 5.0 ± 0.5 ml of DPD solution (C5.6) and 5.0 ± 0.5 ml of buffer solution (C5.5) to a 250 ml conical flask, see note a. Mix well. Carefully, add 100.0 ± 0.5 ml of sample (notes b and c) and mix. Titrate the solution	(a) Alternatively, a combined buffer-DPD reagent (C5.6.1) may be used. (b) Care should be taken to

immediately with standardised ferrous ammonium sulphate solution (C5.9) until the red colour is discharged (volume A ml).

minimize losses of volatile disinfectants from the sample.

(c) If the total available residual chlorine concentration exceeds 5 mg/l, the volume of sample should be correspondingly reduced, i.e. should be less than 100 ml, or a dilution of the sample prepared. An amount of water (C5.1) being the difference between 100 ml and the volume of sample actually taken should be added to the DPD-buffer mixture before the sample is added.

C8.2 Mono-chloramine

C8.2.1 Immediately following the titration in step C8.1.1, add approximately 0.5 mg of potassium iodide (C5.8) see note d, and continue the titration immediately with standardised ferrous ammonium sulphate solution (C5.9) until the red colour is discharged (volume B ml) see note e.

(d) Alternatively, 0.1 ml of 0.5 % m/v potassium iodide solution (C5.8.1) may be used.

(e) The recorded volume is the total volume, i.e. volume A plus the additional titre.

C8.3 Di-chloramine

C8.3.1 Following the titration in step C8.2.1, add approximately 1 g of potassium iodide (C5.8) and mix to dissolve. Leave the solution to stand for two minutes and continue the titration with standardised ferrous ammonium sulphate solution (C5.9) until the red colour is discharged (volume C ml) see notes f and g. If nitrogen trichloride is present (note h) correct the result, see section C8.6.

(f) The recorded volume is the total volume, i.e. volume B plus the additional titre.

(g) Any drift-back of colour at the end point when titrating relatively large amounts of di-chloramine may indicate that the reaction with iodide, which is not instantaneous, is still incomplete. In such cases, allow the solution to stand a further two minutes before commencing the titration. When di-chloramine concentrations are known to be low, add only 0.5 g of potassium iodide (C5.8).

(h) In the absence of free available residual chlorine, nitrogen trichloride may also be taken as being absent. Moreover, nitrogen trichloride is unlikely to be present in waters containing mono-chloramine, but see section C9.

C8.4 Simplified procedure for free available residual chlorine and combined available residual chlorine

C8.4.1 Add 5.0 ± 0.5 ml of DPD solution (C5.6) and 5.0 ± 0.5 ml of buffer solution (C5.5) to a 250 ml conical flask, see note a. Mix well. Carefully, add 100.0 ± 0.5 ml of sample (notes b and c) and mix. Titrate the solution immediately with standardised ferrous ammonium sulphate solution (C5.9) until the red colour is discharged (volume A ml). See note i.

(i) This gives free available residual chlorine.

C8.4.2 Immediately following the titration in step C8.4.1, add approximately 1 g of potassium iodide (C5.8) and mix to dissolve. Leave the solution to stand for two minutes and titrate the solution with standardised ferrous ammonium sulphate solution (C5.9) until the red colour is discharged (volume C ml) see notes e, g and j. If nitrogen trichloride is present (see note h) correct the result, see section C8.6.

(j) This gives combined available residual chlorine.

C8.5 Simplified procedure for total available residual chlorine

C8.5.1 To obtain total available residual chlorine with one titration, add approximately 1 g of potassium iodide (C5.8) to a 250 ml conical flask. Add 5.0 ± 0.5 ml of DPD solution (C5.6) and 5.0 ± 0.5 ml of buffer solution (C5.5) see note a. Mix well. Carefully, add 100.0 ± 0.5 ml of sample (notes b and k) and mix. Leave the solution to stand for two minutes and titrate with standardised ferrous ammonium sulphate solution (C5.9) until the red colour is discharged (volume C ml). In the presence of nitrogen trichloride the result will require an appropriate correction, see section C8.6.

(k) If the total available residual chlorine concentration exceeds 5 mg/l, the volume of sample should be correspondingly reduced, i.e. should be less than 100 ml, or a dilution of the sample prepared. An amount of water (C5.1) being the difference between 100 ml and the volume of sample actually taken should be added to the potassium iodide-DPD-buffer mixture before the sample is added.

C8.6 Nitrogen trichloride

C8.6.1 See note l. To determine nitrogen trichloride separately, add approximately 0.5 mg of potassium iodide (C5.8) to a 250 ml conical flask, see note d. Carefully, add 100.0 ± 0.5 ml of sample and mix (note b). Quantitatively transfer this mixture to a

(l) When present, nitrogen trichloride will normally appear to the extent of one-half of its available chlorine content with di-chloramine.

second flask containing 5.0 ± 0.5 ml of buffer solution (C5.5) and 5.0 ± 0.5 ml of DPD solution (C5.6) see note a. Titrate the mixed solution immediately with standardised ferrous ammonium sulphate solution (C5.9) until the red colour is discharged (volume N ml).

C8.7 Correction for interference caused by oxidized manganese

C8.7.1 See note m. Add 5.0 ± 0.5 ml of buffer solution (C5.5) to a conical flask. Add 0.50 ± 0.05 ml of sodium arsenite solution (C5.7). Add 100.0 ± 0.5 ml of sample (notes b and n) and mix. See note o. Then add 5.0 ± 0.5 ml of DPD solution (C5.6) and again mix. Titrate any red colour with standardised ferrous ammonium sulphate solution (C5.9) until the red colour is discharged. Subtract this titre from volume A (free available residual chlorine) as obtained in steps C8.1 or C8.4 or from total available residual chlorine volume in section C8.5.1.

(m) This is particularly important when determining low levels of chlorine and chloramines in waste waters and effluents.

(n) Alternatively, instead of using sodium arsenite solution, add 0.50 ± 0.05 ml of the thioacetamide solution (C5.7) to 100.0 ± 0.5 ml of sample and add this solution to the flask containing the buffer solution (C5.5).

(o) If the total available residual chlorine concentration exceeds 5 mg/l, the volume of sample should be correspondingly reduced, i.e. should be less than 100 ml, or a dilution of the sample prepared. An amount of water (C5.1) being the difference between 100 ml and the volume of sample actually taken should be added to the buffer solution before the sample is added.

C9 Calculation of results

For 100 ml of sample, 1.0 ml of standardised ferrous ammonium sulphate solution (C5.9) is equivalent to 1.0 mg/l available chlorine. (See final paragraph in section C5.9).

The following table may be used for calculating the concentrations of individual components.

Volumes A, B, C and N are defined in steps C8.1, C8.2, C8.3 and C8.6 respectively.

Determination	Nitrogen trichloride absent	Nitrogen trichloride present
Free chlorine (i)	A	A
Mono-chloramine (ii)	B - A	
Di-chloramine	C - B	C - N
Nitrogen trichloride (i) and (iii)		2(N - A)
Combined chlorine (iii)	C - A	C + N - 2A
Total chlorine (i) and (iii)	C	C + N - A

(i) If oxidized manganese is present, determine the correction as in step C8.7 and apply to the determinations as follows:

free chlorine - deduct correction from volume A
total chlorine - deduct correction from volume C

(ii) The above formulae assume that if nitrogen trichloride is present, mono-chloramine is absent, i.e. B = A.

(iii) If in exceptional circumstances, mono-chloramine and nitrogen trichloride should be present at the same time, volume N will include mono-chloramine. In this case,

nitrogen trichloride = 2(N - B)
combined available residual chlorine = C + N - A - B
total available residual chlorine = C + N - B.

C9.1 Hypochlorous acid concentration

Except in very acid waters below a pH value of about 4, when chlorine may be present, the free available residual chlorine, as normally determined, comprises a mixture of chlorine, hypochlorous acid and hypochlorite ion, the relative proportions depending on pH and temperature. Hypochlorous acid is the most active germicide of all these substances. To obtain an estimate of the hypochlorous acid concentration, multiply volume A by the appropriate factor in the table below. More detailed information is available in standard references on disinfection.

	pH value								
	6.6	7.0	7.2	7.4	7.6	7.8	8.0	8.4	9.0
Factor at 10 °C	0.93	0.83	0.76	0.66	0.55	0.44	0.33	0.16	0.05
Factor at 25 °C	0.90	0.78	0.69	0.58	0.46	0.35	0.26	0.12	0.03

Table C1 Performance data

Chlorine concentration (mg/l)	Standard deviation* (mg/l)	Degrees of freedom
1.0	0.014	9
5.0	0.044	9

* as total available residual chlorine.

Data provided by Newcastle & Gateshead Water Company Laboratory.

D Spectophotometric determination of free available residual chlorine and total available residual chlorine using diethyl-*p*-phenylenediamine

This method describes a spectrophotometric method for determining residual chlorine levels (usually carried out in a laboratory, though not always) based on colours produced using DPD reagent. Portable spectrophotometers are also available for use, either within a laboratory or on-site.

A secondary option may involve colour comparison of the DPD colours but with final estimation made by comparison with permanent glass standards.

Reagents are available in stable powder or tablet form.

Standard glass discs are available in a series of ranges covering 0.01 - 10.0 mg/l of available chlorine, involving sample volumes varying from 4 ml to 50 ml, and viewing depths varying from 5 mm to 113 mm. Such discs should be checked against standard solutions, for example as described in section D8.1.

D1 Performance characteristics of the method

D1.1	Substance determined	Total available residual chlorine, or if separately determined, the amount of free available residual chlorine and combined available residual chlorine.
D1.2	Type of sample	Raw and drinking waters, swimming pool waters, waste waters, effluents and sea waters.
D1.3	Basis of method	Development of red colour with diethyl-*p*-phenylenediamine (DPD) followed by spectrophotometric absorption measurement at 510 nm or 550 nm.
D1.4	Range of application	Typically, 0.01 - 5 mg/l (without dilution of the sample).
D1.5	Calibration curve	Linear to approximately 2 mg/l. The concentration-response curve follows Beer's law and passes through the origin.
D1.6	Standard deviation	See Table D1.
D1.7	Limit of detection	Typically, 0.004 mg/l in a 10 mm path length cell with 10 degrees of freedom
D1.8	Sensitivity	Molar extinction coefficient = 9800.
D1.9	Time required for analysis	Typically, 3 - 5 minutes per sample for free available residual chlorine and combined

available residual chlorine, and 5 - 10 minutes for differential procedure.

D2 Principle

Free available residual chlorine reacts with diethyl-*p*-phenylenediamine (DPD) to produce a red colour. The addition of a small amount of potassium iodide causes mono-chloramine to produce a colour with the same reagent. Further addition of an excess of iodide causes di-chloramine and any nitrogen trichloride present to produce a colour. However, a change in the order of addition of reagents causes the nitrogen trichloride to react and produce a colour in the first free available residual chlorine fraction. Using this, an estimation of the concentration of nitrogen trichloride can be made. The individual fractions can be determined spectrophotometrically at 510 nm or 550 nm.

D3 Interferences

Oxidizing agents, other than those being determined which are capable of reacting with DPD under the experimental conditions, can interfere. Ethylenediaminetetraacetic acid (EDTA) added to the mixture avoids interference in some cases, for example from copper, and from turbidity caused by formation of calcium phosphate in the test. Section D8.8 describes a modified procedure to avoid interference from oxidized manganese. Other oxidizing disinfecting agents, if present, may also react. In these cases, it may be more appropriate to use the procedures described in section E.

Sea water and corresponding sodium chloride solutions have been found to lower the absorbance sensitivity by about 12 - 15 %. When analysing sea waters or other comparable salt solutions, the standard solutions should be prepared in a simulated sea water.

D4 Hazards

Mercuric chloride and sodium arsenite are toxic compounds, and care should be taken in their handling. Diethyl-*p*-phenylenediamine may cause dermatitis; the low concentrations used in the procedures may, however, not be a cause for concern.

D5 Reagents

All chemicals should be of analytical reagent grade quality unless otherwise specified. Store reagents in glass bottles.

D5.1 Water. Deionised or distilled free from oxidising agents and having negligible chlorine demand.

D5.2 Sulphuric acid (10 % v/v). Slowly add 10.0 ± 0.1 ml of concentrated sulphuric acid (SG 1.84) to about 80 ml of water. Cool the solution and make to 100 ± 1 ml with water (D5.1). This solution may be stored at room temperature for up to one year.

D5.3 Disodium ethylenediaminetetraacetate dihydrate (40 g/l). Add 40.0 ± 0.1 g of disodium ethylenediaminetetraacetate dihydrate to approximately 200 ml of water (D5.1). Mix well. Make to 1000 ± 20 ml with water. Mix well. This solution may be stored at room temperature for up to 3 months.

