Chemical Disinfecting Agents in Water and Effluents, and Chlorine Demand 1980

Methods for the Examination of Waters and Associated Materials

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CORRECTIONS

Page 7, para 4, line 13	*for* 'ratio' *read* 'ratios'.
Page 20, step Ca 7.7, line 2	*for* 0.5±0.5 ml' *read* 0.5±0.05 ml'.

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Chemical Disinfecting Agents in Water and Effluents, and Chlorine Demand 1980

Methods for the Examination of Waters and Associated Materials

This booklet contains three basic methods, one iodometric and two using diethyl-p-phenylenediamine (DPD), titrimetric and colorimetric. These latter can be modified for the determination of a variety of disinfectant combinations. In addition the booklet also contains a related method for the determination of Chlorine Demand. The methods are arranged in the following order:

i. Determination of Total Available Chlorine in Waters by Iodometric Titration

ii. Determination of Free Chlorine, Combined Chlorine and Total Available Chlorine using Diethyl-p-phenylenediamine
   a. Titrimetric method
   b. Spectrophotometric and colour comparison methods

iii. Determination of Other Disinfecting Agents, alone and in the presence of Free Chlorine and Chloramines using DPD by titrimetric and other methods.
   a. Chlorine Dioxide and Chlorite
   b. Bromine and Bromamines
   c. Iodine
   d. Ozone
   e. Chloroisocyanurates

   Advice is also given on the determination of other possible disinfecting agents such as hydrogen peroxide, the ferrates and so on.

iv. Determination of Chlorine Demand

The status of these various methods varies from fully tested to tentative. The position is discussed in greater detail in the section immediately preceding the Introduction.

Chemical disinfectants are also used in water treatment as oxidants and although when so used the stoichiometry of their reactions may vary with the conditions of use, the methods which follow are still suitable for their determination.

References are provided for several alternative methods for the determination of available chlorine not normally required in routine British practice.

Contents

Warning to users

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

There are numerous handbooks on first aid and laboratory safety. One such publication is *Code of Practice for Chemical Laboratories* issued by the Royal Society of Chemistry, London. Another such publication, which includes biological hazards, is *Safety in Biological Laboratories*, (editors, E Hartree and V Booth), Biochemical Society Special Publication No 5, The Biochemical Society, London.

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

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

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About this series

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

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

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

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

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

TA DICK
Chairman

LR PITTWELL
Secretary

20 *July* 1977

Status of the Various Methods

Testing of the methods given in this booklet to the degree given in some other booklets in this series has proved impossible. Most of the determinands are not stable enough for the circulation of master solutions. In many cases, preparation of solutions of accurately known strength was not directly possible, though in some instances the strength of a test solution could be deduced indirectly as a cross check. Often a reproducible drift in results obtained in repeated analysis of a series of samples showed that they were not stable enough for precision tests to be made on successive aliquots of sample, and only by analysing samples all at the same time could customary precision data be obtained. Data have been obtained for method B and much of part C, which are presented in the tabular form customary in this series. Data were also obtained for the main and total determinands for the variants given in part D. These are similar to that given for part C. An investigation of the efficiencies of the various separations given in parts C and D and the effectiveness of method B with a range of disinfectants has been made either by panel members or colleagues and associated groups throughout the world. As these are more in the nature of research exercises than normal tests of accuracy, no data are presented beyond those in the appendix though some references to the literature have been given. Acknowledgement made in the various performance characteristics sections is only for the results actually quoted. Acknowledgement of corroborative testing is made at the end of the membership section.

The main determination of a single determinand and of total determinand should therefore be regarded as fully tested for samples normally encountered in Britain. Although some have been used for a long time by many laboratories, the testing of the separations given below cannot be as thorough as might be desired by some analysts. Nevertheless, with the exception of ozone-chlorine mixtures, for which tentative methods are presented, the validity of the different methods has been established by independent laboratory results. Typical results are given in the appendix.

A Introduction

The methods that follow give details for the determination of the various agents used in the treatment of water including 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 the above oxidants and disinfectants 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 molecular chlorine hydrolyses to form hypochlorous acid, which in turn partly dissociates to produce hydrogen ions and hypochlorite ions. These three forms of chlorine exist in equilibrium, their relative proportions being determined by the pH value and temperature. (See Section Ca 8.2 and Ref 32a).

In the presence of ammonia, which is found to a lesser or greater extent in pure and polluted waters, important substitution reactions occur. The hydrogen atoms of the ammonia molecule can be successively replaced by chlorine atoms forming monochloramine, dichloramine and nitrogen trichloride. These chloramines still have disinfecting properties, but like those of hypochlorite ion are on a much reduced level compared with hypochlorous acid. Chloramines, however, are generally more stable than hypochlorous acid and hypochlorite ion and are therefore more persistent. In the presence of excess chlorine, mono and di-chloramines can, with time, undergo breakpoint reactions to produce mainly nitrogen. The so-called breakpoint is reached when all the ammonia 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 ammonia nitrogen originally present in the water is about 10:1, although for heavily polluted waters the ratio may be considerably greater. Any residual chlorine after the production of a breakpoint is substantially in the form of hypochlorous acid and hypochlorite ion. A fuller discussion of the chemistry of water chlorination may be obtained from textbooks dealing with the subject, for example, G C White's *Handbook of Chlorination*[1,32] or from some appropriate articles, such as A T Palin's *Chemistry of Modern Water Chlorination*[2].

When chlorine is in a form which will release free iodine from an acid solution of potassium iodide it 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", although if this is done it is important to appreciate that the "available chlorine" content in the case of some compounds is not a true measure of their disinfecting power. For example the disinfecting power of chlorine dioxide is only equivalent to one fifth of its available chlorine content. In the case of chlorine dioxide and chlorite, some analysts prefer to express results in terms of ClO_2 and ClO_2^-. Other disinfectants, such as bromine and ozone, are normally expressed as the substance itself.

From an analytical point of view, the forms of chlorine which are usually determined are separated into two 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 or organic nitrogen compounds.

The sum of i and ii is known as **total available residual chlorine.**

The residual chlorine content of water and particularly effluent samples decreases after collection. The effect is greater with both rising temperatures and in the presence of organic matter; in addition, it is accelerated by exposure to sunlight. It is important therefore that residual chlorine tests should be carried out with a minimum of delay, preferably at the time of sampling. These results are likely to be more significant since such changes in the amount and nature of the residual chlorine as might arise in transit to a laboratory are eliminated. For such on-site testing, commercial test kits are useful and may provide an adequate degree of accuracy.

A1 Iodometric Titration

The iodometric method given here is only for the determination of chlorine; but it can be adapted to the determination of the other disinfecting agents. It is used for the calibration of chlorine solutions which may be required subsequently to standardize the 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 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. However, the method is so rarely used for these other determinations at present, that these variants have been omitted from this edition.

A2 Diethyl-p-phenylenediamine (DPD) Method

In addition to the iodometric method used as a reference method for total disinfectant, this document also describes titrimetric and colorimetric procedures using DPD for the determination in water of various oxidizing disinfectants including free chlorine, chloramines, chloroisocyanurates, chlorine dioxide, bromine, bromamines, iodine and ozone.

Methods for the separate determination of free chlorine and chloramines in chlorinated waters using DPD[3,4,5] are well established. The use of DPD was extensively tested in the United Kingdom by the then Water Research Association[6,7,8], where in comparative studies on nine analytical methods, for overall use, it was rated the most precise and accurate method.

More recent studies in the United States by Wei and Morris[9] confirmed that the DPD method gave accurate results. In particular its ability to provide unambiguous determinations of free chlorine, the most potent species available for disinfection, without interference from nitrogen trichloride was considered important. These findings were corroborated by Saunier[10] at the University of California, Berkeley, who concluded after carrying out more than fifteen hundred determinations that the DPD titrimetric method was a very reliable method for measuring free chlorine, mono and dichloramine and even nitrogen trichloride provided care was taken during sampling to avoid any escape of nitrogen trichloride gas. This method has been further evaluated by the Analytical Reference Service of the USA Environmental Protection Agency[11, 12] it has been included in APHA Standard Methods[13], and it is now officially laid down in the USA National Primary Drinking Water Regulations[14] that DPD shall be used for the analysis of residual chlorine in all publicly maintained water supply systems. The method is officially recommended in many other countries, such as, for example, West Germany[15].

The most recent reports have come from France where experimental results of a study by N Strupler[16] showed that nitrogen trichloride in concentrations up to at least 4 mg/l as chlorine produced no perceptible response in the free chlorine fraction. In addition the accuracy of the supplementary DPD procedure for nitrogen trichloride[17] was confirmed by extensive comparison against corresponding specific UV absorption data. It was further established[18] that the determination of free chlorine by the DPD method was not affected by the presence of dichloramine and that monochloramine in concentrations of up to 4 mg/l available chlorine gave no perceptible coloration in the absence of iodide, in the titrimetric and spectrophometric procedures. With a field test kit using a visual comparison method, a faint positive response was observed giving an apparent free chlorine reading of the order of two per cent of the monochloramine present. Additional information is also available in an Appendix (Section G).

A3 References to methods for special circumstances rarely encountered in British Practice

A3.1 General

A variety of alternative reagents are compared in References 6, 7 and 8

A3.2 Very High Total Available Chlorine Residuals

Levels of total available chlorine higher than are recommended here for the DPD methods are determined by predilution of the sample or, if total available chlorine will suffice, by the iodometric method. Commercial test kits are also available for approximate direct measurement at these high ranges. Usually such high levels are only found in cannery cooling waters and in heavily chlorinated sewage; the latter is contrary to normal British sewage works practice. For this latter sample type see also A3.3 which follows.

A3.3 Very High Monochloramine Levels

If very high levels of ammonia or sewage are present resulting, after chlorination, in the formation of exceptionally high monochloramine values the free available chlorine may be determined by the syringaldazine method[19]. This method is not widely used but may find application in the field evaluation of free chlorine residuals where polluted sources are in use. The limit of detection is relatively high at 0.1 to 0.2 mg/l Cl_2 and the results are subject to strong positive interference by nitrogen trichloride amounting to about seventy per cent of the amount present[18, 20]. The syringaldazine method has been adapted to the determination of combined chlorine and ozone, but efforts at differentiating between monochloramine and dichloramine were unsuccessful[21]. For specific determination of free available chlorine in the above conditions the DPD – thioacetamide procedure may be used; in addition to being free from nitrogen trichloride interference the thioacetamide reagent used therein effectively eliminates any interference by high levels of monochloramine[22].

