Chloride in Waters, Sewage and Effluents 1981

Methods for the Examination of Waters and Associated Materials

London Her Majesty's Stationery Office £3.80 net

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Methods for the Examination of Waters and Associated Materials

This booklet contains four full methods (one of them tentative) and notes on three more. Throughout this booklet, chloride is expressed as the ion Cl^-.

Contents

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Warning to users

The analytical procedures given in this booklet should only be carried out by competent trained persons, with adequate supervision when necessary. Local Safety Regulations must be observed. Laboratory procedures should be carried out only in properly equipped laboratories. Field operations should be conducted with due regard to possible local hazards, and portable safety equipment should be carried. Care should be taken against creating hazards. 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 specifications. Specifications for reagents, apparatus and equipment are given in manufacturers' catalogues and various published standards. If contamination is suspected, reagent purity should be checked before use.

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

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

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

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About this series

This booklet is part of a series intended to provide recommended methods for the determination of water quality. In addition the series contains short reviews of the more important analytical techniques of interest to the water and sewage industries. In the past, the Department of the Environment and its predecessors, in collaboration with various learned societies, have issued volumes of methods for the analysis of water and sewage culminating in 'Analysis of Raw, Potable and Waste Waters'. These volumes inevitably took some years to prepare, so that they were often partially out of date before they appeared in print. The present series will be published as 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 the attention of the user is drawn to any special known hazards which may occur with the use of any particular method, responsibility for proper supervision and the provision of safe working conditions must remain with the user.

The preparation of this series and its continuous revision is the responsibility of the Standing Committee of Analysts (to review Standard Methods for Quality Control of the Water Cycle). The Standing Committee of Analysts is 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 nonmetallic 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.

Whilst an effort is made to prevent errors from occurring in the published text, a few errors have been found in booklets in this series. Correction notes for booklets in this series are given in the Reports of The Standing Committee of Analysts, published by the Department of the Environment but sold by the National Water Council, 1 Queen Anne's Gate, London SW1H 9BT. Should an error be found affecting the operation of a method, the true sense not being obvious, or an error in the printed text be discovered prior to sale, a separate correction note will be issued for inclusion in the booklet.

* These two working groups are in process of being wound up. Their tasks are being redistributed among the other Working Groups.

T A DICK
Chairman

L R PITTWELL
Secretary

25 September 1981

Choice of Method

There are many methods in use for chloride, each with its advantages and disadvantages. Hence a selection of four methods has been given and short notes have also been included on three other methods, which are useful for some samples. For many samples, the choice will be determined by the equipment available and the number of samples to be analysed.

Table 1 summarizes the information on choice of method.

Table 1 Summarized Information of Methods in this Booklet

Method	Interferences	Range[a]	Sample	Rate	Special Requirements
A. Silver nitrate titration with chromate (or alternative) indicators	Bromide, iodide and phosphate interfere. Sulphide, sulphite, thiocyanate, thiosulphate, simple and complex cyanides, lead, bismuth, barium, iron III, organic reducing agents, carbonate, ammonia, and some suspended matter and dark coloured solutions may also interfere but can usually be removed by procedures given in the method.	2–500 mg/l	Most waters and effluents	About 20/h	None
B. Mercuric nitrate titration with diphenylcarbazone indicator	Bromide, iodide. Chromate, iron III, all simple and complex cyanides, thiocyanate, thiosulphate, sulphide and ammonia.	5–1000 mg/l main method. A variant with a lower range is also given, see Section B14.	Clean waters and certain effluents, especially those containing phosphate.	About 20/h	None
C. Potentiometric titration with silver nitrate	Bromide, iodide, sulphide, sulphite, thiocyanate, thiosulphate, simple and complex cyanides, chromates, iron III, polyphosphates and large amounts of organic matter. Surfactants may interfere at low concentrations of chloride.	1–200 mg/l	Most waters and effluents, especially colourful and turbid samples	About 10/h	Electrodes and millivoltmeter
D. Automated mercuric-ferric thiocyanate colorimetry	Bromide, sulphide, thiocyanate, cyanides, including complex cyanides, nitrite, ammonia and non-ionic detergents.	4–200 mg/l	Most waters and effluents	60 per 100 minutes	An air segmented continuous flow automatic analyser
E. Chloride Ion Selective Electrode	Varies with electrode. All electrodes: bromide, iodide, solid electrodes: sulphide, thiosulphate, cyanides, ammonia, reducing agents, EDTA and some amines. Liquid electrodes: perchlorate, nitrate, sulphate.	0.1–350 mg/l	Clean and river waters – chiefly field use	Over 50/h	A suitable electrode and millivoltmeter
F. Silver Coulometry	Bromide, iodide, phosphate. Sulphide, sulphite, thiocyanate, thiosulphate, simple and complex cyanides, lead, bismuth, barium, iron/III, organic reducing agents, carbonate, ammonia, and some suspended matter and dark coloured solutions interfere but can usually be removed by procedures given in the method.	10–300 mg/l	Clean waters and effluents	About 10/h	A silver coulometer
G. Ion chromatography	Almost no interference.	<<1 mg/l upwards to saturation. Often down to microgram /l level	Clean waters and effluents	Very dependent on other anions present in sample	Ion chromatograph

Note (a) Ranges can often be adjusted by quantitative dilution or concentration by evaporation.

A. Silver Nitrate Titration with Chromate Indicator (Mohr's Method)

A1 Performance Characteristics of the Method (9)

A1.1	Substance determined	Soluble chloride.
A1.2	Type of sample	Most waters and effluents.
A1.3	Basis of method	Titration with standard silver nitrate, using potassium chromate indicator in approximately neutral solution.
A1.4	Range of application	Up to 250 mg/l Cl^- using a 25 ml burette and to 500 mg/l using a 50 ml burette. For low concentrations the potentiometric titration method, method C, is recommended.
A1.5	Standard deviation (a) (b)	See table below.
A1.6	Limit of detection (a)	2.0 mg/l Cl^-. (c)
A1.7	Bias	There is a slight positive bias which can be eliminated if an indicator blank or the double end point technique is used. (See Section A10 and 11).
A1.8	Interferences	Bromide, simple and complex cyanide, iodide, phosphate, sulphides, sulphite thiocyanate, thiosulphate, organic reducing agents and metals with insoluble chromates interfere. All except bromide and iodide can be overcome, see Section A3. Carbonate and ammonia may cause problems, but are easily removed, See Section A3.
A1.9	Time required for analysis	Twenty titrations per hour is a typical rate, excluding any pre-treatment procedures.