D5.4 Mercuric chloride solution (2 % m/v). Add 2.0 ± 0.1 g of mercuric chloride to 100 ± 10 ml of water (D5.1) warm to dissolve and mix well. Cool the solution. This solution may be stored at room temperature for up to three months.

D5.5 Buffer solution. Add 2.60± 0.05 g of disodium hydrogen phosphate and 3.0 ± 0.5 g of potassium dihydrogen phosphate to approximately 50 ml of water (D5.1). Add 25 ± 1 ml of ethylenediaminetetraacetate solution (D5.3) and make to 100.0 ± 0.5 ml with water (D5.1). Add two drops (0.1 ml) of 2 % m/v mercuric chloride solution (D5.4) to prevent mould growth and to prevent interference in the free available residual chlorine test caused by trace amounts of iodide. This solution may be stored at room temperature for up to one month.

D5.6 Diethyl-*p*-phenylenediamine (DPD) solution. Add 0.300 ± 0.005 g of DPD sulphate pentahydrate (or 0.220 ± 0.005 g of anhydrous DPD sulphate) to approximately 50 ml of water (D5.1) containing 2.0 ± 0.1 ml of 10 % v/v sulphuric acid (D5.2) and 0.5 ± 0.1 ml of disodium ethylenediaminetetraacetate dihydrate (D5.3). Mix well. Make to 100.0 ± 0.5 ml with water (D5.1). The solution may be stored in an amber glass bottle at room temperature for up to 1 week. Discard the solution if it becomes discoloured.

D5.6.1 A combined DPD-buffer reagent is commercially available in powder or tablet form.

D5.7 Sodium arsenite solution (0.5 % m/v). Dissolve 0.50 ± 0.05 g of sodium arsenite in 100.0 ± 0.5 ml of water (D5.1). Alternatively, 0.25 % m/v thioacetamide solution may be used. Add 0.25 ± 0.02 g of thioacetamide to 100.0 ± 0.5 ml of water (D5.1) and mix well. These solutions may be stored at room temperature for up to one month.

D5.8 Potassium iodide crystals.

D5.8.1 Potassium iodide solution (0.5 % m/v). This solution may be used in some situations as an alternative to the potassium iodide crystals, i.e. 0.1 ml of potassium iodide solution is equivalent to 0.5 mg of potassium iodide crystals. Weigh out 0.50 ± 0.05 g of potassium iodide and dissolve in 100 ± 2 ml of water (C5.1). Prepare fresh on the day of use as this solution soon becomes discoloured.

D5.9 Ferrous ammonium sulphate solution (0.00282M). Boil approximately 200 ml of water (D5.1). Cool. Add 2.5 ± 0.1 ml of 10 % v/v sulphuric acid (D5.2). Add 1.106 ± 0.005 g of ferrous ammonium sulphate hexahydrate (FAS). Mix well. Quantitatively transfer the solution to a 1000 ml volumetric flask and make to 1000 ml with water (D5.1). Transfer the solution to a stoppered amber glass bottle. The stability of this solution varies with storage conditions and with the amount of free air space above the solution in the bottle. This solution may be stored at room temperature for up to one week. Before use it should be checked against standard potassium dichromate. (1 ml of 0.00282M ferrous ammonium sulphate solution is equivalent to 100 µg of chlorine).

To 100.0 ml of 0.00282M ferrous ammonium sulphate solution, add 20.0 ± 0.5 ml of 10 % v/v sulphuric acid (D5.2) 5 ml of phosphoric acid (D5.11) and 2 ml of barium diphenylaminesulphonate solution (D5.12). Titrate with the potassium dichromate solution to a violet end point that persists for 30 seconds. Repeat the titration twice more and calculate the average titre, T ml.

If the ferrous ammonium sulphate solution is made accurately, 100.0 ml of 0.00282M ferrous ammonium sulphate solution is equivalent to 28.2 ml of 0.01N potassium dichromate solution (D5.10). If the ferrous ammonium sulphate solution requires significantly less than 28.2 ml of potassium dichromate solution, discard the ferrous ammonium sulphate solution and prepare a fresh ferrous ammonium sulphate solution. For ferrous ammonium sulphate solutions which are slightly under the required concentration then a standardisation factor can be used. For 0.01N potassium dichromate solution, the factor is T/28.2, where T is the volume (ml) of standard potassium dichromate solution.

D5.10 Potassium dichromate solution (0.01N, i.e. M/600). Dry just over 0.5 g of potassium dichromate at 105 - 120 °C to constant weight. Add 0.4903 ± 0.0005 g of this potassium dichromate to a 1000 ml volumetric flask and add approximately 800 ml of water (D5.1). Mix well. Make to 1000 ml with water. Mix well. This solution may be stored at room temperature for up to one month.

D5.11 Phosphoric acid (SG 1.83).

D5.12 Barium diphenylaminesulphonate solution (0.1 % m/v). Dissolve 0.10 ± 0.02 g of barium diphenylaminesulphonate in 100 ml of water (D5.1). It may be necessary to warm the water to dissolve the reagent. Store the solution in a glass stoppered bottle at room temperature for up to one week.

D5.13 Potassium permanganate solution (0.891 g/l). Add 0.8910 ± 0.0005 g of potassium permanganate to a 1000-ml volumetric flask, dissolve in 200 ml of water (D5.1) and mix well. Make to 1000 ml with water (D5.1). This solution may be stored at room temperature for up to two months. (1 ml of this solution is equivalent to 1 milligram of chlorine, i.e. 1000 mg/l as chlorine.)

D5.14 Potassium permanganate solution (0.0891 g/l). Add 10.00 ml of potassium permanganate solution (D5.13) to a 100-ml volumetric flask. Make to 100 ml with water (D5.1). This solution should be prepared on the day of use. This solution is equivalent to 100 mg/l as chlorine.

D5.15 Simulated sea water. Dissolve 66 ± 1 g of sodium chloride (which has been heated at 600 ± 25 °C for 1 hour) and 0.167 ± 0.001 g of sodium bromide in approximately 1500 ml of water (D5.1). Make to 2000 ml with water (D5.1). Mix well. This solution may be stored at room temperature for up to one year.

D6 Apparatus

D6.1 Common laboratory glassware, including pipettes, conical and volumetric flasks and measuring cylinders.

D6.2 Microburette. Measuring up to 5 ml, graduated to 0.02 ml

D6.3 Spectrophotometer. For use at a wavelength of 510 nm or 550 nm with 10 mm or 40 mm path length glass cells. Alternatively, an estimation of the chlorine levels can be determined using a comparator and standard glass discs.

D7 Sample collection and preservation

In aqueous solutions, chlorine is not stable and the chlorine content of samples tends to decrease over time. Exposure to sunlight or other strong light or agitation accelerates the rate of this decrease.

The determination of chlorine should be carried out immediately after sampling and collection. If this is not possible, chlorinated final drinking waters may be stored for up to three hours without significant loss of disinfectant occurring provided the sample is taken in an amber glass bottle where no air-gap or head-space volume is allowed to be left in the fully filled bottle and stored in a refrigerator.

When determinations are not carried out immediately after sampling and collection, the time between sampling and analysis, and the conditions of storage and transport should be recorded. This is so that such factors may be taken into account in assessing the reported result.

D8 Analytical procedure

The quantities of reagents given are suitable for concentrations of total available residual chlorine up to 5 mg/l. When the concentration exceeds this figure, dilution of the sample with water (D5.1) is required. However, care should be taken to ensure no losses of residual chlorine levels occur. For very high concentrations, it is important to dilute the sample, as bleaching of the colour can occur leading to erroneous results. This is indicated by the appearance of a transient red colour followed by rapid fading.

Glassware should be rinsed thoroughly between determinations. Any carry-over of traces of iodide can lead to mono-chloramine breakthrough into the free chlorine fraction of the subsequent determination.

Step	Procedure	Notes
D8.1	Standard solutions	
D8.1.1	Add 5.00 ± 0.05 ml of the 0.0891 g/l potassium permanganate solution (D5.14) into a 100-ml volumetric flask and make to 100 ml with water (D5.1) note a.	(a) When analysing sea water samples, use simulated sea water (D5.15) for the preparation of standard solutions.
D8.1.2	Add 5.00 ± 0.05 ml of DPD solution (D5.6) and 5.00 ± 0.05 ml of buffer solution (D5.5) in a 250-ml conical flask, note b. Mix well. Add the 100 ml of potassium permanganate standard solution (step D8.1.1) to the flask and mix thoroughly. Immediately measure the absorbance of the solution at 510 nm in a 40 mm path length cell (notes c and d) using water (D5.1) in the reference cell.	(b) Alternatively, a combined buffer-DPD reagent (D5.6.1) may be used. (c) Alternatively, a wavelength of 550 nm may be used. (d) Smaller path length cells (but not less than 10 mm) may be used.

D8.1.3 Titrate a known volume of the solution from D8.1.2 against standardised ferrous ammonium sulphate solution (D5.9) until the colour is discharged (note e).

(e) This serves as a check on the concentration of the potassium permanganate standard solution.

D8.1.4 Repeat steps D8.1.1 - D8.1.3 using, in sequence, 4.00, 3.00, 2.00, 1.00, 0.50 and 0.0 ml of the 0.0891 g/l potassium permanganate solution (D5.14). See note f.

(f) Each standard solution should be treated separately before proceeding to the next standard solution.

D8.1.5 The 100 ml solutions of potassium permanganate (D8.1.1) are equivalent to 5.0, 4.0, 3.0, 2.0, 1.0, 0.5 and 0.0 mg/l of chlorine, respectively.

D8.1.6 Prepare a calibration curve of the absorbance (D8.1.2) against corresponding equivalent chlorine concentration, see section D5.9.

D8.2 Free available residual chlorine

D8.2.1 Add 5.00 ± 0.05 ml of DPD solution (D5.6) and 5.00 ± 0.05 ml of buffer solution (D5.5) in a 250-ml conical flask, note b. Mix well. Carefully, add 100.0 ± 0.5 ml of sample (note g) and mix (note h). Immediately measure the absorbance at 510 nm in a 40 mm cell (notes c and d) using water in the reference cell. Record the reading, A.

(g) Care should be taken to minimize losses of volatile disinfectants from the sample.

(h) If the total available residual chlorine concentration exceeds 5 mg/l, the volume of sample should be correspondingly reduced, i.e. should be less than 100 ml, or a dilution of the sample prepared. An amount of water (D5.1) being the difference between 100 ml and the volume of sample actually taken should be added to the DPD-buffer mixture before the sample is added.

D8.3 Mono-chloramine

D8.3.1 To the total solution after carrying out step D8.2.1, add approximately 0.5 mg of potassium iodide (D5.8) and mix, note i. Immediately measure the absorbance at 510 nm in a 40 mm cell (notes c and d) using water in the reference cell. Record the reading, B.

(i) Alternatively, 0.1 ml of 0.5 % m/v potassium iodide solution (D5.8.1) may be used.

D8.4 Di-chloramine

D8.4.1 To the total solution after step D8.3.1, add about 1 g of potassium iodide (D5.8) and mix to dissolve. Leave the solution to stand for two minutes, then measure the absorbance at 510 nm in a 40 mm cell (notes c and d) using water in the reference cell, see note j. Record the reading, C. If nitrogen trichloride is present (note k) correct the result, see step D8.7.

(j) A drifting absorbance measurement may indicate that the reaction with the iodide, which is not instantaneous, is still incomplete. In such cases, allow the solution to stand a further two minutes before measuring the absorbance. When di-chloramine concentrations are known to be low, add only 0.5 g of potassium iodide (D5.8).

(k) In the absence of free available residual chlorine, nitrogen trichloride may also be taken as being absent. Moreover, nitrogen trichloride is unlikely to be present in waters containing mono-chloramine, but see section D9.

D8.4.2 Read off the equivalent chlorine concentrations (from the readings A, B and C) from appropriate calibration graphs.

D8.4.3 Repeat procedures in steps D8.2.1 - D8.4.2 for each sample.

D8.5 Simplified procedure for free available residual chlorine and combined available residual chlorine

D8.5.1 Determine free chlorine as follows. Add 5.00 ± 0.05 ml of DPD solution (D5.6) and 5.00 ± 0.05 ml of buffer solution (D5.5) in a 250-ml conical flask, note b. Mix well. Carefully, add 100.0 ± 0.5 ml of sample (note g) and mix (note h). Immediately measure the absorbance at 510 nm in a 40 mm cell (notes c and d) using water in the reference cell. Record the reading, A.