A3.4 Demand for Other Disinfectants or Oxidants

The method for chlorine demand could also be adapted for other disinfectant or oxidant demands, but such additional methods are not considered necessary at present. Ozone, for instance, is used for oxidation and decolorization, and the demand is usually determined by direct plant adjustment, based on effect, not on residual concentrations.

A4 Expression of results

Throughout these methods results are given as available chlorine (Cl_2) or its equivalent unless otherwise stated.

B Determination of Total Available Chlorine in Waters by Iodometric Titration

B1 Performance Characteristics of the Method

B1.1	Substance determined	Total available chlorine
B1.2	Types of sample	Raw, drinking and swimming pool waters (but see Introduction and Diethyl-p-phenylenediamine method).
B1.3	Basis of method	Quantitative liberation of iodine from an acid solution of potassium iodide followed by iodometric titration.
B1.4	Range of application	1 to 20 mg/l of available chlorine (without dilution)
B1.5	Standard deviation (b)	*Equivalent Chlorine Concentration (a)* mg/l: 2; 20 — *Standard Deviation* mg/l: 0.044–0.074; 0.077–0.13 — *Degrees of Freedom*: 11; 11
B1.6	Limit of detection (b)	Approximately 0.15 mg/l of available chlorine (as Cl_2). (based on the criterion of detection with the specified procedure).
B1.7	Sensitivity (b)	1 ml of 0.0125M sodium thiosulphate is equivalent to 0.89 mg/l of available chlorine (as Cl_2).
B1.8	Bias (b)	Potential negative bias due to loss of chlorine and iodine and a tendency to undertitrate slightly to the end point.
B1.9	Interferences (b)	See section B3
B1.10	Time required for analysis (b)	Total analytical and operator time is approximately five minutes per sample. A further five minutes is required for reagent standardization with each sample batch.

(a) Data obtained using standard potassium iodate solutions equivalent to the listed concentrations.

(b) A summary of data obtained by:
The Southern Water Authority (Hampshire River & Water Div.), and Wallace & Tiernan Ltd., Tonbridge, Kent.

B2 Principle

Free and combined chlorine liberate iodine quantitatively from an acid solution of potassium iodide. The free iodine is determined by titration with sodium thiosulphate using starch to indicate the end point.

B3 Interferences

Oxidizing agents, other than those being determined, which are capable of liberating iodine from iodide can interfere. Nitrite, manganese in the trivalent and higher oxidation states, chromate, ferric iron, cupric copper, or, very rarely, ceric cerium can occur in samples of the type being analysed and may interfere. The extent of the interference will depend on the overall composition of the sample. If any of these species are present at a concentration which could cause significant interference (see note e in section B8) a modified method is advised as in steps B8.5 and B8.6 of the procedure.

B4 Hazards

Glacial acetic acid should be handled with care due to corrosivity to skin and eye irritancy properties.

B5 Reagents

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

B5.1 **Water**

Deionized or distilled, free from oxidizing agents and having no chlorine demand. (See also Part F1).

B5.2 **Potassium iodide,** crystals

B5.3 **Sodium acetate,** trihydrate

B5.4 **Acetic acid,** glacial

B5.5 **Starch solution**

Grind 0.5 ± 0.1g of soluble starch into a smooth paste with a little cold water and pour into 100 ± 10ml boiling water with constant stirring. Boil for one minute and allow to cool before use. The reagent remains stable for up to one week if stored in a refrigerator, otherwise prepare fresh solution as required. Solid indicators are available commercially and may be used in place of starch solution. Use in accordance with manufacturer's instructions.

B5.6 **Sodium thiosulphate**

Two alternative strengths of solution may be used: either 0.0125M (B5.7a), which is the commonly used reagent for many purposes and with which the performance data given were obtained; or 0.014M (B5.7b), which gives a simple relationship between volume of titrant used and chlorine concentration of the sample (the difference in performance between the two variants is negligible). Both are prepared from a common 0.125M solution (B5.6.1).

B5.6.1 *Sodium thiosulphate* 0.125M
Dissolve 31.2 ± 0.05g of sodium thiosulphate pentahydrate in about 200ml of water, transfer quantitatively to a 1-litre calibrated flask, dilute with water to the mark and mix. Shelf life is variable and limited. Store in an amber glass bottle. Turbid solutions should be discarded. Also discard as soon as the dilute solutions (B5.7a or B5.7b), prepared daily, show a significant loss of strength (see steps B8.1 and B8.2).

B5.7a *Sodium thiosulphate* 0.0125M Pipette 50.00ml of sodium thiosulphate 0.125M into a 500-ml calibrated flask and dilute with water to the mark. Prepare fresh solution daily.

Alternatively

B5.7b *Sodium thiosulphate* 0.014M Measure out 56.00±0.05ml of sodium thiosulphate 0.125M using a suitable burette into a 500-ml calibrated flask and make up to mark with water. 1ml of this solution is equivalent to 1 mg/l of chlorine in the sample when used as specified in this method. Prepare fresh solution daily.

B5.8 **Potassium iodate 0.0208M** (for standardizing) (ie. M/48)

Dissolve 4.46 ± 0.005g of potassium iodate dried at 110 ± 5° C for 1 hour, in about 200ml of water, transfer quantitatively to a 1-litre calibrated flask, dilute with water to the mark and mix. Properly stored in a clean, glass stoppered, bottle the solution should be stable at least 1 year.

B5.9 **Potassium iodate 0.00208M** (for standardizing) (ie. M/480)

Pipette 50.0ml of potassium iodate 0.0208M into a 500-ml calibrated flask and make up to the mark with water. Properly stored in a clean glass stoppered bottle the diluted solution should be stable for at least 1 week.

B6 Apparatus

Unless otherwise specified all glassware for the handling of specified volumes of reagents should be accurate to a Class B tolerance or better as defined in relevant standards of the British Standards Institution. (see also Part F2).

B6.1 **Common laboratory glassware**

Including pipettes, conical flasks, measuring cylinders and beakers.

B6.2 **A microburette**

Measuring up to 5ml and graduated to 0.02 ml is recommended for available chlorine concentrations up to 4 mg/l. For higher concentrations up to 20 mg/l use a 25 ml burette graduated to 0.1 ml.

B7 Sample Collection and Preservation

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

Chlorine determinations should therefore be carried out immediately after sampling. If this is not possible, chlorinated final drinking waters may be stored for up to three hours before analysis without significant loss of disinfectant provided the samples are taken in amber glass bottles, no air gap is present, and they are stored in a refrigerated container without freezing.

In any case, when determinations are not carried out immediately after sampling, the time between sampling and analysis and conditions of storage and transport should be recorded, so that such factors may be taken into account in the final assessment of the results obtained.

B8 Analytical Procedure

READ SECTION B4 ON HAZARDS BEFORE STARTING THIS PROCEDURE.

Step	Procedure	Notes
	Standardization of Sodium Thiosulphate 0.0125M (note a)	
B8.1	Pipette 10.0ml of 0.00208M potassium iodate into 500 ± 5ml of water in a 1 litre conical flask. Add 0.5 ± 0.1g potassium iodide crystals and 5 ± 1 ml acetic acid, mix and allow to stand for 60 ± 5 seconds.	(a) This should be carried out immediately before the use of sodium thiosulphate for the analysis of samples.
B8.2	Titrate with 0.0125M sodium thiosulphate until the colour of the liberated iodine is nearly discharged. Add 2± 0.5 ml starch solution (or its equivalent if using an alternative indicator) and titrate rapidly until the blue colour disappears for 30 seconds. Note the titration volume V_1 ml (note b).	(b) Any deviation from 0.0125M in the strength of the thiosulphate is taken into account in the final calculation.
	Analysis of Samples	
B8.3	Using a measuring cylinder (note c) transfer 500±5 ml of sample to a 1-litre conical flask. Add 5 ± 1 ml acetic acid and 0.5 ± 0.1g potassium iodide crystals. Mix by gentle swirling.	(c) Care should be taken to minimize losses when transferring the solution containing volatile disinfectant *to* and *from* the measuring cylinder.
B8.4	Immediately titrate with standardized 0.0125M sodium thiosulphate (see steps B8.1 and B8.2) until the colour of the liberated iodine is nearly discharged. Add 2 ± 0.5ml of starch solution (or its equivalent if using an alternative indicator) and titrate rapidly until the blue colour disappears (note d). Note the titration volume V_2 ml.	(d) 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.
	Modification in the Presence of Interferences (notes e and f)	
B8.5	Adjust the pH value of the sample to between 4.5 and 8.0 by addition of acetic acid or sodium acetate as necessary.	(e) It is recommended that this procedure be used where the following limits are exceeded: Nitrite (as N) 0.5 mg/l, Mn^{III} and higher valency manganese (as Mn) 0.03 mg/l, Ferric iron (as Fe) 2 mg/l, or where other oxidizing agents are present which the analyst has reason to suspect could cause interference.
B8.6	Proceed as in steps B8.3 and B8.4 but omitting the addition of further acetic acid in step B8.3	(f) For samples containing dichloramine and related forms of available chlorine the neutral titration (steps 8.5 and 8.6) may give low results, due to incomplete reaction in neutral solution of some forms of combined chlorine[23]. While such circumstances are uncommon with raw and drinking waters they may sometimes occur. In such cases it is suggested that the DPD method be used. (See section C.)