Chloride Concentration mg/l Cl^-	Total Standard Deviation mg/l Cl^-	Degrees of Freedom
20	0.39	9
50	0.45	
100	0.40	
200	0.36	

Note: (a) information supplied by the Colne Valley Water Company.
(b) synthetic samples made with sodium chloride.
(c) not determined in accordance with Ref 7; but estimated from the discriminatory interval of the method and the indicator blank for a coefficient of variation of 10%.

A2 Principle

Chloride is precipitated as silver chloride, in the presence of chromate ion. The red coloured silver chromate being more soluble is not precipitated permanently until virtually all the chloride has reacted. A pH of between 5.0 and 9.5, suitable for the precipitation of silver chromate, must be maintained throughout the titration. Procedures are given for the removal of the more common interferents (1) (2). An alternative indicator is also available when the use of chromate is unsuitable (A14).

A3 Interferences

A3.1 Iodide and bromide titrate as chloride – see Section A13.1.

A3.2 Phosphate titrates as chloride – see Section A13.2

A3.3 Simple and complex cyanides and thiocyanate titrate as chloride, but can be removed – see Section A13.4.

A3.4 Sulphide and hydrogen sulphide titrate as chloride and may decompose the chromate indicator, but can be removed – see Section A13.3.

A3.5 Sulphite and thiosulphate precipitate silver and react with the indicator, but the reactions are complex and vary with concentration. Organic reducing agents interfere by reducing silver ions to metal. All such substances can be removed – see Section A13.4.

A3.6 Carbonate may interfere, but is easily removed – see Section A13.7.

A3.7 Lead, bismuth, barium, iron and a few less common metals with insoluble chromates react with the indicator, but are either removable, or a different indicator may be used – see Sections A13.5 and A14.

A3.8 Highly coloured or turbid solutions may obscure the end point. A clarification procedure is given – see Section A13.6, and a potentiometric method is also included in the booklet (Method C).

A3.9 High concentrations of ammonia and similar compounds may cause problems by complexing the silver – see Section A13.8.

A4 Hazards

Silver salts temporarily stain the skin brown. They are toxic if swallowed in large amounts.
Chromate dust should not be inhaled as it damages the inner lining of the nose. Chromates are toxic if swallowed in large amounts.

A4.1 Hazards in interference removal

If certain interferences have to be removed, toxic gases may be liberated. Such operations must be carried out in a good fume cupboard.

Hydrogen peroxide solution causes temporary skin irritation which stops after a few minutes, which may be mistaken for more insidious irritation. Washing is recommended.

Strong ammonia solution is a caustic alkali with an irritant vapour which can blind if splashed into the eyes. Wear goggles when handling. Do not pipette by mouth or breath the fumes.

Hydrogen sulphide is highly toxic and can temporarily paralyse and alter the sense of smell, even causing the victim to go unwittingly to an area of high concentration. Only use with adequate ventilation. If the smell becomes strong (c20 ppm) and then fades but the eyes continue to itch (c30 ppm), turn off the supply and leave the room at once. If necessary use an oxygen apparatus for rescue or clean up. Unconscious victims require expert medical attention and oxygen. Rely on test papers (such as lead acetate paper) rather than smell when testing for re-entry.

A5 Reagents

Silver salts and their solutions are sensitive to light. They should be stored in dark brown glass bottles, preferably with glass stoppers.

Analytical reagent grade chemicals are preferred, and (except A5.3 and A6.2.2) should, if possible, be halide-free (see steps A10.2).

Both silver nitrate and sodium chloride, if pure, are primary standard substances. The accuracy of the method can be improved by checking standard solutions of one against the other in control analyses using this method or method C.

A5.1 **Water**

Distilled or deionized water is suitable. (50 ml of water in a 50 ml Nessler Cylinder should not give any opalescence when a few drops of silver nitrate solution (A5.2) followed by one drop of N/10 nitric acid (A5.6) are added to it. Alternatively the specific conductance should be below 20 μS/cm).

A5.2 **Silver nitrate solution** 1.0 ml is equivalent to 1.0 mg Cl^-

Dissolve 4.791 ± 0.001 g silver nitrate (dried at 105°C, in clean air) in water and dilute to 1 litre with water in a calibrated flask. Other strengths of silver nitrate are often used to accommodate chloride concentrations outside the range quoted above (Section A1.4). For such solutions a correction factor is needed in the calculation step below. One gram mole of silver nitrate (169.875 g) is equivalent to 35.453 g of chloride. If stored in the dark, this solution is stable indefinitely.

A5.3 **Sodium chloride solution 1.0 ml contains 1.0 mg Cl^-**
(needed only if the double end point technique is used (see Section A1.1)).

Dissolve 1.6484 ± 0.0005 g sodium chloride (dried to constant weight at 120–250°C) in approximately 200 ml of water, and dilute with water to 1 litre in a calibrated flask. Stored in a stoppered glass bottle, this solution is stable indefinitely.

A5.4 **Potassium chromate indicator**

Dissolve 5 ± 0.5 g of potassium chromate in 100 ± 5 ml of water. Add silver nitrate solution (A5.2) until a slight red precipitate forms, then filter. This solution is stable for at least a week.

A5.5 **Calcium carbonate powder.**

A5.6 **Nitric acid N/10 (approximate)**

Dilute 6.3 ± 0.2 ml nitric acid (d_{20} 1.42) to 1 litre with water in a measuring cylinder. Stored in a glass bottle, this solution is stable indefinitely.

Alternatively:

A5.6.1 *Sulphuric acid N/10 (approximate)*

Stir 2.8 ± 0.1 ml of sulphuric acid (d_{20} 1.84) into 1 litre ± 10 ml of cold water. Stored in a glass of plastic bottle, this solution is stable indefinitely.

A5.6.2 *Sulphuric acid 2N (approximate) needed for ammonia removal (Section A13.8).*

Stir 56 ± 1 ml of sulphuric acid (d_{20} 1.84) into 1 litre ± 10 ml of cold water. Stored in a glass or plastic bottle, this solution is stable indefinitely.