D8.5.2 To determine combined available residual chlorine, to the total solution after step D8.5.1, add about 1 g of potassium iodide (D5.8) and mix to dissolve. Leave the solution to stand for two minutes, then measure the absorbance at 510 nm in a 40 mm cell (notes c and d) using water in the reference cell, see note j. Record the

reading, C. If nitrogen trichloride is present (note k) correct the result, see step D8.7.

D8.5.3 Read off the equivalent chlorine concentrations (from the readings A and C) from appropriate calibration graphs.

D8.5.4 Repeat procedures in steps D8.5.1 - D8.5.3 for each sample.

D8.6 Simplified procedure for total available residual chlorine

D8.6.1 To obtain total available residual chlorine in one reading, add approximately 1 g of potassium iodide (D5.8) 5.00 ± 0.05 ml of DPD solution (D5.6) and 5.00 ± 0.05 ml of buffer solution (D5.5) to a 250-ml conical flask, note b. Mix well. Carefully, add 100.0 ± 0.5 ml of sample (note g) and mix (note l). Leave the solution to stand for two minutes, then measure the absorbance at 510 nm in a 40 mm cell (notes c and d) using water in the reference cell, see note j. Record the reading, C. If nitrogen trichloride is present (note k) correct the result, see step D8.7.

(l) If the total available residual chlorine concentration exceeds 5 mg/l, the volume of sample should be correspondingly reduced, i.e. should be less than 100 ml, or a dilution of the sample prepared. An amount of water (D5.1) being the difference between 100 ml and the volume of sample actually taken should be added to the potassium iodide-DPD-buffer mixture before the sample is added.

D8.7 Nitrogen trichloride

D8.7.1 See note m. To determine nitrogen trichloride separately, add approximately 0.5 mg of potassium iodide (D5.8) note i, into a 250-ml conical flask. Carefully, add 100.0 ± 0.5 ml of sample (note g) and mix (note n). Transfer the contents of this flask to a separate flask containing 5.0 ± 0.05 ml of buffer solution (D5.5) and 5.0 ± 0.05 ml of DPD solution (D5.6) note b. Mix and immediately measure the absorbance at 510 nm in a 40 mm cell (notes c and d) using water in the reference cell (reading N). Calculate the equivalent chlorine concentrations from appropriate calibration graphs as in steps D8.2, D8.3 and D8.4.

(m) When present, nitrogen trichloride will normally appear to the extent of one-half of its available chlorine content with the di-chloramine.

(n) If the total available residual chlorine concentration exceeds 5 mg/l, the volume of sample should be correspondingly reduced, i.e. should be less than 100 ml, or a dilution of the sample prepared. An amount of water (D5.1) being the difference between 100 ml and the volume of sample actually taken should be added to the potassium iodide before the sample is added.

D8.8 Correction for interference by oxidised manganese

D8.8.1 See note o. Add 5.0 ± 0.5 ml of buffer solution (D5.5) to a conical flask. Add 0.50 ± 0.05 ml of sodium arsenite solution (D5.7). Add 100.0 ± 0.5 ml of sample (notes g and p) and mix. See note q. Then add 5.0 ± 0.5 ml of DPD solution (D5.6) and again mix. Measure the absorbance at 510 nm in a 40 mm cell (notes c and d) using water in the reference cell, and subtract the reading from the free chlorine absorbance as obtained in steps D8.2 or D8.5 or from the total available chlorine absorbance obtained in step D8.6.

(o) In determining low levels of chlorine and chloramine in waste waters and effluents, a sodium arsenite or thioacetamide blank solution should always be used.

(p) Alternatively, instead of using sodium arsenite solution, add 0.50 ± 0.05 ml of the thioacetamide solution (D5.7) to 100.0 ± 0.5 ml of sample and add this solution to the flask containing the buffer solution (D5.5).

(q) If the total available residual chlorine concentration exceeds 5 mg/l, the volume of sample should be correspondingly reduced, i.e. should be less than 100 ml, or a dilution of the sample prepared. An amount of water (D5.1) being the difference between 100 ml and the volume of sample actually taken should be added to the buffer before the sample is added.

D9 Calculation of results

The following table may be used for calculating the concentrations of individual components.

Volumes A, B, C and N are defined in steps D8.2, D8.3, D8.4 and D8.7 respectively.

Determination	Nitrogen trichloride absent	Nitrogen trichloride present
Free chlorine (i)	A	A
Mono-chloramine (ii)	B - A	
Di-chloramine	C - B	C - N
Nitrogen trichloride (ii) and(iii)		2(N - A)
Combined chlorine (iii)	C - A	C + N - 2A
Total chlorine (i) and (iii)	C	C + N - A

(i) If oxidized manganese is present, determine the correction as in step D8.8 and apply to the determinations as follows:

free chlorine - deduct correction from volume A
total chlorine - deduct correction from volume C

(ii) The above formulae assume that if nitrogen trichloride is present, mono-chloramine is absent, i.e. B = A.

(iii) If in exceptional circumstances, mono-chloramine and nitrogen trichloride should be present at the same time, volume N will include mono-chloramine. In this case, nitrogen trichloride is obtained using 2(N - B).

Table D1 Performance data

Chlorine concentration (mg/l)	Standard deviation (mg/l)	Degrees of freedom
0.1	0.004	19
0.5	0.01	19
0.15	0.01	9

Data provided by Water Research Centre

E Titrimetic determination of selected disinfectants in the presence (or absence) of chlorine and chloramines

E1 Performance characteristics of the methods

With the exception of chlorine dioxide, the performance characteristics of these supplementary procedures are similar to those of the DPD method for free chlorine and chloramines. If conversion factors are used, the numerical values should be adjusted accordingly. In the case of chlorine dioxide, it is necessary to use a factor of 5, if expressed in terms of available chlorine. Alternatively, if results are expressed in terms of chlorine dioxide the required factor is 1.9.

E2 Principle

The procedures are extensions of the DPD method for free chlorine and chloramines.

E2.1 Chlorine dioxide and chlorite

Chlorine dioxide is determined with free chlorine in step E7.1.1, but only to the extent of one-fifth of its total available chlorine, corresponding to the first stage reduction to chlorite. If the sample is then acidified in the presence of potassium iodide, chlorite also reacts. The colour produced after subsequent neutralisation corresponds to the total available residual chlorine content of the chlorine dioxide. Any chlorite present in the original sample will be included in the step involving acidification and neutralisation. The presence of chlorite is to be expected since, apart from the possibility of incomplete conversion to chlorine dioxide in the generation process, some reversion in the treated water may occur, as chlorite is the first stage reduction product of the applied chlorine dioxide. Alternative procedures are given (sections E7.1.2 and E8) using thioacetamide which prevents colour drift-back at end points caused by chlorite being present. In practice, chlorine dioxide treatment is unlikely to produce significant amounts of nitrogen trichloride in the water so that a separate procedure for its determination is not normally required. Should trace amounts be present, it is adequate to include them as di-chloramine or as combined chlorine where a separate determination of mono-chloramine and di-chloramine is not performed, thus simplifying the differential procedures. The same simplification is introduced in the other procedures involving bromine, iodine, ozone and chloroisocyanurates, since the use of these chemicals in water treatment does not produce nitrogen trichloride.

E2.2 Bromine and bromamine

Bromine and bromamines are chemically similar in reacting with the DPD indicator to produce a red colour. In the DPD method (E10) therefore, the result obtained in the first step after allowing for any free chlorine present, corresponds to free bromine plus bromamines, which two forms are taken together as residual bromine. As there are not the same differences in chemical and bacteriological behaviour as occur with free chlorine and the chloramines, the need for their separate determination is not important, although it may be accomplished, if required, by the use of sodium nitrite as a supplementary reagent.

E2.3 Iodine

Iodine reacts with the DPD indicator in the same manner as free chlorine so that it is necessary only to perform the same procedure as given in the first step of the DPD free chlorine-chloramines method (section C8.1).

E2.4 Ozone

Ozone gives a colour with the DPD indicator; but this, in the absence of potassium iodide, corresponds to only a fraction of its total equivalent available chlorine concentration. Subsequent addition of iodide has little effect upon this colour. On the other hand, if the reaction takes place in the presence of potassium iodide, added either before or with the DPD indicator, a full response is obtained; this is therefore the preferred procedure.

E2.5 Chloroisocyanurate

Chloroisocyanurate dissociates in water to form an equilibrium with free chlorine and cyanuric acid. Because the equilibrium is a dynamic one, the reading of the DPD free chlorine-chloramine method (section E14.1) includes both the free chlorine and the reserve chlorine, since as fast as the free chlorine reacts with the DPD indicator, more chloro-compound is decomposed, thus releasing all the bound chlorine.

E2.6 Differential analysis of mixtures

Differential analysis of mixtures of other disinfecting agents with free chlorine and chloramines is based upon the use of glycine. This supplementary reagent converts free chlorine instantaneously into chloraminoacetic acid thus removing it from the first step of the DPD method and effecting a separation from chlorine dioxide, residual bromine and iodine respectively, the volumes for which are not affected. In the case of chlorine-iodine differentiation it is necessary to add a small amount of mercuric chloride in order to supress any premature iodide ion activation of combined chlorine. Should bromine and chlorine dioxide be present together their separation may be effected by an additional procedure using sodium nitrite.

The separate determination of ozone and residual chlorine is based on the fact that glycine destroys the ozone practically completely, leaving the total available chlorine unchanged. Any free chlorine present is converted to chloraminoacetic acid which, together with any combined chlorine originally present, responds fully to the DPD indicator in the presence of excess iodide. Where excess iodide is used for activation of di-chloramine in the DPD method, a standing period of about two minutes is specified to ensure that the colour reaction is complete should very high levels of di-chloramine be encountered. Where glycine is used in the chlorine-ozone differential procedure it is advisable to omit this standing period because of a tendency for the developed colours to change. If the proportion of ozone is high, a slight increase may occur; if the proportion of chlorine, either free or combined, is high, a slight decrease may occur. Since drinking waters are unlikely to contain high amounts of di-chloramine, omission of this pre-cautionary two-minute waiting period should not introduce any significant error. In the case of swimming pools, while high levels of stable di-chloramine-type compounds can build up, any errors in measurement due to omission of the waiting period are of little or no significance in practice and would, in any event, be minimized in on-site testing by the relatively higher temperature of the water samples compared with raw and drinking waters. No method is at

present available for the separate determination of free chlorine in chloroisocyanurate-treated waters because of the dynamic equilibrium existing between the free chlorine and the chloro-compound.

E2.7 Other disinfecting agents

Other disinfecting agents are used in limited quantities and usually as solutions of the pure compound. It is suggested that their residuals be determined as for chlorine and stoichiometric adjustment made in the calculation if desired (methods B or C).

E3 Correction for interferences

In these supplementary procedures, any interference by oxidized manganese may be allowed for as in the DPD method for free chlorine and chloramines. Since manganese interference appears as an increase in the first stage titration volumes after addition of DPD with or without potassium iodide and irrespective of whether or not there has been prior addition of glycine as used in differential methods for mixed residuals, the volumes may be corrected. This correction should be applied before any multiplying factor is used in the calculation. (See note (i) in each of sections E7.9, E10.9, E12.9, E13.7 and E14.4).

E4 Hazards

Mercuric chloride and sodium arsenite are potentially hazardous chemicals used in these methods. Diethyl-*p*-phenylenediamine may cause dermatitic reactions in some sensitive individuals; the low concentrations in the prepared liquid and solid reagents may, however, not be a cause for concern.

E5 Reagents

All chemicals should be of analytical reagent grade quality unless otherwise specified. Store reagents in glass bottles.

E5.1 Water. Deionised or distilled free from oxidising agents and having negligible chlorine demand.

E5.2 Sulphuric acid (10 % v/v). Slowly add 10.0 ± 0.1 ml of concentrated sulphuric acid (SG 1.84) to about 80 ml of water. Cool the solution and make to 100 ± 1 ml with water (E5.1). This solution may be stored at room temperature for up to one year.

E5.3 Disodium ethylenediaminetetraacetate dihydrate (40 g/l). Add 40.0 ± 0.1 g of disodium ethylenediaminetetraacetate dihydrate to approximately 200 ml of water (E5.1). Mix well. Make to 1000 ± 20 ml with water. Mix well. This solution may be stored at room temperature for up to 3 months.

The iron contributed to the sample by the addition of the ferrous ammonium sulphate solution may activate the chlorite in such a way as to interfere with the first end point of the titration. For complete suppression of this effect, additional disodium ethylenediaminetetraacetate is required with the DPD reagents, with a supplementary thioacetamide procedure for higher levels of over approximately 2 mg/l chlorine dioxide (ClO_2) measured as available chlorine. Additional ethylenediaminetetraacetate is not required in the colourimetric procedures.