B9 Calculation of Results

Using 0.0125M sodium thiosulphate solution:

$$\text{Total available chlorine} = \left(V_2 \times \frac{10}{V_1} \times 0.89\right) \text{ mg/l as } Cl_2$$

Using 0.014M sodium thiosulphate solution:

$$\text{Total available chlorine} = \left(V_2 \times \frac{10}{V_1}\right) \text{ mg/l as } Cl_2$$

C Determination of Free Chlorine, Chloramines and Total Available Chlorine using Diethyl-P-Phenylenediamine (DPD)

C1 Performance Characteristics of the Methods

	a. Titrimetric	b. Spectrophotometric
C1.1 Substance determined	Total available chlorine, or separately, the amount of free chlorine and the different chloramines present.	As titrimetric
C1.2 Type of sample	Raw and drinking waters, swimming pool waters, waste waters and effluents	As titrimetric plus seawater.
C1.3 Basis of method	Development of red colour with diethyl-p-phenylene diamine (DPD) followed by titration with ferrous ammonium sulphate solution to a colourless end point.	Development of red colour with diethyl-p-phenylenediamine (DPD) followed by spectrophotometric absorption measurement at 550 nm.
C1.4 Range of application	0.02 to 5 mg/l (without dilution) (d)	0.01 to 5 mg/l (without dilution) (d)
C1.5 Calibration curve	–	Linear to approximately 1 mg/l. Obeys Beer's law and passes through the origin. (c) For the curve to 4 mg/l see Ref 18.
C1.6 Standard deviation	*Chlorine concentration* mg/l: 1.0; 5.0 *Standard deviation(a)* mg/l: 0.014; 0.044 *Degrees of freedom*: 9; 9	*Chlorine concentration* mg/l: 0.1; 0.5; 0.15 *Standard deviation* mg/l: 0.004 (b); 0.01 (b); 0.01 (d) *Degrees of freedom*: 19; 19; 9
C1.7 Limit of detection	0.011 mg/l (b) (see Ca 5.2) with 10 degrees of freedom	0.004 mg/l 1 cm cell (c) with 10 degrees of freedom
C1.8 Sensitivity	1 ml of 0.00282M ferrous ammonium sulphate is equivalent to 0.1mg of chlorine.	Molar extinction coefficient = 9,800 (b)
C1.9 Bias	No information.	No information
C1.10 Interferences	Manganese III and its higher oxidation states may interfere and cause high results. See procedure step Ca 7.7. (d)	As titrimetric (d)
C1.11 Time required for analysis	3-5 minutes per sample for free and combined chlorine and 5-10 minutes for differential procedure. (d)	As titrimetric (d)

(a) These data were obtained at the Newcastle & Gateshead Water Company Laboratory and refer to total chlorine estimation.
(b) Data obtained at the Water Research Centre, see references 6, 7 and 8.
(c) Data obtained at the Water Research Centre, see reference 24.
(d) Data obtained by panel members.

Ca DPD Titrimetric Method

Ca 1 Principle

Free chlorine reacts with diethyl-p-phenylenediamine (also called p-aminodiethylaniline) to produce a red colour. The addition of a small amount of potassium iodide causes monochloramine to produce a colour with the same reagent. Further addition of a considerable excess of iodide causes dichloramine 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 chlorine fraction. Using this fact an estimation of the concentration of nitrogen trichloride can be made. The individual fractions are determined by titration with standard ferrous ammonium sulphate solution to colourless end points.

Ca 2 Interferences

Oxidizing agents, other than those being determined which are capable of reacting with DPD under the experimental conditions, can interfere. EDTA added as part of the method avoids interference in some cases, for example copper. Section Ca 7.7 gives a modified procedure to avoid interference from oxidized manganese. Other oxidizing disinfecting agents, if present, may also react, in which case also consider the procedures given in Section D.

Ca 3 Hazards

Mercuric chloride and sodium arsenite are toxic compounds used in this method, and care should be taken in their handling. Diethyl-p-phenylenediamine may cause dermatitis in some sensitive individuals; the low concentrations in the prepared liquid and solid reagents appear, however, to present no such hazard.

Ca 4 Reagents

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

Ca 4.1 **Water**

Deionized or distilled free from oxidizing agents and having no chlorine demand. (See also Part F1).

Ca 4.2 **Diethyl-p-phenylenediamine (DPD) sulphate solution** laboratory reagent quality.

Ca 4.2.1 10% *V/V sulphuric acid*

Measure out 10 ± 0.1 ml of sulphuric acid (d_{20} 1.84) and slowly add with stirring and cooling to about 80 ml of water, dilute with water to 100 ± 1 ml. This solution, which is stable indefinitely is needed for the preparation and standardization of other reagents.

Ca 4.2.2 8 *g/l disodium ethylenediamine-tetraacetate dihydrate*

Weigh out 8.0 ± 0.1 g of disodium ethylenediamine-tetraacetate dihydrate, dissolve in about 200 ml of water and dilute with water to 1000 ± 20 ml. This solution, which is stable for at least 3 months is needed for the preparation of other reagents.

Ca 4.2.3 *Diethyl-p-phenylenediamine (DPD) reagent solution*

Dissolve 0.15 ± 0.005g of DPD sulphate pentahydrate (or 0.11 ± 0.005g of anhydrous DPD sulphate) in about 50 ml of chlorine-free water to which 2.0 ± 0.1 ml of 10% V/V sulphuric acid and 2.5 ± 0.1 ml of 8 g/l disodium ethylenediamine-tetraacetate dihydrate (EDTA) have been added. Dilute with water to 100 ± 0.5 ml. The solution is stable for at least 1 week if kept in a brown glass bottle. (See also Ca 4.3.1 for a combined reagent). Discard the solution if it becomes discoloured.

Ca 4.3 **Buffer solution**

Dissolve 2.4 ± 0.05g of disodium hydrogen phosphate and 4.6 ± 0.5g potassium dihydrogen phosphate in water, add 10 ± 1 ml of 8 g/l EDTA and dilute with water to 100.0 ± 0.5 ml. Add two drops of 2% m/V mercuric chloride solution (Ca 4.3.2) to prevent mould growth and to prevent interference in the free chlorine test caused by any trace amounts of iodide in the reagents.

Ca 4.3.1 A stable combined DPD-buffer reagent in powder or tablet form is commercially available,[17, 25, 26], and can be used if desired.

Ca 4.3.2 *2% m/V mercuric chloride solution.*

SEE SECTION Ca3 HAZARDS before preparing this reagent. Weigh out 2 ± 0.1g of mercuric chloride, add 100 ± 10 ml of water, warm to dissolve and cool. This solution is only used as a preservative, and to remove interference due to reagent impurities.

Ca 4.4a **(0.5% m/V) Sodium arsenite solution** (or alternatively see Ca 4.4b)

Dissolve 0.5 ± 0.05g of sodium arsenite in 100.0 ± 0.5 ml of water.

Ca 4.4b **(0.25% m/V) Thioacetamide solution**

Dissolve 0.25 ± 0.02g of thioacetamide in 100.0 ± 0.5 ml of water. (This may be used as an alternative reagent to the sodium arsenite solution, Ca 4.4a).

Ca 4.5 **Potassium iodide** crystals

Ca 4.5.1 *0.5% m/V potassium iodide solution* may be used as an alternative.

Weigh out 0.5 ± 0.05g of potassium iodide and dissolve in 100 ± 2 ml of water. Prepare fresh solution as soon as it becomes discoloured.

Ca 4.6 **0.00282M Ferrous ammonium sulphate (FAS) solution** (1 ml is equivalent to 100 μg chlorine)

Dissolve 1.106 ± 0.005g of ferrous ammonium sulphate hexahydrate in about 200 ml of freshly boiled and cooled water to which has been added 2.5 ± 0.1 ml of 10% V/V sulphuric acid. Quantitatively transfer the solution to a 1-litre calibrated flask and dilute with water to the mark. Transfer to a stoppered brown 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. It should be checked regularly against standard potassium dichromate, as frequently as local experience finds necessary; at the worst, daily checking is sufficient, but the minimum for use in routine work with ideal storage is monthly. If this solution should become turbid, discard at once and prepare fresh solution.

Ca 4.6.1 Standardization of Ferrous Ammonium Sulphate Solution

If a 5-ml microburette accurately calibrated in 0.01-ml divisions[31] is available, prepare an 0.100N (M/60) potassium dichromate solution using the procedure given in Section Ca 4.6.1.1, but taking 4.903 ± 0.0005g of potassium dichromate and omitting the final tenfold dilution step. Then carry out procedure Ca 4.6.1.4 using this solution and the microburette. Then see Section Ca 4.6.1.5.

If such a burette is not available, proceed with Sections Ca 4.6.1.1 – Ca 4.6.1.5 as given.

Ca 4.6.1.1 *0.0100N (M/600) Potassium dichromate solution*

Dry just over 5g of analytical reagent grade potassium dichromate at 105–120°C to constant weight. Weigh out 0.4903 ± 0.00005g, transfer quantitatively with rinsing to a 250-ml beaker and dissolve in water. Transfer the solution completely to a 1-litre class A calibrated flask with glass stopper, rinsing the beaker thoroughly into the flask, make up almost to the mark with water, stopper, mix thoroughly and allow to stand to come to room temperature. Make sure that no drops of liquid are above the calibration mark, and make up to the mark with water. Restopper and mix thoroughly. (If made up with sufficient attention to detail and stored properly, this solution is a primary standard). Alternatively, weigh out 4.903 ± 0.0005g of potassium dichromate, make up as above, pipette 100 ml of this solution into a 1-litre calibrated flask, dilute to the mark with water, stopper and mix thoroughly.

Ca 4.6.1.2 *Phosphoric acid* (d_{20} 1.83)

Ca 4.6.1.3 *0.1% m/V Barium diphenylaminesulphonate solution*

Weigh out 0.10 ± 0.02g of barium diphenylaminesulphonate and dissolve in about 100 ml of water by warming. Store in a glass stoppered bottle. (A solution of diphenylamine in concentrated sulphuric acid is occasionally substituted for this reagent).

Procedure (for apparatus specifications see Section B6)

Ca 4.6.1.4

To a 100-ml sample of FAS, add 20.0 ±0.5 ml of 10% V/V sulphuric acid, 5 ml of phosphoric acid (d_{20} 1.83) and about 2 ml of 0.1% m/V barium diphenylaminesulphonate solution and titrate with the M/60 potassium dichromate solution to a violet end point that persists 30 seconds. Repeat the standardization twice more as a check on accuracy.

Ca 4.6.1.5 Calculation, factor and FAS solution life

If accurately made up, 100 ml of 0.00282M ferrous ammonium sulphate solution (FAS) is equivalent to either 2.82 ml of 0.100N potassium dichromate solution or 28.2 ml of the 0.0100N solution. When the FAS solution requires significantly less than this amount of dichromate solution, discard it and prepare a fresh FAS solution. For FAS solutions which are slightly off the required strength use a standardization factor. If 0.1N dichromate is used, this factor is T/2.82, whilst for 0.01N dichromate the factor is T/28.2, where T is the number of millilitres of standard dichromate solution required in Section Ca 4.6.1.4 above.

Ca 5 Apparatus

Ca 5.1 **Common laboratory glassware**

Including pipettes, conical flasks and measuring cylinder (For specification see Section B6). (See also part F2).

Ca 5.2 **Microburette**

Measuring up to 5 ml graduated to 0.02 ml is recommended for the titration with FAS.

Ca 6 Sample Collection and Preservation

See Section B7 (Iodometric Method).

Ca 7 Procedure

Note 1 The quantities of reagents given are suitable for concentrations of total available chlorine up to 5 mg/l. When the total concentration exceeds this figure dilution with chlorine-free water is necessary. This is particularly important for very high concentrations of disinfecting agents otherwise bleaching of the colour can occur leading to erroneous results. This would be indicated by the appearance of a transient red colour followed by rapid fading.