A5.7 **Phenolphthalein solution**

Dissolve 1 ± 0.1 g of phenolphthalein in 100 ± 5 ml of ethanol, and add 100 ± 5 ml of water; filter if necessary (other recipes given in the literature are equally suitable). Stored in a glass bottle, this solution is stable indefinitely.

A5.8 **Test papers** (optional)

A5.8.1 *For pH* indicating to at least 0.2 pH unit steps, (for step A9.1 and also A6.4.1)

A5.8.2 *Permanganate or dichromate paper* for detecting sulphur dioxide (for A13.4).

A6 Additional Reagents for the Removal of Interferences.

A.6.1 **For Sulphide Removal** (Section A13.3).

A6.1.1 *Zinc sulphate* – powdered.

A6.1.2 *Sodium hydroxide solution 2N (approximate)*

Dissolve 80 ± 1 g of sodium hydroxide in water and dilute with water to 1 litre in a measuring cylinder. Stored in a plastic bottle, this solution is stable for at least one year.

A6.2 **For oxidation of interfering substances** (reducing agents, see Section A13.4).

A6.2.1 *Hydrogen peroxide (10 volume)*

(Commercially available 3%). (If other strengths are available, adjust amount used accordingly). Store in a cool place.

A6.2.2 *Ferric chloride test solution*

Dissolve 13.5 ± 0.5 g of ferric chloride hexahydrate in 100 ± 10 ml of water to which 2 ± 0.2 ml of hydrochloric acid (d_{20} 1.18) has been added. Stored in a glass bottle, this solution is stable for at least one year.

A6.2.3 *Sodium carbonate (anhydrous).*

A6.2.4 *Nitric Acid (d_{20} 1.42).*

A6.3 **For Removal of Interfering Metals** (Section A13.5).

A6.3.1 *Ammonium acetate solution*

Dissolve 231 ± 2 g of ammonium acetate in 1 litre ± 10 ml of water. Stored in a glass or plastic bottle, this solution is stable for at least one year.

A6.3.2 *Ammonia solution (d_{20} 0.90 or 0.88)*

A6.3.3 *Hydrogen sulphide gas*

(If made from ferrous sulphide in a Kipp's Apparatus use sulphuric acid to generate, and wash the gas with water. If a cylinder is used as source of supply use an open beaker when bubbling through the sample).

A6.4 **For Adsorption of Colour, and Turbidity** (Section A13.6)

A6.4.1 *Aluminium hydroxide suspension*

Dissolve 100 ± 1 g of potassium aluminium sulphate dodecahydrate (alum) in 1 litre ± 50 ml of water. Slowly add ammonia solution (Solution A6.3.2 above, prediluted approximately 1 to 7 with water is suitable) with continuous stirring until there is no more precipitation, and the solution is slightly ammoniacal, or alternatively, until the pH is greater than 7.5. Allow the precipitate to settle and water wash by decantation until the washings are no longer ammoniacal, or alternatively until the pH is less than 7.2. Test a sample of the final decanted liquid for absence of chloride as in Section A5.1 above. If chloride is present either continue washing until chloride free, or start the preparation again after first testing the reagents used for absence of chloride. Dilute the washed suspension to about one litre with water. Shake well before use. (An equivalent amount of sodium or ammonium aluminium sulphate may be used instead of the potassium salt above, or hydrated aluminium sulphate may be substituted, though in this latter case, a small amount of sulphuric acid should be added to the water to speed solution). Store in a glass or plastic bottle with a screw cap. Replace after one week.

A6.5 **For Alternative Indicator Procedure** (Section A14)

A6.5.1 *2,7 – Dichlorofluorescein (or 4,5 – dibromofluorescein) 1% m/v solution in ethanol.*

Dissolve 0.10 ± 0.01 g of the indicator in 10.0 ± 0.5 ml of ethanol. Store in a glass stoppered dropping bottle. This solution can be used for as long as it continues to fluoresce in daylight.

A7 Apparatus

A7.1 Burettes

Grade B burettes and pipettes are usually of sufficient accuracy. If improved accuracy is required for the determination of chloride concentrations down to 2 mg/l, special burettes calibrated to 0.01 ml are available commercially. For such burettes, immersion of the tip in the sample solution is necessary.

A7.2 Cleanliness

All apparatus must be clean and rinsed with chloride-free water before use.

A8 Sample Collection and Preservation

This is dependent on the nature of the sample, but the sample bottles, made of glass or plastic, must be halide free. No preservative is needed for chloride itself. If prevention of decomposition of other components is necessary, hydrochloric acid, chlorides, and disinfectants containing halogens, mercury, or silver must not be used for preservation of the sample.

A9 Analytical Procedure

Step	Procedure	Notes
A9.1	If necessary, remove interferences (note a) (see Section A13). Check the pH to the nearest 0.5 pH units (note b). Use sufficient sample for multiple aliquots to be taken at step A9.3. At least 500 ml is suggested.	(a) Whether interferences are removed prior to taking the sample aliquot (at step A9.1) or after (at step A9.3) is a matter of convenience. If removal is necessary and made at the start, a known volume should be taken and the volume either readjusted to the same volume or correction made for the volume change in the calculation. Consider also step A9.5 and note f.
		(b) pH papers suitable for this test are available. If a pH meter is used, the reference electrode filling solution should not contain chloride (eg. calomel electrode).
A9.2	If necessary, filter the sample (note c).	(c) As sludges and suspended solids can contain chlorides, if total chloride is required, it will be necessary to dissolve such solids and either add to the sample, or analyse separately. The nature of the sample will determine the best method of solution.
A9.3	Pipette 100.0 ± 0.2 ml of sample (or filtrate) into either a white porcelain basin or a 500 ml conical flask or beaker. If a flask or beaker are preferred there should be a white surface underneath (note d). If the pH value is between 5.0 and 9.5 omit steps A9.4 and A9.5. If the sample too highly coloured to see the end point see Section A13.6. Removal of other interferences may also be made at this point (see notes a and f). If the pH value is below 5.0 include step A9.4. If the pH value is above 9.5 include step A9.5.	(d) A white tile is suitable.
A9.4	If the pH value of the sample is below 5.0, add a small amount of calcium carbonate (A5.5) and stir. There should be a small residue of undissolved calcium carbonate remaining before the titration is carried out.	