E5.4 Mercuric chloride solution (2 % m/v). Add 2.0 ± 0.1 g of mercuric chloride to 100 ± 10 ml of water (E5.1) warm to dissolve and mix well. Cool the solution. This solution may be stored at room temperature for up to three months.

E5.5 Buffer solution. Add 2.40 ± 0.05 g of disodium hydrogen phosphate and 4.6 ± 0.5 g of potassium dihydrogen phosphate to approximately 50 ml of water (E5.1). Add 2 ± 1 ml of disodium ethylenediaminetetraacetate dihydrate solution (E5.3) and make to 100.0 ± 0.5 ml with water (E5.1). Add two drops (0.1 ml) of 2% m/v mercuric chloride solution (E5.4) to prevent mould growth and to prevent interference in the free available residual chlorine test caused by trace amounts of iodide. This solution may be stored at room temperature for up to one month.

E5.6 Diethyl-*p*-phenylenediamine (DPD) solution. Add 0.300 ± 0.005 g of DPD sulphate pentahydrate (or 0.220 ± 0.005 g of anhydrous DPD sulphate) to approximately 50 ml of chlorine-free water containing 2.0 ± 0.1 ml of 10% v/v sulphuric acid (E5.2) and 0.5 ± 0.1 ml of disodium ethylenediaminetetraacetate dihydrate (E5.3). Mix well. Make to 100.0 ± 0.5 ml with water (E5.1). The solution may be stored in an amber glass bottle at room temperature for up to 1 week. Discard the solution if it becomes discoloured.

E5.6.1 A combined DPD-buffer reagent is commercially available in powder or tablet form.

E5.7 Sodium arsenite solution (0.5 % m/v). Dissolve 0.50 ± 0.05 g of sodium arsenite in 100.0 ± 0.5 ml of water (E5.1). Alternatively, 0.25 % m/v thioacetamide solution may be used. Add 0.25 ± 0.02 g of thioacetamide to 100.0 ± 0.5 ml of water (E5.1) and mix well. This solution may be stored at room temperature for up to one month.

E5.8 Potassium iodide crystals.

E5.8.1 Potassium iodide solution (0.5 % m/v). This solution may be used in some situations as an alternative to the potassium iodide crystals, i.e. 0.1 ml of potassium iodide solution is equivalent to 0.5 mg of potassium iodide crystals. Weigh out 0.50 ± 0.05 g of potassium iodide and dissolve in 100 ± 2 ml of water (E5.1). Prepare fresh on the day of use as this solution soon becomes discoloured.

E5.9 Ferrous ammonium sulphate solution (0.00282M). Boil approximately 200 ml of water (E5.1). Cool. Add 2.5 ± 0.1 ml of 10 % v/v sulphuric acid (E5.2). Add 1.106 ± 0.005 g of ferrous ammonium sulphate hexahydrate. Mix well. Quantitatively transfer the solution to a 1000 ml volumetric flask and make to 1000 ml with water (E5.1). Transfer the solution to a stoppered amber glass bottle. The stability of this solution varies with storage conditions and with the amount of free air space above the solution in the bottle. This solution may be stored at room temperature for up to one week. Before use it should be checked against standard potassium dichromate. (1 ml of 0.00282M ferrous ammonium sulphate solution is equivalent to 100 µg of chlorine).

To 100.0 ml of 0.00282M ferrous ammonium sulphate solution, add 20.0 ± 0.5 ml of 10 % v/v sulphuric acid (E5.2) 5 ml of phosphoric acid (C5.11) and 2 ml of barium diphenylaminesulphonate solution (E5.12). Titrate with the potassium dichromate solution to a violet end point that persists for 30 seconds. Repeat the titration twice more and calculate the average titre, T ml.

If the ferrous ammonium sulphate solution is made accurately, 100.0 ml of 0.00282M ferrous ammonium sulphate solution is equivalent to 28.2 ml of 0.01N potassium dichromate solution (E5.10). If the ferrous ammonium sulphate solution requires significantly less than 28.2 ml of potassium dichromate solution, discard the ferrous ammonium sulphate solution and prepare a fresh ferrous ammonium sulphate solution. For ferrous ammonium sulphate solutions which are slightly under the required concentration then a standardisation factor can be used. For 0.01N potassium dichromate solution, the factor is T/28.2, where T is the volume (ml) of standard potassium dichromate solution.

E5.10 Potassium dichromate solution (0.01N, i.e. M/600). Dry just over 0.5 g of potassium dichromate at 105 - 120 °C to constant weight. Add 0.4903 ± 0.0005 g of potassium dichromate to a 1000 ml volumetric flask and add approximately 800 ml of water (E5.1). Mix well. Make to 1000 ml with water. Mix well. This solution may be stored at room temperature for up to one month.

E5.11 Phosphoric acid (SG 1.83).

E5.12 Barium diphenylaminesulphonate solution (0.1 % m/v). Dissolve 0.10 ± 0.02 g of barium diphenylaminesulphonate in 100 ml of water (E5.1). It may be necessary to warm the water to dissolve the reagent. Store the solution in a glass stoppered bottle at room temperature for up to one week.

E5.13 Glycine solution (10 % m/v). Dissolve 10.0 ± 0.5 g of glycine in water (E5.1) and make to 100 ± 1 ml with water (E5.1). This solution may be stored at room temperature for up to one month.

E5.14 Sulphuric acid (5 % v/v). Carefully, add 5.0 ± 0.5 ml of sulphuric acid (SG 1.84) to approximately 80 ml of water (E5.1). Cool the solution and make to 100 ± 1 ml with water (E5.1). This solution may be stored at room temperature for up to one year.

E5.15 Sodium hydrogencarbonate solution (5.5 % m/v). Dissolve 27.5 ± 0.5g of sodium hydrogencarbonate in water (E5.1) and make to 500 ± 5 ml with water (E5.1). This solution may be stored at room temperature for up to six months.

E5.16 Sodium nitrite solution (10 % m/v). Dissolve 10.0 ± 0.5 g of sodium nitrite in 100 ± 1 ml of water (E5.1). This solution may be stored at room temperature for up to six months.

E5.17 Mercuric chloride solution (0.5 % m/v). Dissolve 0.5 ± 0.05 g of mercuric chloride in water (E5.1) and make to 100 ± 1 ml with water (E5.1). This solution may be stored at room temperature for up to three months.

E6 Apparatus

E6.1 Common laboratory glassware, including pipettes, conical flasks, measuring cylinders and beakers.

E6.2 Microburette. Measuring up to 5 ml and graduated to 0.02 ml divisions for concentrations up to 4 mg/l. For higher concentrations which exceed 5 mg/l in terms of available chlorine, a 25 ml burette graduated to 0.1 ml may be more appropriate.

E7 Analytical procedure for chlorine dioxide, chlorite, free chlorine and chloramine mixtures

The presence of bromides in waters may result in the formation of free bromine which interferes in the determination of chlorine dioxide. Procedures allowing for this interference are given in section E9.

Unless prior experience suggests that chlorite will be absent, it should be assumed that chlorite is present in waters that have been treated with chlorine dioxide.

Step	Procedure	Notes
E7.1	Chlorine dioxide	
E7.1.1	Add 2.00 ± 0.05 ml of glycine solution (E5.13) to a 250-ml conical flask. Carefully, add 100.0 ± 0.5 ml of sample (note a) and mix (note b). Into a second flask, add 5.00 ± 0.05 ml of DPD solution (E5.6) and 5.00 ± 0.05 ml of buffer solution (E5.5) see note c, and 5.00 ± 0.05 ml of disodium ethylenediaminetetraacetate solution (E5.3) and mix. Carefully, add the contents of the first flask to the second flask and mix, note d. Titrate immediately with standardised ferrous ammonium sulphate solution (E5.9) until the colour is discharged (volume G ml).	(a) Care should be taken to minimize losses of volatile disinfectants from the sample. (b) If the total available residual chlorine concentration exceeds 5 mg/l, the volume of sample should be correspondingly reduced, i.e. should be less than 100 ml, or a dilution of the sample prepared. An amount of water (E5.1) being the difference between 100 ml and the volume of sample actually taken should be added to the second flask containing the DPD-buffer-EDTA mixture before adding the glycine-treated sample. (c) Alternatively, a combined buffer-DPD reagent (E5.6.1) may be used. (d) Alternatively, If the combined DPD-buffer powder (E5.6.1) is used, and sample dilution is not necessary, the powder may be added direct to the glycine-treated sample in the first flask along with the disodium ethylenediamine-tetraacetate solution (E5.16).
E7.1.2	If appreciable colour drift-back occurs after the end point, repeat step E7.1.1 but add 0.50 ± 0.05 ml of thioacetamide solution (E5.7) immediately after mixing the glycine-	

treated sample with the other reagents and before titrating with standardised ferrous ammonium sulphate solution (E5.9) until the colour is discharged (volume G_1 ml). The volume G of E7.1.1 then becomes G_2. If chlorine and chloramines are known to be absent, see section E7.9, Table E1 note (iv) and section E8.

E7.2 Free available residual chlorine

E7.2.1 See note e. Add 5.0 ± 0.5 ml of DPD solution (E5.6) and 5.0 ± 0.5 ml of buffer solution (E5.5) to a 250 ml conical flask, note c. Mix well. Carefully, add 100.0 ± 0.5 ml of sample (notes a and f) and mix. Titrate the solution immediately with standardised ferrous ammonium sulphate solution (E5.9) until the red colour is discharged (volume A ml).

(e) Chlorine dioxide does not react with ammonia to form chloramines; but such compounds may arise from the excess chlorine associated with the on-site generation of chlorine dioxide.

(f) If the total available residual chlorine concentration exceeds 5 mg/l, the volume of sample should be correspondingly reduced, i.e. should be less than 100 ml, or a dilution of the sample prepared. An amount of water (E5.1) being the difference between 100 ml and the volume of sample actually taken should be added to the DPD-buffer mixture before adding the sample.

E7.3 Mono-chloramine

E7.3.1 Immediately following the titration in step E7.2.1, add approximately 0.5 mg of potassium iodide (E5.8) see note g, and continue the titration immediately with standardised ferrous ammonium sulphate solution (E5.9) until the red colour is discharged (volume B ml) see note h.

(g) Alternatively, 0.1 ml of 0.5 % m/v potassium iodide solution (E5.8.1) may be used.

(h) The recorded volume is the total volume, i.e. volume A plus the additional titre.

E7.4 Di-chloramine

E7.4.1 Immediately following the titration in step E7.3.1, add approximately 1 g of potassium iodide (E5.8) and mix to dissolve. Leave the solution to stand for two minutes and titrate the solution with standardised ferrous ammonium sulphate solution (E5.9) until the red colour is discharged (volume C ml) notes i and j.

(i) The recorded volume is the total volume, i.e. volume B plus the additional titre.

(j) Any drift back of colour at the end point when titrating relatively large amounts of di-chloramine indicates that the reaction with iodide, which is not instantaneous,

is still incomplete. In such cases, allow the solution to stand a further two minutes before commencing the titration. When di-chloramine concentrations are known to be low, add only 0.5 g of potassium iodide (E5.8).

E7.5 Simplified procedure for free available residual chlorine and combined available residual chlorine

E7.5.1 Add 5.0 ± 0.5 ml of DPD solution (E5.6) and 5.0 ± 0.5 ml of buffer solution (E5.5) see note c, and add 5.00 ± 0.05 ml of disodium ethylenediaminetetraacetate solution (E5.3) to a 250 ml conical flask. Mix well. Carefully, add 100.0 ± 0.5 ml of sample (notes a and k) and mix. Titrate the solution immediately with standardised ferrous ammonium sulphate solution (E5.9) until the red colour is discharged (volume A ml). See note l.

(k) If the total available residual chlorine concentration exceeds 5 mg/l, the volume of sample should be correspondingly reduced, i.e. should be less than 100 ml, or a dilution of the sample prepared. An amount of water (E5.1) being the difference between 100 ml and the volume of sample actually taken should be added to the DPD-buffer-EDTA mixture before adding the sample.

(l) This gives free available residual chlorine.

E7.5.2 Immediately following the titration in step E7.5.1, add approximately 1 g of potassium iodide (E5.8) and mix to dissolve. Leave the solution to stand for two minutes and titrate the solution with standardised ferrous ammonium sulphate solution (E5.9) until the red colour is discharged (volume C ml) notes h, j and m.

(m) This gives combined available residual chlorine.