Note 2 Glassware must be rinsed thoroughly between determinations. Any carry-over of traces of iodide can lead to monochloramine breakthrough into the free chlorine fraction of the subsequent determination. (See also Part F.2).

Note 3 The method which follows contains several alternative procedures:

i. The various forms of available chlorine may be determined consecutively – steps Ca 7.1, 7.2, 7.3 and perhaps 7.6 and 7.7;

ii. Only free and combined chlorine may be determined – steps Ca 7.4, 7.1, 7.3 and perhaps 7.6 and 7.7;

iii. Total available chlorine may be determined – steps Ca 7.5, 7.1 and perhaps 7.6 and 7.7.

Step	Procedure	Notes
	Free Chlorine	
Ca 7.1	Place 5.0 ± 0.5 ml DPD solution and 5.0 ± 0.5 ml buffer solution in a 250-ml conical flask and mix. Using a measuring cylinder, carefully add 100.0 ± 0.5 ml of sample and mix (note a). Titrate immediately with FAS solution until the red colour is discharged (reading A).	(a) If the total concentration of available chlorine is likely to exceed 5 mg/l, the volume of sample should be correspondingly less than 100 ml. The difference between 100 ml and the volume taken should be made up with chlorine-free water which should be added to the reagents before the sample. (see also note c. of step B8.3).
	Monochloramine NH_2Cl	
Ca 7.2	To the solution after titration for free chlorine, add a very small crystal (approx 0.5 mg) of potassium iodide (note b) and continue the titration immediately to a total reading B.	(b) Alternatively at step Ca 7.2 add 2 drops (about 0.1 ml) of freshly prepared 0.5% m/V potassium iodide solution in place of the very small crystal.
	Dichloramine $NHCl_2$	
Ca 7.3	To the solution after titration for monochloramine add about 1g potassium iodide and mix to dissolve. Set aside for two minutes and continue the titration further to a total reading C (note c). If nitrogen trichloride is present (note d) correct the result by step Ca 7.6.	(c) Any drift back of colour at the end point when titrating relatively large amounts of dichloramine indicates that the reaction with the iodide, which is not instantaneous, is still incomplete. In such cases allow a further 2 minute period of standing. When dichloramine concentrations are known to be low, half the specified amount of potassium iodide may be used. (d) Nitrogen trichloride may, in the absence of free chlorine, also be taken as absent. Moreover it is unlikely to be present in waters containing monochloramine, but see Section Ca 8.1
	Simplified procedure for free and combined chlorine	
Ca 7.4	Step Ca 7.1 gives free chlorine. To obtain monochloramine and dichloramine together as combined chlorine, omit step Ca 7.2 and carry out step Ca 7.3 directly after step Ca 7.1 (reading C). A nitrogen trichloride correction is necessary if present (step Ca 7.6).	
	Simplified procedure for total available chlorine	
Ca 7.5	To obtain total available chlorine in one reading, carry out step Ca 7.1 with the following modifications: add about 1g of potassium iodide (the full amount required for reading C) at the start of step Ca 7.1 along with the specified amounts of DPD and buffer solutions, followed by the 100.0 ± 0.5 ml of sample, mix, and set aside for two minutes before titrating. In the presence of nitrogen trichloride the result will require an appropriate correction (step Ca 7.6). (See notes a and c)	

Step	Procedure	Notes
	Nitrogen trichloride NCl_3	
Ca 7.6	When present, nitrogen trichloride will normally appear to the extent of one half of its available chlorine content with the dichloramine in reading C. To determine it separately proceed as follows:- Into a 250 ml conical flask place a very small crystal of potassium iodide (approx. 0.5 mg). Using a measuring cylinder carefully add 100.0 ± 0.5 ml of sample and mix (note a). Then add the contents to a second flask containing 5.0 ± 0.5 ml each of buffer and DPD solutions. Titrate rapidly with FAS solution (reading N).	
	Correction for interference by Oxidized Manganese (note e)	
Ca 7.7	Place 5.0 ± 0.05 ml of buffer solution, and 0.5 ± 0.5 ml of sodium arsenite solution in a conical flask (note f). Add 100.0 ± 0.5 ml of sample mix, then 5.0 ± 0.5 ml of DPD solution and again mix. Titrate any red colour with FAS solution and subtract this titre from reading A (free chlorine) as obtained in steps Ca 7.1 and 7.4 or from total available chlorine reading in step Ca 7.5.	(e) In determining low levels of chlorine and chloramines in waste waters and effluents it is recommended, as a safeguard against the presence of trace amounts of unidentified interfering substances, that a sodium arsenite blank should always be used. (f) Alternatively the 0.25% m/V thioacetamide solution can be used instead of sodium arsenite, 0.5 ± 0.05 ml of the thioacetamide solution being added to 100.0 ± 0.5 ml sample.

Ca 8 Calculation

For a 100 ml sample 1.0 ml of standardized FAS solution is equivalent to 1.0 mg/l available chlorine. (See Ca 4.6.1.5).

Ca 8.1 The table which follows may be used for calculating the concentrations of individual components.

A, B, C and N are defined in steps Ca 7.1, 7.2, 7.3 and 7.6 above respectively.

Determination	NCl_3 absent	NCl_3 present
Free chlorine (note a)	A	A
Monochloramine (note b)	B–A	
Dichloramine	C–B	C–N
Nitrogen trichloride (notes b and c)		2(N–A)
Combined chlorine (note c)	C–A	C + N – 2A
Total chlorine (notes a and c)	C	C + N – A

Notes

(a) If oxidized manganese is present determine the correction as in step Ca 7.7 and apply to the determinations as follows:
free chlorine – deduct correction from reading A
total chlorine – deduct correction from reading C

(b) The above formulae assume, in conformity with what has been stated earlier, that if nitrogen trichloride is present, monochloramine is absent, ie. B = A.

(c) If in exceptional circumstances monochloramine and nitrogen trichloride should be present at the same time, reading N will include monochloramine, in which case the concentration of nitrogen trichloride is obtained from 2(N–B).
The combined chlorine is then given by C + N – A – B and the total chlorine by C + N – B.

Ca 8.2 **Hypochlorous Acid Concentration**

Except in very acid waters, below about pH 4, when molecular chlorine may be present, the free chlorine residual as normally determined is a mixture of hypochlorous acid and hypochlorite ion, the relative proportions depending on pH and temperature. Hypochlorous acid is by far the most active germicide of all the residual compounds. An estimate of its concentration may be obtained from the following table. To obtain the estimate, multiply reading A by the appropriate factor in the table below.

	pH								
	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

See also Ref 32a

Cb DPD Spectrophotometric Method

Cb 1 Principle

The same principle applies as in the titrimetric method except that final estimation of the individual fractions is made by spectrophotometric measurement of the coloration produced by reaction with diethyl-p-phenylenediamine and not by titration with standardized ferrous ammonium sulphate.

Cb 2 Hazards and Interferences

As in Section Ca 2 and Ca 3.
Sea water and corresponding sodium chloride solutions have been found to lower the absorbance sensitivity by 12 to 15 per cent. When analysing sea waters or other comparable salt solutions the standards should therefore be prepared in a simulated sea water.

Cb 3 Reagents

As titrimetric method Sections Ca 4.1 to Ca 4.6.

Cb 3.1 **0.891 g/l Potassium Permanganate Solution**

Weigh out 0.891 ± 0.0005g of potassium permanganate, dissolve in 200 ml of water, transfer quantitatively to a 1-litre calibrated flask and make up to the mark with water. This solution is stable for at least two months.

Cb 3.2 **Potassium Permanganate Solution** (0.0891 g/l)

Pipette 10 ml of 0.891 g/l potassium permanganate into a 100 ml calibrated flask and make up to the mark with water.

This solution should be freshly prepared when required.

Cb 3.3 **Simulated Sea Water**

Dissolve 66 ± 1g of sodium chloride which has been ignited at 600°C for 1 hour and 0.167 ± 0.01g of sodium bromide in water, transfer quantitatively to a 2-litre calibrated flask and make up to the mark with water.

Cb 4 Apparatus

Cb 4.1 **Common laboratory glassware**

Including pipettes, conical flasks and measuring cylinders (for specification see Section B6). (See also Part F2).

Cb 4.2 **Microburette**

Measuring up to 5 ml graduated to 0.02 ml is recommended for the titration with FAS.

Cb 4.3 **Spectrophotometer**

For use at a wavelength of 550 nm. 10–mm and 40–mm glass cells for use with the spectrophotometer.

Cb 5 Sample Collection and Preservation

See Section B7 (Iodometric Method).

Cb 6 Procedure

Notes 1 *and* 2 in Ca 7 (Titrimetric Method) apply.

Note 3 The procedure which follows contains several alternative steps after the calibration of standards (steps Cb 6.0 – 6.4):

i. The various forms of available chlorine may be determined consecutively – steps Cb 6.5, 6.6, 6.7 and perhaps 6.10 and 6.11;

ii. Only free and combined chlorine may be determined – steps Cb 6.8, 6.5, 6.7 and perhaps 6.10 and 6.11;

iii. Total available chlorine may be determined – steps Cb 6.9, 6.5 and perhaps 6.10 and 6.11.

Step	Procedure	Notes
	Standards	
Cb 6.0	Each standard should be separately carried through steps Cb 6.1 – 6.3 before proceeding with the next.	
Cb 6.1	Measure out 0.0, 0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 ml (to the nearest 0.05 ml) of the 0.0891 g/l potassium permanganate solution into a series of 100-ml volumetric flasks using a microburette and make each up to the mark with water (note a). These solutions are equivalent to 0.0, 0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 mg/l of chlorine respectively when reacted and measured as below.	(a) When analysing sea-water samples use simulated sea-water for preparation of standards (See Section Cb 2)
Cb 6.2	Place 5.0 ± 0.05 ml of DPD solution and 5.0 ± 0.05 ml of buffer solution in a 250-ml conical flask and mix. Add the 100 ml of the 0.5 ml potassium permanganate standard (Step Cb 6.1) equivalent to 0.5 mg/l chlorine), mix thoroughly and immediately measure the absorbance of solution at 550 nm in a 40-mm cell (note b) in the spectrophotometer. Use water in the reference cell. Repeat with the other standards in turn.	(b) Smaller cells may be used, but not less than 1 cm.
Cb 6.3	Titrate known volumes of the solution in step Cb 6.2 against standard FAS solution until the colour is discharged (note c).	(c) This acts as a check on the strength of the permanganate standards.
Cb 6.4	Prepare a calibration curve of absorbance against standard equivalent chlorine concentration.	
	Sample Analysis	
	Although for completeness, all information for each determinand is given in one section step, all the analytical work and readings should be made without stopping to determine readings from the calibration graph until step Cb 6.7 has been completed.	
	Free Chlorine	
Cb 6.5	Place 5.0 ± 0.05 of DPD solution and 5.0 ± 0.05 ml of buffer solution in a 250-ml conical flask and mix. Using a measuring cylinder carefully add 100.0 ± 0.5 ml sample and mix (note d). Immediately measure absorbance at 550 nm in a 40-mm cell (note b) in the spectrophotometer using water in the reference cell. After carrying out step Cb 6.7, read off the equivalent chlorine concentration (reading A) from the appropriate calibration graph.	(d) If the total concentration of the available chlorine is likely to exceed 5 mg/l the volume of sample should be correspondingly less than 100 ml. The difference between 100 ml and the volume taken should be made up with chlorine-free water which should be added to the reagents before the sample. (See also note c of step B8.3).
	Monochloramine NH_2Cl	
Cb 6.6	To the total solution after carrying out step Cb 6.5 add a very small crystal (approx 0.5 mg) of potassium iodide (note e) and mix. Immediately read the absorbance as in step Cb 6.5 After carrying out step Cb 6.7, read off the equivalent chlorine concentration (reading B) from the appropriate calibration graph.	(e) Alternatively at step Cb 6.6 add 2 drops (about 0.1 ml) of freshly prepared 0.5% m/V potassium iodide solution in place of the very small crystal.