Step	Procedure	Notes
A9.5	If the pH value of the sample is above 9.5, add one or two drops of phenolphthalein solution (A5.7), and titrate with N/10 acid (nitric or sulphuric see Section A5.6) until the red colour of the indicator is discharged. Discard this sample, take a fresh 100.0 ± 0.2 ml sample (as in Section A9.3) add the same amount of N/10 acid to it, followed by a small amount of calcium carbonate and stir (notes e and f).	(e) If the alternative procedure given in A14 is to be used, replace the next step A9.6 by that procedure. (f) If an interference removal step is entailed after the aliquot has been taken a pH meter may be used instead of an indicator, but consideration should be given to removing the interference right at the start (see note a, above). If a pH meter is used the reference electrode should not be calomel.
A9.6	Add 1 ± 0.2 ml of Potassium Chromate Indicator (A5.4) and titrate with standard silver nitrate solution (A5.2) with constant stirring or shaking until the slightest perceptible reddish coloration persists. Note the burette reading. If, due to the colour of the sample itself, there is difficulty in deciding the end-point proceed as in Section A11 (note g).	(g) Specimen end-point samples may be used for comparison purposes. Prepare by titrating a sample as in Sections A9 and A11, then add further silver nitrate solution to this sample, a drop at a time, and so arrive at a specimen end point with which to match subsequent titrations. As these specimens darken in light, they can only be used for a few samples before being discarded.

A10 Blank Determination

A10.1 **Indicator blank:**

Repeat the procedure above, starting at step A9.3, using 100 ± 0.2 ml of water instead of the sample.

A10.2 **Reagent Blank:**

As this titration requires moderately accurate pH adjustment of the solution, and as the initial sample may not have the same pH or buffer capacity as the water used for the blank, and as any of the pretreatments used would give a different final pH with water to that which they would give with the sample, a full reagent blank determination can only be made by determining and deducting the amount of chloride added with each reagent addition. Such a blank is unnecessary if all the reagents used are chloride free.

A11 Back-Titration Technique

A11.1 The analytical accuracy may sometimes be improved by taking the titrated sample from step A9.6 and back titrating with the standard sodium chloride solution (Section A5.3) until the reddish colour just disappears.

A11.2 From the titration obtained in step A9.6 deduct half the chloride back titration obtained in step A11.1, and use this corrected value instead of the "Volume of Silver Nitrate" in the calculation (Section A12), but note that this procedure is only valid if the initial direct titration has not been taken beyond the first apparent end-point to confirm that the end-point has been reached.

A12 Calculation of Results

$$\text{mg/l Chloride} = \frac{\text{Volume of silver nitrate solution (ml)} \times 1000}{\text{Volume of sample (ml)}}$$

A12.1 If the back titration technique (Section A11) is used, use the corrected titration value explained therein in the above formula.

A12.2 If a blank titration (indicator blank) is used, deduct the mean blank value from the mean titration volume and use as volume of silver nitrate solution in the above formula.

A12.3 If, after the removal of interfering substances, a separate aliquot rather than the whole sample is taken for the titration, correct for any volume changes by multiplying the found chloride concentration by the factor:

$$\frac{\text{final sample volume}}{\text{initial sample volume}}$$

A13 Removal of Interferences

A13.1 **Bromide and iodide**

There is no simple method of suppressing the stoichiometric interference due to bromide and iodide. If necessary these must be determined separately and deducted from the final result.

A13.2 **Phosphates**

There is no simple method of suppressing the stoichiometric interference of phosphate with this method; but methods B, C and D, suitable for solutions containing orthophosphate, are included in this booklet.

A13.3 **Sulphide and hydrogen sulphide**

Sulphides interfere and obscure the end point and must be removed. (See also A13.4). At step A9.1, add about 50 ± 5 mg of powdered zinc sulphate, stir or shake well, then add two drops of 2N sodium hydroxide solution. Stir or shake again, allow to settle and filter. Test one drop of the filtrate with silver nitrate solution, followed by a drop of nitric acid (d_{20} 1.42). A permanent black precipitate would indicate incomplete sulphide removal. (Discard this small test sample). If necessary repeat this treatment with zinc sulphate etc until the silver nitrate test gives no permanent black precipitate.

A13.4 **Thiosulphate, sulphite, thiocyanate, cyanide, and also many organic substances that reduce Silver (I) ions.**

These substances all interfere. The anions may react with silver to form insoluble salts, or soluble complexes depending on concentration, some of which decompose to other compounds on warming or standing. Some deposit metallic silver. All must be removed. If sulphide is also present it can be removed along with these other substances by hydrogen peroxide oxidation in acid solution.

A13.4.1 Measure a suitable volume of sample and pour into a conical flask. Add 1 ± 0.1 ml nitric acid (d_{20} 1.42) and if necessary dilute with water. In a fume cupboard, cautiously add 25 ± 1 ml of 10 volume Hydrogen Peroxide and boil for 15 minutes, add 10 ± 1 ml more hydrogen peroxide and boil for 5 minutes.

A13.4.2 Test a drop of the solution with ferric chloride to confirm absence of thiocyanate. If a red colour develops, thiocyanate removal is incomplete.

A13.4.3 Test another drop of the solution with a few drops of dilute sulphuric acid and warm. If Sulphur dioxide can be detected by test paper (A5.8.2) removal of either thiosulphate or sulphite is incomplete.

A13.4.4 If organic reducing agents were present in the initial sample, take a few drops of solution, remove any excess peroxide with a crystal of ferrous sulphate and test the liquid with a drop of silver nitrate. A black precipitate or silver mirror, insoluble in dilute sulphuric acid, indicates incomplete oxidation. A black precipitate is also obtained if sulphide removal is incomplete.

A13.4.5 Should removal of any of these substances be incomplete, add more hydrogen peroxide to the remainder of the sample and continue digestion until a satisfactory test is obtained indicating removal of the interferant.

A13.4.6 When the oxidation is complete, add five drops of potassium chromate solution and boil for two minutes to decompose excess hydrogen peroxide, cool slightly, add 1.5 ± 0.1 g of anhydrous sodium carbonate and bring the sample to the boil for one minute. Cool to room temperature, filter and using a calibrated flask make up to a known volume. Proceed to step A9.3. In the final calculation (Section A12), correct for any volume change entailed by this operation.