E7.6 Simplified procedure for total available residual chlorine

E7.6.1 To obtain total available residual chlorine with one titration, add approximately 1 g of potassium iodide (E5.8) to a 250 ml conical flask. Add 5.0 ± 0.5 ml of DPD solution (E5.6) and 5.0 ± 0.5 ml of buffer solution (E5.5) see note c, and 5.00 ± 0.05 ml disodium ethylenediaminetetraacetate solution (E5.3). Mix well. Carefully, add 100.0 ± 0.5 ml of sample (notes a and n) and mix. Leave the solution to stand for two minutes and titrate with standardised ferrous ammonium sulphate solution (E5.9) until the

(n) If the total available residual chlorine concentration exceeds 5 mg/l, the volume of sample should be correspondingly reduced, i.e. should be less than 100 ml, or a dilution of the sample prepared. An amount of water (E5.1) being the difference between 100 ml and the volume of sample actually taken should be added to the potassium iodide-DPD-buffer-EDTA mixture before

red colour is discharged (volume C ml) see notes j and o.

adding the sample.

(o) If any difficulty still remains with the end point (volume C ml) add 0.50 ± 0.05 ml of thioacetamide solution (E5.7) immediately to the potassium iodide (E5.8) and mix before continuing. In this event, the total available residual chlorine procedure should be carried out as follows. Add a fifth 100.0 ± 0.5 ml portion of the sample to a flask containing 5.0 ± 0.5 ml of DPD solution (E5.6) and 5.0 ± 0.5 ml of buffer solution (E5.5) see note c, and 5.00 ± 0.05 ml of disodium ethylenediaminetetraacetate solution (E5.3). Following mixing, add the potassium iodide and thioacetamide mixture, followed by 1.00 ± 0.05 ml of sulphuric acid (E5.14) and leave the solution to stand for two minutes. Then add 5.00 ± 0.05 ml of sodium hydrogencarbonate solution (E5.15). Mix and titrate with standardised ferrous ammonium sulphate solution (E5.9).

E7.7 Total available residual chlorine including chlorite

E7.7.1 After obtaining volume C (note o) add 1.00 ± 0.05 ml of sulphuric acid (E5.14) to the titration flask (E7.6.1). Mix and leave the solution to stand for two minutes. Then add 5.00 ± 0.05 ml of sodium hydrogen-carbonate solution (E5.15). Mix and titrate the solution, to a total volume D ml.

E7.8 Correction for interference caused by oxidized manganese

E7.8.1 See note p. Add 5.0 ± 0.5 ml of buffer solution (E5.5) to a conical flask. Add 0.50 ± 0.05 ml of sodium arsenite solution (E5.7). Add 100.0 ± 0.5 ml of sample (notes a and q) and mix (note r). Then add 5.0 ± 0.5 ml of DPD solution (E5.6) and again mix. Titrate any red colour with standardised ferrous ammonium sulphate

(p) This is particularly important when determining low levels of chlorine and chloramines in waste waters and effluents.

(q) Alternatively, instead of using sodium arsenite solution, add 0.50 ± 0.05 ml of the

solution (E5.9) until the red colour is discharged. Subtract this titre from volume A (free available residual chlorine) as obtained in sections E7.2 or E7.5 or from total available residual chlorine volume in section E7.6.1.

thioacetamide solution (E5.7) to 100.0 ± 0.5 ml of sample and add this solution to the flask containing the buffer solution (E5.5).

(r) If the total available residual chlorine concentration exceeds 5 mg/l, the volume of sample should be correspondingly reduced, i.e. should be less than 100 ml, or a dilution of the sample prepared. An amount of water (E5.1) being the difference between 100 ml and the volume of sample actually taken should be added to the buffer solution before adding the sample.

E7.9 Calculations

For 100 ml of sample, 1.0 ml of standardised ferrous ammonium sulphate solution (E5.9) is equivalent to 1.0 mg/l available chlorine. (See final paragraph in section E5.9).

Table E1 may be used for calculating the concentrations of individual components, unless thioacetamide has been used in which case, see Table E2.

Volumes A, B, C, D, G, G_1 and G_2 are defined in steps E7.1.1 - E7.7.1.

Table E1 Normal calculations where thioacetamide procedure not used, note (vii)

	Volume	
Determination	(Chlorite absent)	(Chlorite present)
Chlorine dioxide, notes (i) (ii) and (v)	5G	5G
Chlorite, notes (i) (iv) (v) and (vi)	-	D - C - 4G
Free chlorine	A - G	A - G
Monochloramine, note (iii)	B - A	B - A
Dichloramine, note (iii)	C - B	C - B
Total available chlorine, note (i)	C + 4G	D

(i) If oxidized manganese is present determine the correction as in step E7.8 and apply to the determinations as follows:

chlorine dioxide -	deduct correction from volume G
chlorite -	deduct correction from volume G
total available chlorine -	deduct correction from volumes C, G and D.

(ii) All fractions are expressed as mg/l available Cl. To obtain chlorine dioxide in terms of ClO_2, multiply G by 1.9 instead of 5.

(iii) If the step leading to volume B is omitted, mono-chloramine and di-chloramine are obtained together as combined chlorine = C - A.

(iv) To check whether or not chlorite is present in the original sample it is necessary to obtain volume D. The presence of chlorite is indicated if D is greater than C + 4G.

(v) Under treatment conditions where chlorine and chloramines may be assumed absent, the use of glycine is unnecessary since volume A then equals volume G, thus chlorine dioxide = 5A mg/l as chlorine or 1.9A if required in terms of ClO_2 and chlorite equals D - 5A as chlorine.

(vi) All chlorite results as calculated above in terms of chlorine may be converted to mg/l ClO_2^- by multiplying by 0.48.

(vii) If the raw water contained bromide see also section E9.

Table E2 Modified calculations where thioacetamide procedure required, note (iii)

Determination	Volume	
	(Chlorite absent)	(Chlorite present)
Chlorine dioxide, note (i)	$5G_1$	$5G_1$
Chlorite, note (i)	-	$D - C - 5G_1 + G_2$
Free chlorine	$A - G_2$	A - G2
Monochloramine	B - A	B - A
Dichloramine	C - B	C - B
Total available chlorine, note (i)	$C + 5G_1 - G_2$	D

(i) If oxidized manganese is present determine the correction as in step E7.8 and apply to the determinations as follows:

chlorine dioxide-	deduct correction from volume G_1
chlorite -	deduct correction from volume G_1 and G_2
total available chlorine -	deduct correction from volumes G_1 and D

(ii) Unless chlorite is known to be absent, assume chlorite is present.

(iii) If the raw water contained bromide see also section E9.

E8 Simplified thioacetamide procedure when chlorine and chloramines are absent

Step	Procedure	Notes
E8.1	Free available residual chlorine	
E8.1.1	Add 5.0 ± 0.5 ml of DPD solution (E5.6) and 5.0 ± 0.5 ml of buffer solution (E5.5) to a 250 ml conical flask, note a. Mix well. Carefully, add 100.0 ± 0.5 ml of sample (notes b and c) and mix. Add 0.50 ± 0.05 ml of thioacetamide solution (E5.7). Mix well.	(a) Alternatively, a combined buffer-DPD reagent (E5.6.1) may be used. (b) Care should be taken to minimize losses of volatile

Titrate the solution immediately with standardised ferrous ammonium sulphate solution (E5.9) until the red colour is discharged (volume A ml).

disinfectants from the sample.

(c) If the total available residual chlorine concentration exceeds 5 mg/l, the volume of sample should be correspondingly reduced, i.e. should be less than 100 ml, or a dilution of the sample prepared. An amount of water (E5.1) being the difference between 100 ml and the volume of sample actually taken should be added to the DPD-buffer mixture before adding the sample.

E8.1.2 Add a second 100.0 ± 0.5 ml portion of sample into a flask containing 5.00 ± 0.05 ml of DPD solution (E5.6) and 5.00 ± 0.05 ml of buffer solution (E5.5) see note a. Mix well. Add 1.0 ± 0.1 g of potassium iodide (E5.8). Mix well. Add 1.00 ± 0.05 ml of sulphuric acid (E5.14). Mix and leave the solution to stand for two minutes. Add 5.00 ± 0.05 ml of sodium hydrogencarbonate solution (E5.15). Mix and titrate immediately with ferrous ammonium sulphate (E5.9) until the red colour is discharged (volume D ml).

E8.2 Calculations

Chlorine dioxide = 5A
Chlorite = D - 5A

These results are expressed as mg/l available chlorine. For conversion factors to ClO_2 and $[ClO_2]^-$ see step E7.9, Table E1 notes (ii) and (vi) respectively.

E9 Water containing bromide

Any excess of chlorine associated with the chlorine dioxide treatment of waters containing natural bromides may result in disinfectant residuals containing traces of residual bromine. The determination of such traces and any consequent corrections to results for other residual disinfectants may be carried out by an additional procedure (described below) using sodium nitrite as a supplementary reagent.

This procedure is based on the findings that residual bromine, when converted entirely to the bromamine form by the addition of glycine, is unaffected by sodium nitrite, whereas chlorine dioxide is destroyed.

Step	Procedure	Notes
E9.1	Residual bromine	
E9.1.1	Add 2.00 ± 0.05 ml of glycine solution (E5.13) to a 250-ml conical flask. Carefully, add 100.0 ± 0.5 ml of sample (note a) and mix (note b). Add 0.50 ± 0.05 ml of sodium nitrite solution (E5.16). Mix well. Into a second flask, add 5.00 ± 0.05 ml of DPD solution (E5.6) and 5.00 ± 0.05 ml of buffer solution (E5.5) see note c, and 5.00 ± 0.05 ml of disodium ethylenediaminetetraacetate solution (E5.3) and mix (note d). Carefully add the contents of the first flask to the second flask, mix and titrate immediately with standardised ferrous ammonium sulphate solution (E5.9) until the colour is discharged (volume BR ml).	(a) Care should be taken to minimize losses of volatile disinfectants from the sample. (b) If the total available residual chlorine concentration exceeds 5 mg/l, the volume of sample should be correspondingly reduced, i.e. should be less than 100 ml, or a dilution of the sample prepared. An amount of water (E5.1) being the difference between 100 ml and the volume of sample actually taken should be added to the glycine solution before adding the sample. (c) Alternatively, a combined buffer-DPD reagent (E5.6.1) may be used. (d) Alternatively, If the combined DPD-buffer powder (E5.6.1) is used, and sample dilution is not necessary, the powder may be added direct to the glycine-treated sample in the first flask along with the disodium ethylenediamine-tetraacetate solution (E5.3).

E9.2 Calculations

Having obtained volume BR, the calculations in Tables E1 and E2 of section E7.9 require correction as follows:-

Subtract the BR volume from the G, G_1 and G_2 volumes before applying any given multiplication factor in the calculations for chlorine dioxide, chlorite and total available chlorine. In the case of the total available chlorine result thus obtained and that from volume D the residual bromine (as mg/l Cl_2) will be included.

E10 Procedure for bromine (including bromamines) and mixtures with free chlorine and chloramine

See section E13 for procedures for the separate determination of bromine and bromamines

Step	Procedure	Notes
E10.1	Bromine (including bromamines) in the absence of free chlorine and chloramines	
E10.1.1	Add 5.0 ± 0.5 ml of DPD solution (E5.6) and 5.0 ± 0.5 ml of buffer solution (E5.5) to a 250 ml conical flask, see note a. Mix well. Carefully, add 100.0 ± 0.5 ml of sample (notes b and c) and mix. Titrate the solution immediately with standardised ferrous ammonium sulphate solution (C5.9) until the red colour is discharged (volume BR ml).	(a) Alternatively, a combined buffer-DPD reagent (E5.6.1) may be used. (b) Care should be taken to minimize losses of volatile disinfectants from the sample. (c) If the total available residual chlorine concentration exceeds 5 mg/l, the volume of sample should be correspondingly reduced, i.e. should be less than 100 ml, or a dilution of the sample prepared. An amount of water (E5.1) being the difference between 100 ml and the volume of sample actually taken should be added to the flask containing the DPD-buffer mixture before adding the sample.
E10.2	Bromine (including bromamines) in the presence of free chlorine and chloramines	
E10.2.1	Add 2.0 ± 0.5 ml of glycine solution (E5.13) to a 250 ml conical flask. Carefully, add 100.0 ± 0.5 ml of sample and mix (note d).	(d) If the total available residual chlorine concentration exceeds 5 mg/l, the volume of sample should be correspondingly reduced, i.e. should be less than 100 ml, or a dilution of the sample prepared. An amount of water (E5.1) being the difference between 100 ml and the volume of sample actually taken should be added to the second flask containing the DPD-buffer solution.

E10.2.2 Into a second flask, add 5.0 ± 0.5 ml of DPD solution (E5.6) and 5.0 ± 0.5 ml of buffer solution (E5.5) see note a, and mix (note e). Add the contents of the first flask to the second flask, mix, and titrate with standardised ferrous ammonium sulphate solution (E5.9) until the colour is discharged (volume BR ml).

(e) Alternatively, If the combined DPD-buffer powder (E5.6.1) is used, and sample dilution is not necessary, the powder may be added direct to the glycine-treated sample in the first flask.