Step	Procedure	Notes
	Dichloramine $NHCl_2$	
Cb 6.7	To the total solution after step Cb 6.7 (for monochloramine), add about 1g of potassium iodide and mix to dissolve. Set aside for 2 minutes, then measure the absorbance and read off the equivalent chlorine concentration (reading C) as in steps Cb 6.5 and Cb 6.6 (note f). If nitrogen trichloride is present (note g), correct the result using step Cb 6.10.	(f) A drifting absorbance signal indicates that the reaction with the iodide, which is not instantaneous, is still incomplete. In such cases allow a further 2 minute period of standing. When dichloramine concentrations are known to be low, half the specified amount of potassium iodide may be used. (g) Nitrogen trichloride may, in the absence of free chlorine, also be taken as absent. Moreover it is unlikely to be present in waters containing monochloramine, but see Section Ca 8.1.
	Simplified procedure for free and combined chlorine	
Cb 6.8	Determine free chlorine as in step Cb 6.5. To determine monochloramine and dichloramine together as combined chlorine, omit step Cb 6.6 and carry out step Cb 6.7 (reading C). A nitrogen trichloride correction (step Cb 6.10) is necessary if present.	
	Simplified procedure for total available chlorine	
Cb 6.9	To obtain total available chlorine in one reading, carry out step Cb 6.5 with the following modifications: add about 1g (the full amount of potassium iodide required for Reading C) at the start of step Cb 6.5 along with the specified amounts of DPD solution and buffer solution. After carefully adding the 100.0 ± 0.5 ml of sample, mix and set aside for two minutes before measuring the absorbance. In the presence of nitrogen trichloride the result will require an appropriate correction (step Cb 6.10).	
	Nitrogen Trichloride NCl_3	
Cb 6.10	When present, nitrogen trichloride will normally appear to the extent of one half of its available chlorine content with the dichloramine in reading C. To determine it separately proceed as follows:- Into a 250 ml conical flask place a very small crystal of potassium iodide (approx 0.5 mg) (note e). Using a measuring cylinder add carefully 100.0 ± 0.5 ml of sample and mix (note d). Then add the contents to a flask containing 5.0 ± 0.05 ml each of buffer and DPD solution. Mix and immediately measure absorbance and calculate equivalent chlorine concentration from the appropriate calibration graph as in steps Cb 6.5, 6.6 and 6.7 (reading N).	

Step	Procedure	Notes
	Correction for interference by Oxidized Manganese (note h)	
Cb 6.11	Place 5.0 ± 0.05 ml of buffer, and 0.5 ± 0.05 ml of sodium arsenite solution or 0.5 ± 0.05 ml of thioacetamide solution in a conical flask. Add 100.0 ± 0.5 ml of sample, mix then 5.0 ± 0.05 ml of DPD solution and mix again. Measure the absorbance and subtract the reading from the free chlorine absorbance as obtained in steps Cb 6.5 and 6.8 or from the total available chlorine absorbance obtained in step Cb 6.9.	(h) In determining low levels of chlorine and chloramine in waste waters and effluents it is recommended, as a safeguard against the presence of trace amounts of unidentified interfering substances, that a sodium arsenite or thioacetamide blank should always be used.

Cb 7 Calculation

As for the titrimetric method from step Ca 8.1, except that the manganese correction referred to in the note to Ca 8.1 should be determined by step Cb 6.11 and not by step Ca 7.7.

A, B, C and N are here defined in steps Cb 6.5, 6.6, 6.7 and 6.10

Cc DPD Laboratory and Field Test Colour Comparison Procedures for the Estimation of Free Chlorine, Chloramines and Total Available Chlorine

Colour comparison procedures involving visual estimation of the DPD colours produced are normally used to estimate chlorine species in the field, and quite commonly in laboratories also. Colours are produced as described in the spectrophotometric method but final estimation is made by comparison with permanent glass standards.

Reagents are available in stable powder or tablet form for convenient use[17, 25, 26]. Standard glass discs are available in a series of ranges overall covering 0.01 to 10.0 mg/l of available chlorine, involving sample volumes varying from 50 ml to 4 ml, and viewing depths varying from 113 mm to 5 mm[26, 27]. Such discs should be checked against chemical standards prepared as in Section Cb 6 (steps 6.0-6.4).

D. Determination of Chlorine Dioxide, Chlorite, Bromine, Bromamine, Iodine, Ozone and Chloroisocyanurates, alone and in the presence of Chlorine and Chloramines, and also the Determination of Other Disinfectants

Da Titrimetric Methods

Da 1 Performance Characteristics of the Methods

With the exception of chlorine dioxide the performance characteristics of the supplementary procedures are similar to those of the DPD method for free chlorine and chloramines when the determinands are expressed in terms of available chlorine. If conversion factors are used the numerical values of the characteristics must be adjusted to suit.

In the case of chlorine dioxide it is necessary to introduce a factor of 5 if the conventional mode of expression in terms of available chlorine is followed. Alternatively if results are expressed in terms of ClO_2 the required factor is 1.9.

Da 2 Principles

The procedures are extensions of the DPD method for free chlorine and chloramines[5, 20, 28, 29].

Da 2.1 Chlorine Dioxide and Chlorite

Chlorine dioxide appears with free chlorine in Step Da 7.1 of this procedure, 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 the chlorite also is caused to react. The colour produced after subsequent neutralization corresponds to the total available chlorine content of the chlorine dioxide. Any chlorite present as such in the original sample will be included in the step involving acidification and neutralization. The presence of such chlorite is in fact 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 (step Da 7.1 note b and Section Da 7.5) using thioacetamide which prevents colour drift-back at end points caused by much chlorite being present.[29]. 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 dichloramine or as total combined chlorine where a separate determination of mono and dichloramine is not performed, thus simplifying the differential procedures. The same simplification is introduced in the other differential procedures involving bromine, iodine, ozone and chloroisocyanurates, since the use of these chemicals in water treatment does not produce nitrogen trichloride.

Da 2.2 Bromine and Bromamines

Bromine and bromamines are chemically similar in reacting with the DPD indicator to produce a red colour. In the DPD method (Da 8), 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[30].

Da 2.3 **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 (Ca 7.1).

Da 2.4 **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.

Da 2.5 **Chloroisocyanurates**

Chloroisocyanurates dissociate 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 (step Da 11.1) 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.

Da 2.6 **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 readings 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[30].

The basis of the separate determination of ozone and residual chlorine is 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 use for activation of dichloramine 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 dichloramine be encountered. Where glycine is used in the chlorine-ozone differential procedure it is advisable to omit this waiting 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 dichloramine, omission of this precautionary two-minute waiting period should not introduce any significant error. In the case of swimming pools, while high levels of stable dichloramine-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.

Da 2.7 **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).

Da 3 Correction for Interference

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 readings 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 readings may be corrected. This correction must be applied before any multiplying factor is used in the calculation. (See note a in each of Sections Da 7.4, Da 8.4, Da 9.4, Da 10.6 and Da 11.3).

Da 4 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 appear, however, to present no such hazzard.

Da 5 Reagents

The following extra reagents are required for the supplementary procedures, in addition to those required for the DPD free chlorine-chloramines method (see Section Ca 4). All chemicals should be of analytical reagent quality unless otherwise stated.

Da 5.1 **For the Determination of Chlorine Dioxide, Chlorite, Free Chlorine and Chloramines** (Section Da 7)

Da 5.1.1 10% *m/V Glycine solution*:
Dissolve 10 ± 0.5g of glycine in water and dilute to 100 ± 1 ml.

Da 5.1.2 5% *V/V Sulphuric acid*:
Pour 5 ± 0.5 ml of sulphuric acid (d_{20} 1.84) into water, cool and dilute to 100 ± 1 ml.

Da 5.1.3 5.5% *m/V Sodium bicarbonate solution*:
Dissolve 27.5 ± 0.5g of sodium bicarbonate in water and dilute to 500 ± 5 ml.

Da 5.1.4 4% *m/V Disodium EDTA solution*:
Dissolve 4 ± 0.5g of disodium ethylenediaminetetraacetate dihydrate in 100 ± 1 ml of water.

Note: The iron contributed to the sample by the addition of the FAS titrant 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 EDTA is required with the DPD reagents, with a supplementary thiocetamide procedure for higher levels of over approximately 2 mg/l ClO_2 measured as available chlorine. Additional EDTA is not required in the colorimetric procedures.

Da 5.1.5 10% *m/V Sodium nitrite solution*:
Dissolve 10 ± 0.5g of sodium nitrite in 100 ± 1 ml of water.

Da 5.2 **For the Determination of Bromine, Free Chlorine and Chloramines** (Section Da 8)

Da 5.2.1 *Glycine solution*: as above (see Da 5.1.1)

Da 5.2.2 *Sodium nitrite solution*: as above (see Da 5.1.5)

Da 5.3 **For the Determination of Iodine, Free Chlorine and Chloramines** (Section Da 9)

Da 5.3.1 *Glycine solution*: as above (see Da 5.1.1)

Da 5.3.2 0.5% *m/V Mercuric chloride solution*
Dissolve 0.5 ± 0.05g of mercuric chloride in water and dilute to 100 ± 1 ml.