A13.5 Lead, bismuth, barium, iron

Lead, bismuth, barium and iron interfere with the indicator, and so cause interference at almost all concentrations. These metals must either be removed or the alternative indicator procedure A14 must be used. Choice is dependent on the clarity of the solution and ability to observe the colour of the precipitated silver chloride.

A13.5.1 *Barium* is best removed by addition of sulphuric acid and filtration, though traces of chloride may be lost by adsorption onto the precipitate. If the concentration of barium is high, use the mercuric nitrate method which follows (Method B). Note and correct for any volume change (see Section A12.3).

A13.5.2 *Lead, bismuth and iron* can be removed by addition of a small amount of ammonium acetate solution and making alkaline with ammonia solution, followed by treatment with hydrogen sulphide. Precipitated sulphides are filtered off. Precise details cannot be given as they are dependent on the amounts of these metals present. Remove any excess hydrogen sulphide by procedure A13.3. Note and correct for any volume changes (see Section A12.3).

A13.5.3 Alternatively, use 2, 7 dichlorofluorescein or 3, 4 dibromofluorescein as indicator instead of potassium chromate (see A14), or use the potentiometric method that follows in this booklet (Method C).

A13.6 Highly coloured or turbid solutions

The pH value of the sample should be between 5 and 9. Adjust if necessary.*

Add 3 ± 0.5 ml of aluminium hydroxide suspension (Section A6.4.1) to the 100 ml sample from step A9.3. Stir or shake to mix thoroughly. Allow to stand for a few minutes, then filter. Wash the precipitate with 10–15 ml of water, collecting the washing with the filtrate and continue with steps A9.4, 9.5 or 9.6 as appropriate. If this treatment is not sufficient, or there is risk of loss of chloride by adsorption to suspended matter in the sample, use another method such as a potentiometric titration (Method C).

A13.7 Carbonates

If much carbonate is present acidify the sample with a few drops of nitric acid (d_{20} 1.42) and warm to expel carbon dioxide. Small amounts of carbonate usually have no effect.

A13.8 Ammonia and related compounds

Take a known volume of sample, make alkaline with sodium hydroxide (A6.1.2) to a pH value >12 and simmer in an open beaker in a fume cupboard until all the ammonia etc has been volatilized, cool.

A14 Alternative Indicator Procedure (Ref. 1)

Add a few drops of 2, 7 – dichlorofluorescein solution (or 4, 5 dibromofluorescein solution) to the sample and titrate with standard silver nitrate solution with constant shaking until the silver chloride precipitate, which is at first dyed a pale yellow, turns a mauvish pink colour.

If no precipitate at all forms after the addition of the first few drops of silver nitrate solution, discontinue titration, take a fresh sample as a check against error and repeat the analysis. If the same happens again, the chloride content is below the solubility limit for silver chloride. Without a precipitate to change colour there can be no end point. Should the precipitate turn bright yellow check the pH. It is probably less than 4.0. If so, discard the sample and start again checking the sample pH value prior to titration.

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*If the sample is markedly acid or alkaline part or all of the suspension may dissolve. Colour and/or turbidity may not be removed and Aluminium hydroxide may be re-precipitated when the pH is adjusted before the titration.

A15. Chlorinity, Chlorosity and Salinity Determinations

These terms are arbitrary conventions used in sea water analysis. For an explanation of these terms, other special information on the adaptation of this method to Sea and Estuarine Water and other methods used for the analysis of such waters, see References 3–5 and 30. For reasons of time and cost, accurate measurements of these three determinands are usually deduced from conductivity data.

A16 Accuracy of Results

Analytical Quality Control Procedures are recommended. Suitable procedures are described in References 6–9.

A17 Effluent Disposal and Silver Recovery

In order to recover some of the cost of an expensive reagent, and remove any risk to the environment, silver may be recovered from the wastes. See Section H1. Silver Chloride is a notifiable waste and must not be disposed to land or water without consent.

B. Mercuric Nitrate Titration with Diphenylcarbazone Indicator

B1 Performance Characteristics of the Method (9)

B1.1	Substance determined	Soluble chloride.
B1.2	Type of sample	Most waters and effluents, especially those containing phosphate.
B1.3	Basis of method	Titration with standard mercuric nitrate using diphenylcarbazone indicator at pH 2.9 – 3.4.
B1.4	Range of application	Up to 1000 mg/l Cl^- using a 50 ml sample and a 50 ml burette (but see also Sections B8 and B11 for change of range).
B1.5	Standard deviation (c)	

Chloride Concentration mg/l Cl^-	Total Standard Deviation mg/l Cl^-	Degrees of Freedom
20 (a)	0.29	9
250 (b)	3.3	11
500 (b)	3.0	11
1000 (b)	3.1	11

B1.6	Limit of detection (b)	5 mg/l Cl^- using a 50 ml sample (but see notes (a) and (e).
B1.7	Bias	No information.
B1.8	Interferences	i. Iodide, bromide, simple and complex cyanides readily decomposed to cyanide, and thiocyanates, titrate stoichiometrically as chloride (d) ii. Cyanoferrates (II) titrate non-stoichiometrically (d) iii. Cyanoferrates (III) and thiosulphates interfere with the end point (d). iv. Chromate and Iron (III) salts interfere. v. Ammonia may interfere. All the above ions except iodide and bromide can be removed, see Section 3. Phosphate and Sulphite do not interfere (d).
B1.9	Time required for analysis	Each analysis must be performed individually. Analytical time which is the same as operator time varies with chloride concentration. Twenty titrations per hour is a typical rate.

Notes: (a) information made available by the DOE committee for Analytical Quality Control (Harmonized Monitoring) using a 250 ml sample. The Relative Standard Deviation is almost the same as that obtained for 250 mg/l Cl^- on a 50 ml sample.

(b) information supplied by the Colne Valley Water Company, 50 ml sample.

(c) synthetic samples made with sodium chloride.

(d) data confirmed by North West Water Authority.

(e) not determined in accordance with Ref 7; but estimated from the discriminatory interval of the method and the indicator blank for a coefficient of variation of 10%.