E10.3 Free available residual chlorine

E10.3.1 Using a second portion of sample, add 5.0 ± 0.5 ml of DPD solution (E5.6) and 5.0 ± 0.5 ml of buffer solution (E5.5) to a 250 ml conical flask, see note a. Mix well. Carefully, add 100.0 ± 0.5 ml of sample (notes b and f) and mix. Titrate the solution immediately with standardised ferrous ammonium sulphate solution (E5.9) until the red colour is discharged (volume A ml).

(f) If the total available residual chlorine concentration exceeds 5 mg/l, the volume of sample should be correspondingly reduced, i.e. should be less than 100 ml, or a dilution of the sample prepared. An amount of water (E5.1) being the difference between 100 ml and the volume of sample actually taken should be added to the flask containing the DPD-buffer solution before adding the sample.

E10.4 Mono-chloramine

E10.4.1 Immediately following the titration in step E10.3.1, add approximately 0.5 mg of potassium iodide (E5.8) see note g, and titrate the solution immediately with standardised ferrous ammonium sulphate solution (E5.9) until the red colour is discharged (volume B ml) note h.

(g) Alternatively, 0.1 ml of 0.5 % m/v potassium iodide solution (E5.8.1) may be used.

(h) The recorded volume is the total volume, i.e. volume A plus the additional titre.

E10.5 Di-chloramine

E10.5.1 Immediately following the titration in step E10.4.1, add approximately 1 g of potassium iodide (E5.8) and mix to dissolve. Leave the solution to stand for two minutes and titratethe solution with standardised ferrous ammonium sulphate solution (E5.9) until the red colour is discharged (volume C ml) notes i and j.

(i) The recorded volume is the total volume, i.e. volume B plus the additional titre.

(j) Any drift-back of colour at the end point when titrating relatively large amounts of di-chloramine indicates that the reaction with iodide, which is not instantaneous, is still incomplete. In such cases, allow the solution to stand a further two minutes before commencing the titration. When di-chloramine concentrations are known to be low, add only 0.5 g of

potassium iodide (E5.8).

E10.6 Simplified procedure for free available residual chlorine and combined available residual chlorine

E10.6.1 Add 5.0 ± 0.5 ml of DPD solution (E5.6) and 5.0 ± 0.5 ml of buffer solution (E5.5) to a 250 ml conical flask see note a. Mix well. Carefully, add 100.0 ± 0.5 ml of sample (notes b and c) and mix. Titrate the solution immediately with standardised ferrous ammonium sulphate solution (E5.9) until the red colour is discharged (volume A ml). See note k.

(k) This gives free available residual chlorine.

E10.6.2 Immediately following the titration in step E10.6.1, add approximately 1 g of potassium iodide (E5.8) and mix to dissolve. Leave the solution to stand for two minutes and titrate the solution with standardised ferrous ammonium sulphate solution (E5.9) until the red colour is discharged (volume C ml) notes g, j and l.

(l) This gives combined available residual chlorine.

E10.7 Simplified procedure for total available residual chlorine

E10.7.1 To obtain total available residual chlorine with one titration, add approximately 1 g of potassium iodide (E5.8) to a 250 ml conical flask. Add 5.0 ± 0.5 ml of DPD solution (E5.6) and 5.0 ± 0.5 ml of buffer solution (E5.5) see note a. Mix well. Carefully, add 100.0 ± 0.5 ml of sample (notes b and m) and mix. Leave the solution to stand for two minutes and titrate with standardised ferrous ammonium sulphate solution (E5.9) until the red colour is discharged (volume C ml) see note j.

(m) If the total available residual chlorine concentration exceeds 5 mg/l, the volume of sample should be correspondingly reduced, i.e. should be less than 100 ml, or a dilution of the sample prepared. An amount of water (E5.1) being the difference between 100 ml and the volume of sample actually taken should be added to the flask containing the potassium iodide-DPD-buffer solution.

E10.8 Correction for interference caused by oxidized manganese

E10.8.1 See note n. Add 5.0 ± 0.5 ml of buffer solution (E5.5) to a conical flask. Add 0.50 ± 0.05 ml of sodium arsenite solution (E5.7). Add 100.0 ± 0.5 ml of sample (note o) and mix (note p). Then add 5.0 ± 0.5 ml of DPD solution (E5.6) and again mix. Titrate any red colour with

(n) This is particularly important when determining low levels of chlorine and chloramines in waste waters and effluents.

(o) Alternatively, instead of using sodium arsenite solution, add

	standardised ferrous ammonium sulphate solution (E5.9) until the red colour is discharged. Subtract this titre from volume A (free available residual chlorine) as obtained in steps E10.3 or E10.6 or from total available residual chlorine reading in section E10.7.	0.50 ± 0.05 ml of the thioacetamide solution (E5.7) to 100.0 ± 0.5 ml of sample and add this solution to the flask containing the buffer solution (E5.5). (p) If the total available residual chlorine concentration exceeds 5 mg/l, the volume of sample should be correspondingly reduced, i.e. should be less than 100 ml, or a dilution of the sample prepared. An amount of water (E5.1) being the difference between 100 ml and the volume of sample actually taken should be added to the buffer solution before adding the sample.

E10.9 Calculations

For a 100 ml sample, 1.0 ml standard ferrous ammonium sulphate solution (E5.9) is equivalent to 1.0 mg/l available chlorine. (See final paragraph in section E5.9).

In the absence of free chlorine and chloramines, reading BR gives bromine direct.

The following table may be used for calculating the concentrations of individual components of mixtures of bromine with free chlorine and chloramines.

A, B, C and BR are defined in steps E10.1 - E10.3 inclusive.

Determination	Volume
Bromine (plus bromamines) notes (i) and (ii)	BR
Free chlorine	A - BR
Monochloramine, note (iii)	B - A
Dichloramine, note (iii)	C - B

(i) If oxidized manganese is present determine the correction as in section E10.8 and apply to the determinations as follows:
bromine (plus bromamines) - deduct correction from volume BR

(ii) The bromine results are obtained in terms of available chlorine. To convert to bromine multiply by 2.25.

(iii) If the step leading to volume B is omitted mono-chloramine and di-chloramine are obtained together as combined available residual chlorine = C - A.

E11 Procedure for the separate determination of bromine and bromamines

In this procedure, use is made of the ability of sodium nitrite to destroy free bromine but not bromamines.

Step	Procedure	Notes
E11.1	Separate determination of bromine and bromamines	
E11.1.1	Add 5.0 ± 0.5 ml of DPD solution (E5.6) and 5.0 ± 0.5 ml of buffer solution (E5.5) to a 250 ml conical flask, see note a. Mix well. To a second flask, add 0.50 ± 0.05 ml of sodium nitrite solution (E5.16) to 100.0 ± 0.5 ml of sample (see notes b and c) and mix. Carefully, add the contents of the second flask to the first flask and mix well. Titrate the solution immediately with standardised ferrous ammonium sulphate solution (E5.9) until the red colour is discharged (volume BRA ml).	(a) Alternatively, a combined buffer-DPD reagent (E5.6.1) may be used. (b) Care should be taken to minimize losses of volatile disinfectants from the sample. (c) If the total available residual chlorine concentration exceeds 5 mg/l, the volume of sample should be correspondingly reduced, i.e. should be less than 100 ml, or a dilution of the sample prepared. An amount of water (E5.1) being the difference between 100 ml and the volume of sample actually taken should be added to the flask containing the DPD-buffer solution.

E11.2 Calculations

The following additional calculations then apply to those given in the table in section E10.9:

Free bromine = BR - BRA
Bromamines = BRA

E12 Procedure for iodine and mixtures with free chlorine and chloramines

Step	Procedure	Notes
E12.1	Iodine (in the absence of free chlorine and chloramines)	
E12.1.1	Add 5.0 ± 0.5 ml of DPD solution (E5.6) and 5.0 ± 0.5 ml of buffer solution (E5.5) to a 250 ml conical flask, see note a. Mix well. Carefully, add 100.0 ± 0.5 ml of sample (notes b and c) and mix. Titrate the solution immediately with standardised ferrous ammonium sulphate solution (E5.9) until the red colour is discharged (volume I ml).	(a) Alternatively, a combined buffer-DPD reagent (E5.6.1) may be used. (b) Care should be taken to minimize losses of volatile disinfectants from the sample. (c) If the total available residual chlorine concentration exceeds 5 mg/l, the volume of sample should be correspondingly reduced, i.e. should be less than 100 ml, or a dilution of the sample prepared. An amount of water (E5.1) being the difference between 100 ml and the volume of sample actually taken should be added to the flask containing the DPD-buffer solution before adding the sample.
E12.2	Iodine (in the presence of free chlorine and chloramines)	
E12.2.1	Place 2.00 ± 0.05 ml of glycine solution (E5.13) and approximately 0.5 ml of mercuric chloride solution (E5.17) in a 250 ml conical flask. Carefully add 100.0 ± 0.5 ml of sample and mix (note d). Into a second flask, add 5.00 ± 0.05 ml of DPD solution (E5.6)and 5.00 ± 0.05 ml of buffer solution (E5.5) see note a, and mix (see note e). Add the contents of the first flask to the second flask, mix and titrate with standardised ferrous ammonium sulphate solution (E5.9) until the colour is discharged (volume I).	(d) If the total available residual chlorine concentration exceeds 5 mg/l, the volume of sample should be correspondingly reduced, i.e. should be less than 100 ml, or a dilution of the sample prepared. An amount of water (E5.1) being the difference between 100 ml and the volume of sample actually taken should be added to the flask containing the glycine-mercuric chloride solution before adding the sample. (e) If DPD-buffer powder is used,

and sample dilution is not necessary, the powder may be added directly to the glycine-treated sample in the first flask.

E12.3 Free chlorine and chloramines

E12.3.1 Add 5.0 ± 0.5 ml of DPD solution (E5.6) and 5.0 ± 0.5 ml of buffer solution (E5.5) see note a, and approximately 0.5 ml of mercuric chloride solution (E5.17) to a 250 ml conical flask. Mix well. Carefully, add 100.0 ± 0.5 ml of sample (notes b and f) and mix. Titrate the solution immediately with standardised ferrous ammonium sulphate solution (E5.9) until the red colour is discharged (volume A ml).

(f) If the total available residual chlorine concentration exceeds 5 mg/l, the volume of sample should be correspondingly reduced, i.e. should be less than 100 ml, or a dilution of the sample prepared. An amount of water (E5.1) being the difference between 100 ml and the volume of sample actually taken should be added to the flask containing the DPD-buffer-mercuric chloride solution before adding the sample.

E12.4 Mono-chloramine

E12.4.1 Immediately following the titration in step E12.3.1, add approximately 0.5 mg of potassium iodide (E5.8) see note g, and titrate the solution immediately with standardised ferrous ammonium sulphate solution (E5.9) until the red colour is discharged (volume B ml) see note h.

(g) Alternatively, 0.1 ml of 0.5 % m/v potassium iodide solution (E5.8.1) may be used.

(h) The recorded volume is the total volume, i.e. volume A plus the additional titre.

E12.5 Di-chloramine

E12.5.1 Immediately following the titration in step E12.4.1, add approximately 1 g of potassium iodide (E5.8) and mix to dissolve. Leave the solution to stand for two minutes and titrate the solution with standardised ferrous ammonium sulphate solution (E5.9) until the red colour is discharged (volume C ml) notes i and j.

(i) The recorded volume is the total volume, i.e. volume B plus the additional titre.

(j) Any drift back of colour at the end point when titrating relatively large amounts of di-chloramine indicates that the reaction with iodide, which is not instantaneous, is still incomplete. In such cases, allow the solution to stand a further two minutes before commencing the titration. When di-chloramine concentrations are known to be low, add only 0.5 g of potassium iodide (E5.8).

E12.6 Simplified procedure for free available residual chlorine and combined available residual chlorine

E12.6.1 Add 5.0 ± 0.5 ml of DPD solution (E5.6) and 5.0 ± 0.5 ml of buffer solution (E5.5) see note a, and approximately 0.5 ml of mercuric chloride solution (E5.17) to a 250 ml conical flask. Mix well. Carefully, add 100.0 ± 0.5 ml of sample (notes b and f) and mix. Titrate the solution immediately with standardised ferrous ammonium sulphate solution (E5.9) until the red colour is discharged (volume A ml). See note k.

(k) This gives free available residual chlorine.

E12.6.2 Immediately following the titration in step E12.6.1, add approximately 1 g of potassium iodide (E5.8) and mix to dissolve. Set aside for two minutes and continue the titration with standardised ferrous ammonium sulphate solution (E5.9) until the red colour is discharged (volume C ml) notes i, j and l.