Da 5.4 **For the determination of Ozone, Free Chlorine and Chloramines** (Section Da 10)

Da 5.4.1 *Glycine solution*: as above. (See Da 5.1.1)

Da 6 Apparatus and Reagent Quantities

The general recommendations with regard to apparatus, dilution of sample where total concentrations exceed 5 mg/l in terms of available chlorine and rinsing of glassware between determinations are as given for the DPD free chlorine-chloramines procedure (Method C, but for specifications see section B6).

Da 7 Procedure for Chlorine Dioxide, Chlorite, Free Chlorine and Chloramine Mixtures

Note 1: *Bromine Interference* The presence of bromides in waters may result in the formation of free bromine which interferes in the determination of chlorine dioxide. A tentative method allowing for this interference is given in Da 7.6.

Note 2: *Presence of Chlorite* Unless prior experience indicates that chlorite will be absent, it is safest to assume it to be present in waters treated with chlorine dioxide.

Step	Procedure	Notes
	Chlorine Dioxide	
Da 7.1	Place 2.0 ± 0.05 ml glycine solution in a 250-ml conical flask. Using a measuring cylinder add carefully 100 ± 0.5 ml of sample and mix. (Note a). In a second flask place 5.0 ± 0.05 ml DPD solution (Ca 4.2), 5.0 ± 0.05 ml buffer solution (Ca 4.3) and 5.0 ± 0.05 ml disodium EDTA solution and mix (note a). Carefully add the contents of the first flask, mix and titrate immediately with FAS solution until the colour is discharged (reading G) (note b).	(a) Dilution of the sample may sometimes be necessary to keep the titration within burette capacity. If this is required, the volume of sample should be correspondingly less than 100 ml and the volume taken should be made up with chlorine-free water which should be added to the reagents in the second flask before adding the glycine-treated sample. If the combined DPD-buffer powder (Ca 4.3.1) 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 EDTA solution. (b) If appreciable colour driftback occurs after the end point (see note under Section Da 5.1) repeat step Da 7.1 but add 0.5 ± 0.05 ml thiocetamide solution immediately after mixing the sample with the other reagents and before titrating with FAS until the colour is discharged (reading G_1). The reading G of Da 7.1 then becomes G_2. If chlorine and chloramines are known to be absent, see Section Da 7.4 Table 1 note d and Section Da 7.5.

Step	Procedure	Notes
	Free chlorine and chloramines	
Da 7.2	(Note c) Using a second 100.0 ± 0.5 ml sample follow the procedure given in the DPD method for free chlorine and chloramines steps Ca 7.1 to Ca 7.3 (note, the alternative procedures given in steps Ca 7.4 and 7.5 are also applicable), but add 5.0 ± 0.05 ml disodium EDTA solution along with the DPD and buffer solutions, (readings A, B and C) (note d).	(c) Chlorine dioxide does not itself react with ammonia to form chloramines; but such compounds may arise in practice, however, from the excess chlorine associated with the on-site generation of chlorine dioxide.
	Total available chlorine including chlorite (note d)	
Da 7.3	After obtaining reading C add 1.0 ± 0.05 ml sulphuric acid to the same 100 ml sample in the titration flask. Mix and set aside for two minutes. Then add 5.00 ± 0.05 ml sodium bicarbonate solution. Mix and continue the titration further to a total reading D.	(d) If any difficulty still remains with the reading C end point, add 0.5 ± 0.05 ml of thioacetamide solution immediately after mixing in the potassium iodide and mix again before continuing the titration to this end point. In that event the total chlorine procedure must be carried out by adding a fourth 100.0 ± 0.5 ml portion of the sample to a flask containing the DPD reagents and mixing before adding the potassium iodide, acid and, two minutes later, the bicarbonate.

Da 7.4 **Calculations**

For a 100 ml sample 1.0 ml standard FAS solution is equivalent to 1.0 mg/l available chlorine. (See Ca 4.6.1.5).

Table 1 may be used for calculating the concentrations of individual components, unless thioacetamide has been used in which case see Table 2.
A, B, C, D, G, G_1 and G_2 are defined in Steps Da 7.1-7.3 inclusive, including note b therein.

Table 1 Normal calculations (Thioacetamide procedure not used) (note g)

Determination	Reading	
	(Chlorite absent)	(Chlorite present)
Chlorine dioxide (notes a, b and e)	5G	5G
Chlorite (notes a, d, e and f)	–	D – C – 4G
Free chlorine	A – G	A – G
Monochloramine (note c)	B – A	B – A
Dichloramine (note c)	C – B	C – B
Total available chlorine (note a)	C + 4G	D

Notes

(a) If oxidized manganese is present determine the correction as in step Ca 7.7 and apply to the determinations as follows:
chlorine dioxide – deduct correction from reading G
chlorite – deduct correction from reading G
total available chlorine – deduct correction from readings C, G and D.

(b) To obtain chlorine dioxide in terms of ClO_2 multiply G by 1.9 instead of 5.

(c) If the step leading to reading B is omitted, monochloramine and dichloramine are obtained together as combined chlorine = C – A.

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

(e) Under treatment conditions where chlorine and chloramines may be assumed absent the use of glycine is unnecessary since reading A then equals reading G, thus chlorine dioxide = 5A mg/l as Cl_2 or 1.9A if required in terms of ClO_2, and chlorite equals D-5A as Cl_2.

(f) All chlorite results as calculated above in terms of Cl_2 may be converted to mg/l ClO_2^- by multiplying by 0.48.

(g) If the raw water contained bromide see also Section Da 7.6.

Table 2 Modified Calculations Where Thioacetamide Procedure Required (note c)

Reading	Reading	
	(Chlorite absent) (note b)	(Chlorite present)
Chlorine dioxide (note a)	$5G_1$	$5G_1$
Chlorite (note a)	–	$D–C–5G_1+G_2$
Free chlorine	$A–G_2$	$A–G_2$
Monochloramine	B–A	B–A
Dichloramine	C–B	C–B
Total available chlorine (note a)	$C+5G_1–G_2$	D

Notes

(a) If oxidized manganese is present determine the correction as in step Ca 7.7 and apply to the determinations as follows:

chlorine dioxide – deduct correction from reading G_1
chlorite – deduct correction from readings G_1 and G_2
total available chlorine – deduct correction from readings G_1 and D

(b) Unless chlorite is known to be absent, it is safest to assume it is present.

(c) If the raw water contained bromide see also Section Da 7.6.

Da 7.5 **Simplified Thioacetamide Procedure when Chlorine and Chloramines are absent**

Obtain reading A as in steps Ca 7.1, but add 0.5 ± 0.05 ml of thioacetamide solution immediately after the sample has been mixed with the DPD and buffer solutions and before titration with FAS solution. Then take a second 100 ml sample into a flask containing 5.0 ± 0.05 ml of DPD indicator solution and 5.0 ± 0.05 ml of buffer solution, mix and add 1.0 ± 0.1g of potassium iodide. Then proceed as in step Da 7.3 by adding sulphuric acid and, two minutes later, sodium bicarbonate to obtain reading D. This simplified procedure may be used as a general method for all levels of chlorine dioxide and chlorite up to the maximum of the normal available chlorine range of the DPD method, that is without dilution of sample.

Chlorine dioxide = 5A
Chlorite = D–5A

These results are in mg/l available chlorine. For conversion factors to ClO_2 and ClO_2^- see step Da 7.4 Table 1 notes (b) and (f) respectively.

Da 7.6 **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 residuals may be carried out by an additional procedure given below, using sodium nitrite as a supplementary reagent[30].

This tentative method 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.

To determine this residual bromine, repeat step Da 7.1, but add 0.50 ± 0.05 ml of sodium nitrite solution to the 100 ml of sample immediately after the initial mixing with the added glycine. Mix again, then continue with the other reagents as specified and the FAS titration, (reading BR).

Having obtained reading BR the calculations in Tables 1 and 2 of step Da 7.4 require correction as follows:–

Subtract the BR reading from the G, G_1 and G_2 readings 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 reading D the residual bromine (as mg/1 Cl_2) will be included.

Da 8 Procedure for Bromine (Including Bromamines) and Mixtures with Free Chlorine and Chloramine

Note: See step Da 8.5 for a tentative procedure for the separate determination of bromine and bromamines

Step	Procedure	Notes
	Bromine (including bromamines)	
Da 8.1	(In the absence of free chlorine and chloramines). Using 100 ± 0.05 ml sample follow the procedure in step Ca 7.1 of the DPD method for free chlorine-chloramines (reading BR).	
	Bromine (including bromamines)	
Da 8.2	(In the presence of free chlorine and chloramines). Place 2.0 ± 0.5 ml glycine solution in a 250 ml-conical flask Using a measuring cylinder add carefully 100 ± 0.5 ml of sample and mix (note a).	(a) If dilution is required follow the procedure of step Da 7.1 note a.
	In the second flask place 5.0 ± 0.05 ml DPD solution and 5.0 ± 0.05 ml buffer solution and mix (note b). Add the contents of the first flask, mix and titrate with FAS solution until the colour is discharged (reading BR).	(b) If DPD powder is used, and sample dilution is not necessary, this may be added direct to the glycine-treated sample in the first flask.
	Free chlorine and chloramines	
Da 8.3	Using a second 100.0 ± 0.05 ml sample follow the procedures of the DPD free chlorine-chloramines method step Ca 7.1 to Ca 7.3 or Ca 7.4 or Ca 7.5 (readings A, B and C).	

Da 8.4 Calculations

For a 100 ml sample, 1.0 ml standard FAS solution is equivalent to 1.0 mg/l available chlorine. (See Ca 4.6.1.5).

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 Da 8.1–8.3 inclusive.

Determination	Reading
Bromine (plus bromamines) (notes a and b)	BR
Free chlorine	A – BR
Monochloramine (note c)	B – A
Dichloramine (note c)	C – B

Notes

(a) If oxidized manganese is present determine the correction as in step Ca 7.7 and apply to the determinations as follows:

bromine (plus bromamines) – deduct correction from reading BR

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

(c) If the step leading to reading B is omitted monochloramine and dichloramine are obtained together as combined chlorine = C – A.

Da 8.5 **Tentative 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[30].