B2 Principle

Mercuric ions react stoichiometrically with chloride ions to form a stable, soluble complex. The end point is detected by the use of diphenylcarbazone which forms a less stable bluish violet complex when an excess of mercuric ions is present (10–14).

B3 Interferences

B3.1 Chromate and Iron III ions interfere. The interference becomes marked at above 10 mg/l but can be prevented by reduction to chromium III and iron II. See step B8.3.

B3.2 Ammonia can interfere by reaction with the titrant to form complexes other than those desired; which complexes are formed is highly dependent on other variables in the sample. Remove by the procedure given in Section A13.8.

B3.3 Sulphide and hydrogen sulphide interfere. Remove by the procedure given in Section B8.3 note d.

B3.4 Phosphates do not interfere.

B3.5 Simple and complex cyanides interfere (see reference 13). Simple cyanides and thiocyanates titrate as chloride. Cyanatoferrates (II) titrate as chloride, but not stoichiometrically. Cyanatoferrates (III) prevent the formation of an end-point. Remove by the procedure given in Section A13.4 except remove excess hydrogen peroxide as outlined in Section C12.2.2 and not as given in Section A13.4.6.

B3.6 Thiosulphate interferes by obscuring the end point. Remove by the procedure given in Section A13.4 except remove excess hydrogen peroxide as outlined in Section C12.2.2 and not as given in Section A13.4.6.

B3.7 Sulphite does not interfere.

B4 Hazards

Both mercuric salts and diphenylcarbazone are toxic and must not be swallowed. Do not pipette by mouth.

B5 Reagents

Analytical Reagent grade chemicals are preferred.

B5.1 Water

Distilled or deionized water is suitable. (50 ml of water in a 50 ml Nessler Cylinder should not give any opalescence when a few drops of silver nitrate solution (A5.2) are added to it, followed by one drop of N/10 nitric acid; alternatively the specific conductance should be below 20 μS/cm).

B5.2 Mercuric nitrate solution

Two different procedures are in use in the water industry. The test data in Section B1 are valid for both procedures. Either a mercuric nitrate of strength such that exactly 1 ml is equivalent to 1 mg of chloride, or the initial approximate strength mercuric nitrate solution is used for titrations, with a correction factor in the calculation stage. Either procedure requires standardization of the initial approximate strength solution against a primary standard sodium chloride solution (B5.3).

B5.2.1 *Approximate strength Mercuric nitrate solution*

Dissolve 5.24 ± 0.01 g mercuric nitrate hemihydrate in 50 ± 0.5 ml of water containing 0.5 ± 0.1 ml of nitric acid (d_{20} 1.42), dilute to about 1 litre in a stoppered flask, shake well and filter if necessary.

B5.2.2 *Standardization of the mercuric nitrate against the standard sodium chloride solution*

Use the procedure given in steps B8.2 to B8.5, with 10.00 ± 0.05 ml or preferably 25.00 ± 0.05 ml portions of the sodium chloride standard solution (B5.3) instead of sample. Take the mean of at least three titrations.

B5.2.3 *Correction factor*

Multiply titrations (corrected for indicator blank) by V/S, where V is the number of ml of standard chloride solution taken as sample for the standardization of the mercuric nitrate, and S is the mean mercuric nitrate titration.

B5.2.4 *Mercuric nitrate solution 1 ml is equivalent to 1 mg chloride*

Measure 500 ml ± 0.5 ml of the mercuric nitrate solution into a flask and add 500 $(\frac{V}{S} - 1)$ ± 0.5 ml of water. Stopper the flask and shake well. The solution is now 1.0 ml equivalent to 1 mg/Cl^-. Recheck the strength of this solution as in B5.2.2 above.

B5.2.5 This solution is stable for at least one month when stored in glass or plastic bottles.

B5.3 **Sodium chloride standard solution 1.0 ml contains 1.0 mg Cl^-.**

Dissolve 1.6484 ± 0.0005 g sodium chloride, (dried to constant weight at 120 – 250°C) in approximately 200 ml water, and dilute with water to 1 litre in a calibrated flask. Stored in a glass stoppered bottle this solution is stable indefinitely.

B5.4 **Diphenylcarbazone indicator**

Dissolve 0.5 ± 0.1 g of diphenylcarbazone and 0.05 ± 0.2 g bromophenol blue in 100 ± 5 ml of ethanol. Store in a brown glass bottle. This solution is stable for at least one week if stored in a refrigerator.

B5.5 **Nitric acid, N/20 (approximate)**

Dilute 3.2 ± 0.1 ml nitric acid (d_{20} 1.42) to 1 litre ± 10 ml with water.

B5.6 **Sodium hydroxide, N/20 (approximate)**

Dissolve 2.0 ± 0.1 g of sodium hydroxide in water and dilute to 1 litre ± 10 ml. Stored in a polyethylene bottle this reagent can be kept indefinitely.

B5.7 **Additional Reagents for the Removal of Interferences**

B5.7.1 *Hydroquinone solution 1% m/V*

Dissolve 1.0 ± 0.1 g hydroquinone in water and dilute to 100 ± 10 ml. Prepare freshly as required.

B5.7.2 *Barium nitrate solution* (required occasionally to test for completeness of chromate reduction).

Dissolve about 1 g of Barium nitrate in about 20 ml of water. Stored in a glass bottle, this solution is stable indefinitely.

B5.7.3 *Potassium thiocyanate solution* (required occasionally to test for completeness of iron III reduction)

Dissolve about 1 g of Potassium Thiocyanate in about 20 ml of water. Discard if discoloured.

B5.7.4 *pH indicator papers* to cover the range from about pH1 to above pH7 (needed only if sulphide is to be removed).

B6 Apparatus

B6.1 **Burettes**

Grade B burettes and pipettes are usually of sufficient accuracy.

B6.2 **Cleanliness**

All apparatus must be clean and rinsed with chloride-free water before use.

B7 Sample Collection and Preservation

This is dependent on the nature of the sample, but the sample bottles made of glass or plastic must be halide free. No preservative is needed for chloride itself. If prevention of decomposition of other components is necessary, hydrochloric acid, chlorides, and disinfectants containing halogens, silver, or mercury must not be used for preservation of the sample.