(l) This gives combined available residual chlorine.

E12.7 Simplified procedure for total available residual chlorine

E12.7.1 To obtain total available residual chlorine with one titration, add approximately 1 g of potassium iodide (E5.8) to a 250 ml conical flask. Add 5.0 ± 0.5 ml of DPD solution (E5.6) and 5.0 ± 0.5 ml of buffer solution (E5.5) see note a, and approximately 0.5 ml of mercuric chloride solution (E5.17). Mix well. Carefully, add 100.0 ± 0.5 ml of sample (notes b and m) and mix. Leave the solution to stand for two minutes and titrate with standardised ferrous ammonium sulphate solution (E5.9) until the red colour is discharged (volume C ml).

(m) If the total available residual chlorine concentration exceeds 5 mg/l, the volume of sample should be correspondingly reduced, i.e. should be less than 100 ml, or a dilution of the sample prepared. An amount of water (E5.1) being the difference between 100 ml and the volume of sample actually taken should be added to the flask containing the potassium iodide-DPD-buffer-mercuric chloride solution before adding the sample.

E12.8 Correction for interference caused by oxidized manganese

E12.8.1 See note n. Add 5.0 ± 0.5 ml of buffer solution (E5.5) to a conical flask. Add 0.50 ± 0.05 ml of sodium arsenite solution (E5.7). Add 100.0 ± 0.5 ml of sample (note o) and mix. See note p. Then add 5.0 ± 0.5 ml of DPD solution (E5.6) and

(n) This is particularly important when determining low levels of chlorine and chloramines in waste waters and effluents.

again mix. Titrate any red colour with standardised ferrous ammonium sulphate solution (E5.9) until the red colour is discharged. Subtract this titre from volume A (free available residual chlorine) as obtained in steps E12.3 or E12.6 or from total available residual chlorine volume in section E12.7.

(o) Alternatively, instead of using sodium arsenite solution, add 0.50 ± 0.05 ml of the thioacetamide solution (E5.7) to 100.0 ± 0.5 ml of sample and add this solution to the flask containing the buffer solution (E5.5).

(p) If the total available residual chlorine concentration exceeds 5 mg/l, the volume of sample should be correspondingly reduced, i.e. should be less than 100 ml, or a dilution of the sample prepared. An amount of water (E5.1) being the difference between 100 ml and the volume of sample actually taken should be added to the flask containing the buffer solution before adding the sample.

E12.9 Calculations

For a 100 ml sample 1.0 ml of standardised ferrous ammonium sulphate solution (E5.9) is equivalent to 1.0 mg/l available chlorine. (See final paragraph of section E5.9).

In the absence of free chlorine and chloramines, volume I gives iodine direct.

The following table may be used for calculating the concentrations of individual components of mixtures of iodine with free chlorine and chloramines.

Volumes A, B, C and I are defined in steps E.12.1 - E12.7.1 inclusive.

Determination	Volume
Iodine, notes (i) .and (ii)	I
Free chlorine	A - I
Mono-chloramine, note (iii)	B - A
Di-chloramine, note (iii)	C - B

(i) If oxidized manganese is present determine the correction as in step E12.8 and apply to the determinations as follows:
iodine deduct correction from volume I

(ii) The iodine results are obtained in terms of available chlorine. To convert to iodine multiply by 3.6.

(iii) If the step leading to volume B is omitted, monochloramine and dichloramine are, obtained together as combined chlorine = C - A

E13 Procedure for ozone and mixtures with free chlorine and chloramine

Step	Procedure	Notes
E13.1	Ozone (In the absence of free chlorine and chloramines)	
E13.1.1	Place 5.00 ± 0.05 ml of DPD solution (E5.6) and 5.00 ± 0.05 of buffer solution (E5.5) see note a, and about 0.5 g of potassium iodide (E5.8) see note b, in a 250 ml conical flask. Carefully, add 100.0 ± 0.5 ml of sample, see notes c and d, and mix. Titrate immediately with standardised ferrous ammonium sulphate solution (E5.9) until the colour is discharged (volume O).	(a) Alternatively, a combined buffer-DPD reagent (E5.6.1) may be used. (b) Alternatively, 0.1 ml of 0.5 % m/v potassium iodide solution (E5.8.1) may be used. (c) Care should be taken to minimize losses of volatile disinfectants from the sample. (d) If the total available residual chlorine concentration exceeds 5 mg/l, the volume of sample should be correspondingly reduced, i.e. should be less than 100 ml, or a dilution of the sample prepared. An amount of water (E5.1) being the difference between 100 ml and the volume of sample actually taken should be added to the flask containing the DPD-buffer-potassium iodide solution before adding the sample.
E13.2	Ozone plus total available chlorine (in the presence of free chlorine and/or chloramines.)	
E13.2.1	The procedure of step E13.1.1 now gives ozone plus total available chlorine, i.e. free chlorine plus chloramines (volume OTC).	
E13.3	Total available residual chlorine	
E13.3.1	Place 2.00 ± 0.05 ml of glycine solution (E5.13) in a 250 ml conical flask. Carefully, add 100.0 ± 0.5 ml of sample and mix (notes c and f). Into a second flask, add 5.00 ± 0.05 ml of DPD solution (E5.6) and 5.0 ± 0.5 ml of buffer solution (E5.5) see	(e) If DPD powder (or powder and potassium iodide mixture) is used, and sample dilution is not necessary, the powder may be added direct to the glycine-treated sample in the first flask.

	note a, and approximately 0.5 g of potassium iodide (note b) and mix (note e). Add the contents of the first flask to the second flask, mix and titrate immediately with standardised ferrous ammonium sulphate solution (E5.9) (volume TC).	(f) If the total available residual chlorine concentration exceeds 5 mg/l, the volume of sample should be correspondingly reduced, i.e. should be less than 100 ml, or a dilution of the sample prepared. An amount of water (E5.1) being the difference between 100 ml and the volume of sample actually taken should be added to the flask containing the glycine solution before adding the sample.
E13.4	Free available residual chlorine	
E13.4.1	Note g. Place 5.00 ± 0.05 ml of DPD solution (E5.6) and 5.00 ± 0.05 ml of buffer solution (E5.5) in a 250 ml conical flask, see note a. Carefully, add 100.0 ± 0.5 ml of sample and mix (notes c and h). Titrate immediately with standardised ferrous ammonium sulphate solution (E5.9) (volume A, note i).	(g) Steps E13.4.1 and E13.5.1 are necessary if separation of total available chlorine into free chlorine and combined chlorine, ie. mono-chloramine plus di-chloramine, is required. (h) If the total available residual chlorine concentration exceeds 5 mg/l, the volume of sample should be correspondingly reduced, i.e. should be less than 100 ml, or a dilution of the sample prepared. An amount of water (E5.1) being the difference between 100 ml and the volume of sample actually taken should be added to the flask containing the DPD-buffer solution before adding the sample. (i) Reading A includes a proportion of the ozone. The same proportion is included in the subsequent volume C.
E13.5	Combined chlorine (i.e. mono-chloramine plus di-chloramine	
E13.5.1	After obtaining reading A, add about 0.5 g potassium iodide (E5.8) see note b, to the same titration flask, mix and immediately continue the titration to a total volume of C ml.	

E13.6 Correction for interference caused by oxidized manganese

E13.6.1 See note j. Add 5.0 ± 0.5 ml of buffer solution (E5.5) to a conical flask. Add 0.50 ± 0.05 ml of sodium arsenite solution (E5.7). Add 100.0 ± 0.5 ml of sample (note k) and mix. See note l. Then add 5.0 ± 0.5 ml of DPD solution (E5.6) and again mix. Titrate any red colour with standardised ferrous ammonium sulphate solution (E5.9) until the red colour is discharged. Subtract this titre from volume A (free available residual chlorine) as obtained in steps E13.3 or E13.4 or from total available residual chlorine volume in section E13.5.

(j) This is particularly important when determining low levels of chlorine and chloramines in waste waters and effluents.

(k) Alternatively, instead of using sodium arsenite solution, add 0.50 ± 0.05 ml of the thioacetamide solution (E5.7) to 100.0 ± 0.5 ml of sample and add this solution to the flask containing the buffer solution (E5.5).

(i) If the total available residual chlorine concentration exceeds 5 mg/l, the volume of sample should be correspondingly reduced, i.e. should be less than 100 ml, or a dilution of the sample prepared. An amount of water (E5.1) being the difference between 100 ml and the volume of sample actually taken should be added to the flask containing the buffer solution before adding the sample.

E13.7 Calculations

For a 100 ml sample, 1.0 ml of standardised ferrous ammonium sulphate solution (E5.9). is equivalent to 1.0 mg/l available chlorine (see final paragraph of section E5.9).

In the absence of free chlorine and chloramines, volume O gives ozone direct.

The following table may be used for calculating the concentrations of individual components of mixtures of ozone with free and combined chlorine.

Determination	Volume
Ozone, notes (i) and (ii)	OTC - TC
Total available chlorine, note (i)	TC
Free chlorine, note (i)	TC - C + A
Combined chlorine	C - A

Volumes O, OTC, TC, A and C are defined in steps E13.1.1 - E13.5.1 inclusive.

(i) If oxidized manganese is present determine the correction as in step E13.6 and apply to the determinations as follows:

ozone -	deduct correction from volume O
total available chlorine -	deduct correction from volume TC
free chlorine -	deduct correction from volume TC

(ii) The ozone results are obtained in terms of available chlorine. To convert to ozone multiply by 48/71, (0.676) or approximately 0.7.

E14 Procedure for chloroisocyanurate, free chlorine and chloramine mixtures

Step	Procedure	Notes
E14.1	Free available residual chlorine and reserve chlorine	
E14.1.1	Add 5.0 ± 0.5 ml of DPD solution (E5.6) and 5.0 ± 0.5 ml of buffer solution (E5.5) to a 250 ml conical flask, note a. Mix well. Carefully, add 100.0 ± 0.5 ml of sample (notes b and c) and mix. Titrate the solution immediately with standardised ferrous ammonium sulphate solution (E5.9) until the red colour is discharged (volume A ml) see note d.	(a) Alternatively, a combined buffer-DPD reagent (E5.6.1) may be used. (b) Care should be taken to minimize losses of volatile disinfectants from the sample. (c) If the total available residual chlorine concentration exceeds 5 mg/l, the volume of sample should be correspondingly reduced, i.e. should be less than 100 ml, or a dilution of the sample prepared. An amount of water (E5.1) being the difference between 100 ml and the volume of sample actually taken should be added to the flask containing the DPD-buffer solution before adding the sample. (d) This reading includes the free available residual chlorine present in the water plus that available as reserve in the chloroiso-cyanurates.
E14.2	Mono-chloramine	
E14.2.1	Immediately following the titration in step E14.1.1, add approximately 0.5 mg of potassium iodide (E5.8) see note e, and	(e) Alternatively, 0.1 ml of 0.5 % m/v potassium iodide solution (E5.8.1) may be used.

	titrate the solution immediately with standardised ferrous ammonium sulphate solution (E5.9) until the red colour is discharged (volume B ml) note f.	(f) The recorded volume is the total volume, i.e. volume A plus the additional titre.
E14.3	Di-chloramine	
E14.3.1	Immediately following the titration in step E14.2.1, add approximately 1 g of potassium iodide (E5.8) and mix to dissolve. Leave the solution to stand for two minutes and titrate the solution with standardised ferrous ammonium sulphate solution (E5.9) until the red colour is discharged (volume C ml) notes g and h.	(g) The recorded volume is the total volume, i.e. volume B plus the additional titre. (h) Any drift back of colour at the end point when titrating relatively large amounts of di-chloramine indicates that the reaction with iodide, which is not instantaneous, is still incomplete. In such cases, allow the solution to stand a further two minutes before commencing the titration. When di-chloramine concentrations are known to be low, add only 0.5 g of potassium iodide (E5.8).

E14.4 Calculation

For a 100 ml sample 1.0 ml of standardised ferrous ammonium sulphate solution (E5.9) is equivalent to 1.0 mg/l available chlorine. (see final paragraph of section E5.9).

Volumes A, B and C are defined in steps E14.1.1 - E14.3.1.

The following table may be used for calculating the concentrations of individual components.

Determination	Volume
Free and reserve chlorine, notes (i) and (ii)	A
Mono-chloramine, note (iii)	B - A
Di-chloramine, note (iii)	C - B

(i) If oxidized manganese is present determine the correction as in step E14.3.1 and apply to the determination as follows:

free and reserve chlorine - deduct correction from volume A

(ii) The result for the reserve chlorine derived from the chloroisocyanurates remains in terms of available chlorine.

(iii) If the step leading to reading B is omitted mono-chloramine and di-chloramine are obtained together as combined chlorine (C - A).