Repeat step Da 8.1 but first add 0.5 ± 0.05 ml of sodium nitrite solution to the 100 ml of sample and mix. The result obtained corresponds to bromamines (reading BRA), the following additional calculations then apply to those given in the table in step Da 8.4:

Free bromine = BR – BRA
Bromamines = BRA

Da 9 Procedure for Iodine and Mixtures with Free Chlorine and Chloramine

Step	Procedure	Notes
Da 9.1	Iodine *In the absence of free chlorine and chloramines.* Using a 100 ± 0.05 ml sample follow the procedure in step Ca 7.1 of the DPD method for free chlorine and chloramines to obtain reading I.	
Da 9.2	Iodine *In the presence of free chlorine and chloramines.* Place 2.0 ± 0.05 ml glycine solution and about 10 drops (0.5 ml) mercuric chloride solution in a 250 ml conical flask. Using a measuring cylinder carefully add 100 ± 0.5 ml of sample and mix (note a). In a second flask place 5.0 ± 0.05 ml of DPD solution and 5.0 ± 0.05 ml of buffer solution (note b). Add the contents of the first flask, mix and titrate with FAS solution until the colour is discharged (reading I).	(a) If dilution is required follow the procedure of step Da 7.1 note a. (b) If DPD powder is used, and sample dilution is not necessary, the powder may be added directly to the glycine-treated sample in the first flask.

Step	Procedure	Notes
	Free chlorine and chloramines	
Da 9.3	Using a second 100.0 ± 0.05 ml sample follow the procedures given in the DPD free chlorine-chloramines method, steps Ca 7.1 to 7.3 or 7.4 or 7.5 with the addition of about 10 drops (0.5ml) or mercuric chloride solution at the start with the DPD and buffer solutions.	

Da 9.4 **Calculations**

For a 100 ml sample 1.0 ml standard FAS solution is equivalent to 1.0 mg/l available chlorine. (See Ca 4.6.1.5).

In the absence of free chlorine and chloramines reading 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.
A, B, C and I are defined in steps Da 9.1–9.3 inclusive.

Determination	Reading
Iodine (notes a and b)	I
Free chlorine	A – I
Monochloramine (note c)	B – A
Dichloramine (note c)	C – B

Notes

(a) If oxidized manganese is present determine the correction as in step Ca 7.7 and apply to the determinations as follows:
iodine – deduct correction from reading I

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

(c) If the step leading to reading B is omitted, monochloramine and dichloramine are obtained together as combined chlorine = C – A

Da 10 Procedure for Ozone and Mixtures with Free Chlorine and Chloramine

Step	Procedure	Notes
	Ozone *(In the absence of free chlorine and chloramines).*	(a) Alternatively, commercially available DPD powder reagents may be used.
Da10.1	Place 5.0 ± 0.05 ml of DPD solution, 5.0 ± 0.05 of buffer solution and about 0.5g of potassium iodide in a 250 ml-conical flask (note a). Using a measuring cylinder carefully add 100 ± 0.5 ml of sample and mix. Titrate immediately with FAS until the colour is discharged (reading O).	

Ozone plus total available chlorine

Da10.2 (In the presence of free chlorine and/or chloramines.) The procedure of step Da 10.1 above now gives ozone plus total available chlorine i.e. free chlorine plus chloramines (reading OTC).

Total available chlorine (note b)

Da10.3 Place 2.0 ± 0.05 ml of glycine solution in a 250 ml-conical flask. Using a measuring cylinder carefully add 100 ± 0.5 ml of sample and mix (note b). In a second flask place 5.0 ± 0.05 ml of DPD solution, 5.0 ± 0.5 ml of buffer solution and about 0.5g of potassium iodide (note c). Add the contents of the first flask to the second, mix and titrate immediately with FAS solution (reading TC).

(b) If dilution is required follow the procedure of Ca 7.1 note a.

(c) If DPD powder (or powder and KI mixture) is used, and sample dilution is not necessary, the powder may be added direct to the glycine-treated sample in the first flask.

Free chlorine (note d)

Da10.4 Place 5.0 ± 0.05 ml of DPD solution and 5.0 ± 0.05 ml of buffer solution in a 250-ml conical flask. Carefully add 100 ± 0.5 ml of sample and mix. Titrate immediately with FAS solution. (Reading A – note e).

(d) Steps 10.4 and 10.5 are necessary if separation of total available chlorine into free chlorine and combined chlorine, ie. monochloramine plus dichloramine, is required.

(e) Reading A includes a proportion of the ozone. The same proportion is included in subsequent reading C.

Combined chlorine *(ie. monochloramine plus dichloramine* (note d)

Da10.5 After obtaining reading A add about 0.5g potassium iodide to the same 100 ml sample in the titration flask, mix and immediately continue the titration to a total reading C.

Da 10.6 **Calculations**

For a 100 ml sample, 1.0 ml standard FAS solution is equivalent to 1.0 mg/l available chlorine (see Ca 4.6.1.5).

In the absence of free chlorine and chloramines reading 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	Reading
Ozone (notes a and b)	OTC – TC
Total available chlorine (note a)	TC
Free chlorine (note a)	TC – C + A
Combined chlorine	C – A

O, OTC, TC, A and C are defined in steps Da 10.1-10.5 inclusive.

Notes

(a) If oxidized manganese is present determine the correction as in step Ca 7.7 and apply to the determinations as follows:

ozone – deduct correction from reading O
total available chlorine – deduct correction from reading TC
free chlorine – deduct correction from reading TC

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

Da 11 Procedure for Chloroisocyanurates, Free Chlorine and Chloramine Mixtures

Step	Procedure	Notes
	Free and reserve chlorine	
Da11.1	Follow the procedure of the DPD free chlorine-chloramine method (Ca 7.1) to obtain reading A (note a).	(a) This reading includes the free chlorine present in the water plus that available as reserve in the chloroisocyanurates.
	Monochloramine and dichloramine	
Da11.2	Continue on the same 100 ml sample with the DPD method Ca 7.2 and 7.3 to obtain readings B and C (note b)	(b) If dilution of sample is required follow the procedure of Ca 7.1 note a.

Da 11.3 **Calculations**

For a 100 ml sample 1.0 ml of standard FAS solution is equivalent to 1.0 mg/l available chlorine. (see Ca 4.6.1.5)

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

Determination	Reading
Free and reserve chlorine (notes a and b)	A
Monochloramine (note c)	B – A
Dichloramine (note c)	C – B

A, B and C are defined in steps Da 11.1 and 11.2.

Notes

(a) If oxidized manganese is present determine the correction as in step Ca 7.7 and apply to the determination as follows:

free and reserve chlorine – deduct correction from reading A

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

(c) If the step leading to reading B is omitted monochloramine and dichloramine are obtained together as combined chlorine (C – A).

Db Spectrophotometric, Colour Comparison and Field Test Procedure

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 EDTA as specified for the corresponding titrimetric method.

Calibration of spectrophotometers is as given under the DPD method for free chlorine and chloramines (Cb 6.0 – 6.4). Appropriate volume correction factors should be applied when using the supplementary reagents as given in Section Da 5.1.

The reagents required for chlorine species estimations as in Part Cc 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 obviates the need for volume correction factors.

Colour comparison methods against permanent glass standards are commonly used in the laboratory and field. 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.

For further information see reference 5, 25, 26 and 27.

E Determination of Chlorine Demand

E 1 Introduction

In the application of chlorine or other disinfecting agent to water it is important to ensure that sufficient 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 or combined, 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 must, 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 the actual dose applied, the time of contact, the pH value and the water temperature. Hence, when determining the chlorine demand of a raw water ie the difference between the applied chlorine dose and the residual chlorine, these factors must be specified. In addition, it is necessary to state the terms in which the residual is expressed, namely, free, combined or total 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

E 2 Principle

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

E 3 Hazards

Appropriate precautions should be taken when handling strong chlorine solutions.

E 4 Reagents

The following reagent is required in addition to those previously given for the iodometric method (Part B) for total chlorine and the DPD method (Part C) for free chlorine, combined chlorine and total chlorine.

E 4.1 Standard chlorine solution

The chlorine water may be obtained from the plant chlorinator solution pipe or by bubbling chlorine gas through distilled water. 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 Cl_2 so that 1 ml added to 250 ml sample gives a dose of about 1 mg/l Cl_2. Should the dosage range to be covered extend beyond 5 mg/l, a stronger solution should be used. Chlorine solutions should be used immediately after standardization. (see step E5.2).

E5 Procedure

Step	Procedure	Notes
	Standardization of sodium thiosulphate 0.0125 M	
E 5.1	Carry out steps B 8.1 and B 8.2. (notes a, b and c).	Notes a, b and c as in Section B 8
	Standardization of chlorine solution	
E 5.2	Add 0.5 ± 0.1 g potassium iodide crystals and 5 ± 1 ml acetic acid to a 250-ml conical flask. Measure into the flask 25 ± 0.5 ml of chlorine solution, or other suitable volume, and mix by gentle swirling. Titrate in accordance with step B 8.4. (note d)	(d) When applying the calculation step B9, correct for the difference in sample size. Multiply the result from B9 by 500 and divide by the volume (in ml) of chlorine solution taken in step E5.2.
	Preparation of sample	
E 5.3	Measure 10 (or other appropriate number) 250 ± 2 ml portions of the sample into brown glass-stoppered bottles or open flasks, whichever more closely matches plant conditions. The bottles or flasks should be of sufficient size to permit mixing.	
	Addition of chlorine solution	
E 5.4	To cover the required dosage range add the appropriate amounts of chlorine solution in increasing amounts to successive portions of sample in the series. Mix gently but thoroughly while adding. To allow time for the residual determinations to be carried out after the predetermined 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.	
	Examination of sample	
E 5.5	At the end of the appropriate contact period, which may well be the same as that in the treatment plant, each portion of sample is examined by the DPD method for free chlorine and combined chlorine (see part C). The type and the amount of residual chlorine found are recorded.	
	Determination of chlorine demand	
E 5.6	It is convenient to prepare a curve by plotting chlorine dose against chlorine residual. The chlorine demand is the difference between dose and residual at any selected point on the curve. At least the following conditions must be specified: dose, amount and nature of residual, contact time. In addition a note of pH value and temperature should be made.	

F Analytical Quality Control

For work requiring high accuracy, the following guidance may prove helpful.

F 1 Dilution Water Quality

Water used for dilution in the method should be chlorine and chlorine-demand free. For work of the highest accuracy special steps must be taken to ensure that this is the case. Water of the required purity may be obtained by passing distilled water through a mixed-bed ion exchange resin, chlorinating to a level of about 10 mg/l and storing in a well-stoppered carboy for a minimum of sixteen hours. The water is then dechlorinated by exposing it to ultra-violet irradiation for at least half an hour or to sunlight for several hours. This water should then be suitable for use as dilution water in the method. If desired, it may be checked for quality by carrying a sample of water through step Ca 7.1 and noting the absence of the typical chlorine produced colour, and by adding one drop of chlorine water to a second sample as in section E and then repeating step Ca 7.1 to show that chlorine is now present, thus showing the water to be free from chlorine demand. If greater sensitivity is required a more dilute chlorine solution than given in section E may be used.