B8 Analytical Procedure

Step	Procedure	Notes
B8.1	If the chloride concentration is not approximately known, pipette 10.00 ± 0.05 ml of sample into a conical flask and carry out a preliminary determination as detailed in steps B8.3, B8.4, B8.5 and B10. Determine the approximate concentration of the sample.	
B8.2	Accurately measure a volume of sample preferably containing between 5 and 50 mg of chloride and if necessary, either by dilution or evaporation bring the volume to about 50 ml in a conical flask (notes a, b and c).	(a) If necessary use a large flask or beaker which should be well rinsed out into the conical titration flask when the sample is finally transferred. (b) Evaporation will increase the concentration of chromate and iron (III) and may convert iron (II) to (III). If in doubt assume present in subsequent steps. (c) When time and availability of sample permit, steps 8.2–8.6 should be carried out in triplicate.
B8.3	If chromate or iron III are present in the sample in excess of 10 mg/l (note b), add 5 ml of Hydroquinone solution (note d). If sulphide or hydrogen sulphide are present see note e. If ammonia is present, remove as given in Section A13.8. If simple or complex cyanides are present, see Section B3.5. If thiosulphate is present see Section B3.6.	(d) If the solution is still yellow in colour test whether chromate and iron III are still present. Take two separate approximately 1 ml portions of the solution, to one portion add one drop of barium nitrate solution (B5.7.1) followed by one drop of sodium hydroxide solution (B5.6). A yellow precipitate indicates unreduced chromate. To the other portion add one drop of potassium thiocyanate solution. A red coloration indicates unreduced iron III. If need be, repeat the hydroquinone addition until all chromate and iron III are reduced. Preferably, once the amount of hydroquinone solution required has been determined on an aliquot discard the initial aliquot used for the tests, take a fresh sample aliquot, add a slight excess of hydroquinone solution and proceed if required as given in note d, followed by steps B8.4 onwards. (e) If sulphide or hydrogen sulphide are present, using either a pH meter or pH test papers, make sure that the sample is slightly acid, adding nitric acid (B5.5) if necessary, then simmer in a fume cupboard until all hydrogen sulphide has been evolved. Add water if necessary to maintain the approximate sample volume.

Step	Procedure	Notes
B8.4	Add 5 to 10 drops of diphenycarbazone Indicator Solution.	
B8.4.1	If a blue, bluish violet, or red colour develops, add N/20 nitric acid dropwise with stirring until the colour just changes to yellow; then add 1.00 ± 0.05 ml more N/20 nitric acid.	
B8.4.2	If a yellow or orange colour develops, add N/20 sodium hydroxide solution dropwise, with stirring until the colour just changes to blue-violet; then add N/20 nitric acid dropwise with stirring until the colour just returns to yellow; then add 1.00 ± 0.5 ml more nitric acid.	
B8.5	Titrate with standard mercuric nitrate solution to a bluish violet end point.	
B8.6	Indicator Blank Determination. Carry out steps B8.4 and B8.5 using 50.00 ± 0.05 ml portions of water. Deduct the mean indicator blank titration value from the titration value (note c) and use the corrected titration value in step B10.	

B9 Blank Determination

As with other methods requiring pH adjustment of the sample, where the sample may be highly buffered, a true reagent blank is impossible, and use of high purity reagents is advisable. If necessary, determine any chloride increment due to reagents separately and deduct from the final result.

B10 Calculation of Results

$$\text{mg/l Chloride} = \frac{\text{corrected titration value (ml)} \times 1000}{\text{Volume of sample (ml)}}$$

Also, if necessary, multiply the result by the appropriate mercuric nitrate solution factor from step B5.2.3 (see also Sections B8 and 11).

B11 Range of Method

For very dilute samples, use of a more dilute standard mercuric nitrate solution is recommended. See Section B14 for details. Use of large samples or use of aliquots may also extend the range of the method either way. Alternative methods with better precision at lower concentrations are included in this booklet.

B12 Accuracy of Results

Analytical quality control procedures are recommended. Suitable procedures are described in References 6–9.

B13 Effluent Disposal and Mercury Recovery

In order to avoid risk to the environment, eg sewage treatment works, water courses and the sea, and also to recover some of the cost of an expensive reagent, wastes containing mercury should be treated to remove mercury. See Section H2. Mercury compounds are notifiable wastes and must not be disposed to land or water without consent.

B14 Determination of Chloride at lower concentrations

The method which follows is a variant of the main method. It has a sharper end point with more dilute reagents and hence can be used for the analysis of lower concentrations. It has not been tested as thoroughly as the main method.

B14.1 **Performance Characteristics of the Variant** (a)

At 2 mg/l chloride, the total relative standard deviation is 10%.

At higher concentrations, the test data are comparable with those for the main method. 0.2 mg/l chloride can be detected, but not with the above degree of precision.

Interferences and principle are as for the main method.

(a) Data supplied by the Laboratory of the Government Chemist based on monthly checks over many years.

B14.2 **Reagents**

B14.2.1 *Water*

Test the suitability of water for use in this variant by measuring at least 500 ml into a clean beaker, evaporating to 50 ml or less and testing as in B5.1. If necessary redistill the water using a good antisplash device then recheck the quality.

B14.2.2 *Diphenylcarbazone, 0.1% solution in ethanol.*

Disolve 0.100 ± 0.002 g of sym diphenylcarbazone in 100 ± 2 ml of absolute ethanol. This solution is stable for at least one week if stored in a refrigerator.

B14.2.3 *Bromophenol blue, 0.1% solution in ethanol*

Disolve 0.100 ± 0.002 g of bromophenol blue in 100 ± 2 ml of absolute ethanol. This solution is stable for at least one week if stored in a refrigerator.

B14.2.4 *Nitric acid 0.1N*

See Section A5.6.

B14.2.5 *Sodium carbonate solution approx 0.1N*

Weight out 5.3 ± 0.1 g of anhydrous sodium carbonate, dissolve in water, and dilute with water to 1 litre in a measuring cylinder. This solution is stable indefinitely.

B14.2.6 *Ethanol, absolute*

B14.2.7 *Mercuric nitrate solution, approximately 0.01N*

Dissolve 3.43 ± 0.01 g of mercuric nitrate hemihydrate in a mixture of 50.0 ± 0.5 ml of nitric acid 0.1N and 450 ± 1 ml of water. Allow the solution to stand for two days, filter to remove any suspended matter, transfer quantitatively to a 2 litre calibrated flask and make up to the mark with water. This solution is stable for at least one month.