E15 Spectrophotometric, colour comparison and on-site test procedures

Colorimetric methods may be applied to the supplementary procedures for the other disinfecting agents in place of the titrations with ferrous ammonium sulphate solution. Those involving chlorine dioxide and chlorite do not require the additional disodium ethylenediaminetetraacetate solution as specified for the corresponding titrimetric method. Calibration of spectrophotometers should be carried out as described in the DPD method for free chlorine and chloramines (see section D8.1). Appropriate volume correction factors should be applied when using the supplementary reagents as described in section E7.

The reagents required for estimating chlorine species as described in section D are available in powder or tablet form. The supplementary reagents are available in the form of glycine, acidifying and neutralizing tablets, the use of which may obviate the need for volume correction factors.

Colour comparison methods against permanent glass standards are commonly used in laboratories and on-site. Such standards are available covering 0.2 - 10 mg/l as bromine, 0.4 - 14.0 mg/l as iodine and 0.01 - 1.0 mg/l as ozone. Standards calibrated in terms of chlorine may be used provided appropriate stoichiometric corrections are made.

F Determination of chlorine demand

F1 Introduction

In the application of chlorine or other disinfecting agents to waters it is important to ensure that sufficient agent has been applied to achieve the desired result in terms of improved bacteriological quality. In practice, this control consists of frequent determination of the residual chlorine or other agent in the water after a given contact period. In addition to its amount, it is necessary in the case of chlorine to consider the nature of the residual, whether free, combined or total, since impurities in the water, besides destroying active chlorine by reduction to chloride or some other form of non-available chlorine, may combine with it to form compounds of the chloramine type, especially if such impurities are of an ammoniacal or nitrogenous nature. Such combined chlorine compounds contain available chlorine and should, therefore, be included as residual chlorine. Hence, when establishing the optimum dosage level for disinfection, it is necessary to consider both the amount and the nature of the residual.

The extent of chlorine reduction to chloride, or of conversion to chloramines and any subsequent loss of residual through breakpoint reactions depends upon factors such as the actual dose applied, the time of contact, the pH value and temperature of the water. Hence, when determining the chlorine demand of a raw water, i.e. the difference between the applied chlorine dose and the residual chlorine, these factors should be specified. In addition, it is necessary to state the terms in which the residual is expressed, namely, free, combined or total available residual chlorine.

Similar considerations apply where chlorine is used to achieve some improvement in chemical quality. The requirements for maintenance of a residual are first established and thereafter the determination of chlorine demand under the prevailing conditions fixes the amount of chlorine to be applied to produce the desired residual.

Whilst the procedure given below is for chlorination, similar techniques apply for other disinfecting and oxidizing agents

F2 Principle

Increasing known amounts of a standard chlorine solution are added to a series of portions of the sample under conditions of pH, temperature, etc, as close to operating conditions as possible, and, after the appropriate contact time, the residual chlorine is determined. The chlorine solution is standardised iodometrically. Chlorine residuals are determined by either of the DPD methods given above (methods C or D).

F3 Hazards

Appropriate precautions should be taken when handling strong chlorine solutions.

F4 Reagents

All chemicals should be of analytical reagent quality unless otherwise specified. Store reagents in glass bottles.

F4.1 Water. Deionised or distilled, free from oxidising agents and having neglegible chlorine demand.

F4.2 Potassium iodide, crystals.

F4.3 Sodium acetate, trihydrate.

F4.4 Acetic acid, glacial.

F4.5 Starch solution. Grind 0.5 ± 0.1 g of soluble starch into a smooth paste with a little cold water and pour, with constant stirring, into 100 ± 10 ml of boiling water. Boil for one minute and allow the mixture to cool before use. The reagent may be stored in a refrigerator for up to one week. Solid indicators are available commercially and may be used in accordance with manufacturer's instructions.

F4.6 Sodium thiosulphate (0.125M). Dissolve 31.2 ± 0.05 g of sodium thiosulphate pentahydrate in approximately 200 ml of water in a 1000-ml volumetric flask. Make to 1000 ml with water and mix well. Store in an amber glass bottle. The expiry date of this reagent is variable and limited. Turbid solutions should be discarded. This solution may be stored at room temperature for up to one month.

F4.7 Sodium thiosulphate (0.0125M). Add 50.00 ± 0.05 ml of sodium thiosulphate solution (F4.6) into a 500-ml volumetric flask. Make to 500 ml with water and mix well. Prepare fresh on the day of use.

F4.8 Potassium iodate solution (0.0208M) (i.e. M/48). Dissolve 4.460 ± 0.005 g of potassium iodate (previously dried at 110 ± 5 °C for 1 hour) in approximately 200 ml of water in a 1000 ml volumetric flask. Make to 1000 ml with water and mix well. This solution may be stored at room temperature for up to 1 year.

F4.9 Potassium iodate solution (0.00208M) (i.e. M/480). Add 50.00 ml of potassium iodate solution (F4.8) into a 500-ml volumetric flask and make to 500 ml with water. Mix well. This solution may be stored at room temperature for up to 1 year.

F4.10 Standardisation of the sodium thiosulphate solution. This should be carried out immediately before use for the analysis of samples.

Pipette 10.00 ml of 0.00208M potassium iodate solution (F4.9) into 500 ± 5 ml of water in a 1000 ml conical flask. Add 0.5 ± 0.1 g of potassium iodide crystals and 5 ± 1 ml of acetic acid (F4.4) mix and allow to stand for 60 ± 5 seconds. Titrate with the sodium thiosulphate solution to be standardised (F4.7) until the colour of the liberated iodine is nearly discharged. Add 2.0 ± 0.5 ml of starch solution (F4.5) and titrate rapidly until the blue colour disappears and re-appears within for 30 seconds. Note the titration volume, V_1 ml.

F4.11 Standard chlorine solution. The chlorine water may be obtained from the plant chlorinator solution pipe or by bubbling chlorine gas through water (F4.1). If another chlorinating agent, for example sodium hypochlorite, is applied in the treatment plant process, a solution of the same chlorinating agent should be used in this procedure.

A suitable strength of solution is about 250 mg/l (as chlorine) so that 1 ml added to 250 ml of sample equivalent to a dose of about 1 mg/l as chlorine. Should the dosage range to be covered extends beyond 5 mg/l, a stronger solution should be used. Chlorine solutions should be used immediately after standardisation, (see section F6.1).

F5 Apparatus

F5.1 Common laboratory glassware, including pipettes, conical flasks, measuring cylinders and beakers.

F5.2 Microburette. Measuring up to 5 ml and graduated to 0.02 ml divisions for concentrations up to 4 mg/l. For higher concentrations which exceed 5 mg/l in terms of available chlorine, a 25 ml burette graduated to 0.1 ml may be more appropriate.

F6 Analytical procedure

These procedures should be used where the following concentrations are exceeded;

nitrite (as N) -	0.5 mg/l;
Mn(III) and higher valency states (as Mn) -	0.03 mg/l;
Iron(III) (as Fe) -	2 mg/l;

or where other oxidizing agents are present and there is reason to suspect this might cause interference.

Step	Procedure	Notes
F6.1	Standardisation of chlorine solution	
F6.1.1	Add 0.5 ± 0.1 g of potassium iodide crystals (F4.2) and 5 ± 1 ml of acetic acid (F4.4) to a 250 ml conical flask. Add to the flask, a suitable volume (V ml) of chlorine solution (F4.11) typically, 25.0 ± 0.5 ml, and mix by gentle swirling.	
F6.1.2	Immediately titrate with standardised 0.0125M sodium thiosulphate solution (F4.10) until the colour of the liberated iodine is nearly discharged. Add 2.0 ± 0.5 ml of starch solution (F4.5) and titrate rapidly until the blue colour disappears and re-appeasr within 30 seconds (note a). Note the titration volume V_2 ml.	(a) Titrate to the first end point only, since problems may occur due to recurring end points caused by slow oxidation by air and other substances. See F6.
F6.2	Sample	
F6.2.1	Measure 10 (or other appropriate number) of portions or aliquots, each of 250 ± 2 ml of the sample into separate brown glass-stoppered bottles or open flasks, note b.	(b) The bottles or flasks should be of sufficient size to allow adequate mixing.

F6.3 Addition of chlorine solution

F6.3.1 To cover the required dosage range, add the appropriate amounts of chlorine solution in increasing amounts to successive portions or aliquots of the sample. Mix the solutions gently but thoroughly while adding the chlorine solution. See note c.

(c) To allow time for the residual determinations to be carried out after the pre-determined contact time, it is desirable to stagger the timing of the additions. Protect the samples from strong daylight and, preferably maintain them at the same temperature as the water undergoing treatment.

F6.4 Examination of sample

F6.4.1 At the end of the appropriate contact period, each portion or aliquot of sample should be examined for free available residual chlorine and combined available residual chlorine (see methods C or D). The type and the amount of residual chlorine determined should be recorded.

F6.5 Determination of chlorine demand

F6.5.1 Prepare a curve by plotting chlorine dose applied against chlorine residual determined. The chlorine demand is the difference between the dose and the residual at any selected point on the curve, note d.

(d) The following details should be recorded: dose, amount and nature of residual, contact time. In addition, the pH value and temperature should be measured and recorded.

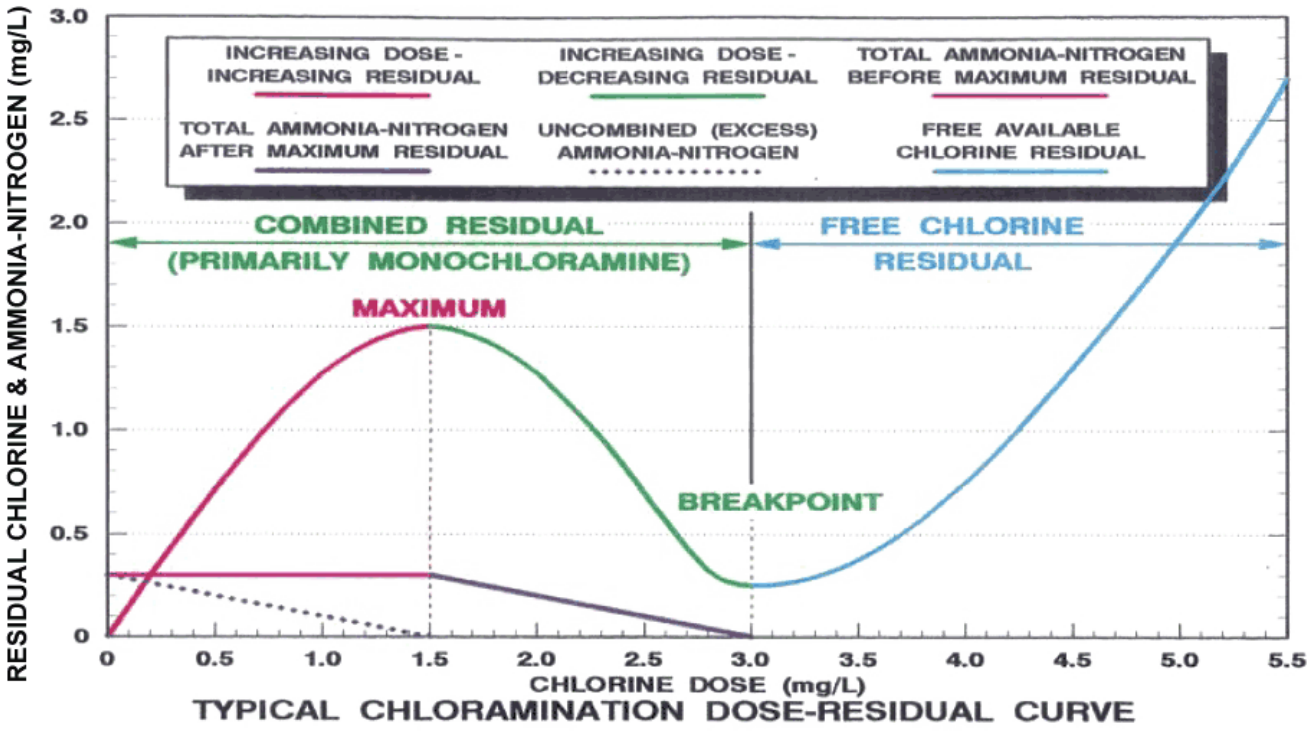
F7 Calculation

Using 0.0125M sodium thiosulphate solution (F4.10):

$$\text{Total available chlorine} = (500 \times V_2 \times 10 \times 0.89) / (V_1 \times V) \quad \text{mg/l as } Cl_2$$

Figure 1 shows a typical break-point curve.

Figure 1 Typical break-point curve



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 wish to receive advance notice of forthcoming publications, please contact the Secretary.

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