F 2 Glassware

Chlorine-demand free glassware can be ensured by storing 10 mg/l chlorine solution in the required glassware overnight and thoroughly rinsing before use with dilution water prepared as in Section F 1.

F 3 Checking the Accuracy of Analytical Results

Once the method has been put into normal routine operation many factors may subsequently adversely affect the accuracy of the analytical results. It is recommended that experimental tests to check certain sources of inaccuracy should be made regularly. Many types of test are possible and should be used as appropriate. As a minimum, however, it is suggested that in the case of the iodometric method a standard solution of potassium iodate of suitable concentration should be analysed at the same time and in exactly the same way as normal samples. The DPD methods should be similarly checked using freshly prepared standardized solutions of potassium permanganate. The results obtained should then be plotted on a quality control chart which will facilitate detection of inadequate accuracy, and will also allow the standard deviation of routine analytical results to be estimated. It must, however, be pointed out that if losses are occurring in handling chlorine solutions, such losses will not be detected by these means. Consideration should also be given, therefore, to the use of hypochlorite solutions for periodic checks.

G Appendix of Independent Test Data

Extra independent test data made available to the panel have already been mentioned with references. Other additional references to test data are given in refs 1,32 and 33.

The results presented in Tables 1, 2, 3 and 4 of this appendix were produced using the DPD titrimetric methods given in this booklet, for the Institute Belge de Normalization, secretariat of ISO Technical Committee 147 Sub-Committee 2, Working Group 16, whose permission for publication here is gratefully acknowledged.

Where a blank appears in the columns of the tables the result obtained was less than 0.03 mg/l. A dash indicates that the particular determination was not performed or was not given.

In their report it was stated that when using chlorine-free and chlorine-demand-free water the recovery of added amounts of free chlorine and monochloramine was better than 97% with good precision, although there was inevitably some uncertainty as to whether added dichloramine and nitrogen trichloride did in fact consist exclusively of the compounds as prepared. Nevertheless more than 90% of the chlorine introduced in these forms was recovered in the DPD determinations.

Table 1 Analysis of Chlorine-Chloramine Mixtures (Samples at about pH4)

Chlorine forms added (as mg/l Cl_2)				Chlorine forms found (as mg/l Cl_2)				Total recovered	
Cl_2	NH_2Cl	$NHCl_2$	NCl_3	Cl_2	NH_2Cl	$NHCl_2$	NCl_3	mg/l	%
0.2				0.20				0.20	100
1.0				1.00				1.00	100
2.0				2.00				2.00	100
4.0				4.06				4.06	102
	0.2				0.20			0.20	100
	1.0				1.00			1.00	100
	2.0				2.00			2.00	100
	4.0				3.96			3.96	99
		0.66				0.57	0.06	0.63	95
		3.3			0.03	3.15	0.06	3.24	98
			1.1	0.06			1.04	1.10	100
			4.3	0.15			4.10	4.25	99
0.2	0.2			0.20	0.20			0.40	100
2.0	1.0			2.00	1.00			3.00	100
		0.66	1.1	0.06		0.55	1.08	1.69	96
0.2			1.5	–	–	–	–	1.70	100

Table 2 Analysis of Chlorine-Chloramine Mixtures (Samples at about pH7)

Chlorine forms added (as mg/l Cl_2)				Chlorine forms found (as mg/l Cl_2)				Total recovered	
Cl_2	NH_2Cl	$NHCl_2$	NCl_3	Cl_2	NH_2Cl	$NHCl_2$	NCl_3	mg/l	%
0.2				0.20				0.20	100
1.0				1.00				1.00	100
2.0				1.98				1.98	99
4.0				3.96	0.03			3.99	100
	0.2				0.20			0.20	100
	1.0				1.00			1.00	100
	2.0				1.95			1.95	98
	4.0				3.93			3.93	98
		0.7		0.03		0.54	0.06	0.63	90
		3.4		0.15	0.09	2.76	0.24	3.24	95
			1.0	0.06		0.03	0.84	0.93	93
			3.8	0.12	0.03	0.09	3.50	3.74	98
0.2	0.2			0.20	0.20			0.40	100
2.0	1.0			1.98	0.97			2.95	98
		3.4	1.0	0.20	0.04	2.90	1.08	4.22	96
0.2			1.5	–	–	–	–	1.70	100

Table 3 Analysis of Chlorine-Chloramine Mixtures (samples at about pH10)

Chlorine forms added (as mg/l Cl_2)				Chlorine forms found (as mg/l Cl_2)				Total recovered	
Cl_2	NH_2Cl	$NHCl_2$	NCl_3	Cl_2	NH_2Cl	$NHCl_2$	NCl_3	mg/l	%
0.2				0.20				0.20	100
1.0				1.00				1.00	100
2.0				1.98				1.98	99
4.0				4.02				4.02	100
	0.2				0.20			0.20	100
	1.0				1.00			1.00	100
	2.0				2.00			2.00	100
	4.0				4.05			4.05	101
		0.66				0.60	0.06	0.66	100
		3.3				3.19	0.12	3.31	100
			1.1	0.05		0.02	1.00	1.07	97
			4.3	0.18		0.05	3.94	4.17	97
0.2	0.2			0.20	0.20			0.40	100
2.0	1.0			2.00	1.05			3.05	102
		0.66	1.1	0.06		0.57	1.04	1.67	100
0.2			1.5	–	–	–	–	1.68	99

Table 4 Analysis of Some Other Disinfectants

Substances added (expressed as mg/l Cl_2)									Substance found (expressed as mg/l Cl_2)							Total recovered	
Cl_2	NH_2Cl	$NHCl_2$	NCl_3	Br_2	$NHBr_2$	I_2	ClO_2	$NaClO_2$	Cl_2	NH_2Cl	$NHCl_2$	NCl_3	Br_2+ $NHBr_2$+I_2	ClO_2	$NaClO_2$	mg/l	%
1.30									1.30							1.30	100
	1.00									1.00						1.00	100
		0.55									0.49	0.06				0.55	100
			1.50								0.10	1.40				1.50	100
				1.00									1.00			1.00	100
					1.25				0.05				1.20			1.25	100
						1.00							1.00			1.00	100
							1.05	0.05						1.00	0.08	1.08	98
								1.00							0.92	0.92	92
0.20			1.50					1.00	0.20		0.10	1.40			0.95	2.65	98
	1.00	0.55				1.00				1.00	0.45	0.10	1.00			2.55	100
			1.50		1.25			1.00			0.10	1.40	1.25		1.00	3.75	100
0.20							1.05	0.05	0.20					1.00	0.10	1.30	100
				1.15			1.05	0.05					1.15	1.00	0.10	2.25	100
	1.00						1.05	0.05		1.00				1.00	0.10	2.10	100
			1.50				1.05	0.05			0.10	1.50		1.00	0.05	2.65	102
0.20									<0.03	–	–	–	–			Tests using	
4.0									<0.03	–	–	–	–			glycine	
				1.0					<0.03	–	–	–	1.03			solution	
2.0				1.0					<0.03	–	–	–	1.00				

H References

(1) White, G. C. *Handbook of Chlorination*, Van Nostrand Reinhold Co, 1972.

(2) Palin A. T., Water Services 1974, **78,** 7 and 53.

(3) Palin A. T., J.Am. Water Wks. Ass. 1957, **49,** 873.

(4) Palin A. T., J.Inst Water Eng. 1967, **21,** 537.

(5) Palin A. T., J.Inst Water Eng. 1974, **28,** 139.

(6) Nicolson, N. J., Water Res. Ass. Tech. Rep. 29 (1963).

(7) Nicolson N. J., Water Res. Ass. Tech. Rep. 47 (1965).

(8) Nicolson N. J., Water Res. Ass. Tech. Rep. 53 (1966).

(9) Wei W. I. & Morris J. C., *Chemistry of Water Supply, Treatment & Distribution*, Ann Arbor Sci. Pub. Inc. USA. 1973.

(10) Saunier, B., Ph.D. Thesis, University of California, Berkeley, USA May 1976. Personal communication, 21st September 1978.

(11) Analytical Reference Service, EPA Cincinnati, Study No. 35 (1969).

(12) Analytical Reference Service, EPA Cincinnati, Study No. 40 (1971).

(13) *Standard Methods for the Examination of Water and Wastewater*, APHA, AWWA & WPCF, Washington D.C. 14th Edn. 1975.

(14) USA Environmental Protection Agency, National Primary Drinking Water Regulation 1975.

(15) Mitteilungen aus dem Bundesgesundheitsamt (29.4.77) 20 No. 9 2 Mitteilung Part 2.4 Bestimmung der Chlorzehrung.

(16) Strupler, N., J. Français d'Hydrologie, 1978, **9,** 19.

(17) Palin A. T., Proc. Soc. Water Treatment and Examination 1967. **16,** 127

(18) Strupler N., Proc. 6th Water Quality Technology Conference, AWWA. Dec. 1978.

(19) Cooper W. J., Sorber C. A. & Meier E. P. J.Am. Water Wks. Ass. 1975. **67.** 34.

(20) Palin A. T., J.Am. Water Wks. Assn. 1975, **67,** 206.

(21) Lieberman J., Meier E. P., Cooper W. J. & Roscher N. M., Am. Chem. Soc. Symposium on Disinfection, Mar. 1978.

(22) Palin A. T., J.Inst. Water Engrs. & Scientists, 1978, **32,** 327.

(23) Metropolitan Water Board, 29th Annual Report 1934, p.62.

(24) Nicolson, N. J., Analyst 1964, **90,** 187.

(25) Palin A. T., J.Am. Water Wks. Ass. 1975, **67,** 32.

(26) *Simple Tablet Tests for Water Analysis and Treatment Control*, Wilkinson & Simpson Ltd., Gateshead, Tyne and Wear, England.

(27) Thomas L. C. & Chamberlin G. J. *Colorimetric Chemical Analytical Methods*. 9th Edn. 1980. The Tintometer Ltd., Salisbury, England.

(28) Palin A. T., Water & Sewage Wks. 1960, **107,** 457.

(29) Palin A. T. & Darrall K. G., J. Inst. Water Engrs. & Scientists, 1979, **33,** 467.

(30) Palin A. T., J. Inst. Water Engrs. & Scientists, 1980, 34, 383.

(31) British Standard 846.

(32) White G. C., *Disinfection of Wastewater and Water for Reuse*, Van Nostrand Reinhold Co, 1978.

(32a) Table 2.4 in the above.

(33) Strupler N. and Rouault J., J. Français d'Hydrologie. 1979, **10,** 113.

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