B14.2.8 *Sodium chloride solution, 0.01N*

Dissolve 0.5844 ± 0.0001 g of sodium chloride (previously dried at 120–250°C for 2 hours), in about 20 ml of water, and dilute with water to 1 litre in a calibrated flask. This solution is stable for at least one month.

B14.3 **Special Apparatus**

A burette calibrated with graduations every 0.01 ml or less.

B14.4 *Analytical procedure*

B14.4.1 Pipette out 20 ml of sample, into a conical flask and add 2 drops of bromophenol blue solution. If the solution is a bluish colour, titrate with nitric acid, 0.1N until the colour just changes to yellow, then add 0.5 ml extra of this nitric acid. If the solution is a yellow colour, titrate with sodium carbonate solution, 0.1N until the colour just becomes bluish, then back titrate to yellow and add 0.5 ml extra of nitric acid 0.1N, as above.

B14.4.2 To the pH adjusted sample, add 50 ml of ethanol and 12 drops of diphenylcarbazone solution and titrate with mercuric nitrate solution, 0.01N to a faint purplish grey end point to obtain the sample titration V. It is suggested that the burette tip be just immersed in the sample during the titration. Drain time should be allowed before reading, especially if finely calibrated burettes are used.

B14.4.3 *Indicator Blank Value*

Carry out a triplicate blank determination through steps B14.4.1 and 2, using water, in place of the sample and determine the mean blank titration B.

B14.4.4 *Standardization*

Carry out steps B14.4.1 and 2 in triplicate using three samples of 5 ml of 0.01N sodium chloride and 15 ml of water. Determine the mean standardization titration S.

B14.5 **Calculation**

The chloride concentration in the sample is $\frac{88.6\ (V-B)\ mg/l}{(S-B)}$

C Potentiometric Titration with Silver Nitrate (Tentative Method)

C1 Performance Characteristics of the Method (9)

C1.1	Substance determined	Soluble chloride.
C1.2	Type of sample	Most waters, including coloured and turbid waters.
C1.3	Basis of method	Potentiometric titration in acid medium with silver nitrate.
C1.4	Range of application	Up to 200 mg/l Cl^- using a 25 ml burette and 50 ml aliquot (See Section C11).
C1.5	Standard deviation (a)(b)	Chloride Concentration mg/l Cl^- / Total Standard Deviation mg/l Cl^- 10 — 0.32 20 — 0.34 30 — 0.55 40 — 0.40 50 — 0.27 100 — 0.23 200 — 0.38 Determined with 9 degrees of freedom
C1.6	Limit of detection (a)	1 mg/1 Cl^- for a 50 ml aliquot, with 9 degrees of freedom.
C1.7	Bias (a)	Recovery tests on canal water gave no evidence of bias. Recovery was 99.1%, with 9 degrees of freedom. The 95% confidence limits are 98.0 – 100.2%
C1.8	Interference (a)	Not removable: Bromide, Iodide Removable: Ferricyanide, Ferrocyanide, Thiocyanate, Sulphide, Sulphite, Cyanide, Thio-sulphate, Chromate ion, Dichromate ion, Iron (III) ion, Polyphosphates, Gross organic contamination (See Section C12). Surfactants may interfere (See Section C3).
C1.9	Time required for analysis (a)	Each analysis is performed separately. Ten analyses per hour is a typical rate, not allowing for sample pre-treatment.

(a) Based on data obtained by South West Water Authority (Countess Wear Laboratories) using the double differential plot technique (step C9.5 note e), 50 ml samples.

(b) All samples were synthetic solutions of sodium chloride in distilled water.

Note: Results quoted in C1.5 and C1.6 were obtained by:

i. following procedure 9.4

ii. reading the burette to nearest 0.01 ml.

C2 Principle

Chloride ion is determined by potentiometric titration in acidic conditions with silver nitrate solution, using a suitable reference electrode and a silver-silver chloride electrode system. A high impedance input millivoltmeter is used to observe potential difference changes in the system. The end point of the titration is indicated by the maximum value of a plot of potential difference changes for a small and constant increment of titrant against the volume of titrant used.

C3 Interferences

C3.1 Bromide and iodide cannot be removed and each titrates stoichiometrically as the equivalent of chloride ion. If the presence of appreciable concentrations of bromide or iodide is suspected then they should be determined separately and a correction applied. (See Part G of this booklet, the respective methods for Bromide and Iodide to be published in this series or Ref 15).

C3.2 Cyanoferrate (III) titrates as three equivalents of chloride but may be removed. (See Section C12.2).

C3.3 Cyanoferrate (II) titrates as four equivalents of chloride but may be removed. (See section C12.2).

C3.4 Cyanide, sulphite, sulphide, thiosulphate and thiocyanates interfere stoichiometrically, but may be removed. (See sections C12.1 and C12.2).

C3.5 Iron III ion interferes if present in amounts substantially greater than the chloride ion, but is also removed by section C12.2.1.

C3.6 Organic material interferes but may be removed. (See section C12.2).

C3.7 Chromate and dichromate interfere and may be reduced and removed. (See section C12.2).

C3.8 Polyphosphates and other macromolecules may be adsorbed on the electrode membrane and so inhibit the electrode performance. (See sections C12.1 and C12.2).

C3.9 Tests made at the South West Water Authority Countess Weir Laboratory indicate that some but not all surfactants can cause slight interference. If such interference is suspected these substances can be removed. See Section C12.2 for details.

C3.10 Chromium (III) ion, iron (II) ion and ortho-phosphate do not interfere. Chromic and ferrous ions interfere with some silver titrations by reacting with the chemical indicator, but have no effect on the electrode system used here. Orthophosphate will precipitate with silver nitrate at above about pH4 but not in the highly acid solution used in this method. This is in contrast with Method A, given in this booklet.

C3.11 Hydrogen peroxide damages the electrodes and must be removed. See C12.2.2.

C4 Hazards

Silver salts are toxic if ingested and temporarily stain the skin brown.

C4.1 Hazards in Interference Removal

Cyanides and complexed cyanides, sulphides, sulphites, thiocyanates and thiosulphates release toxic gases on acidification and must be treated in a fume cupboard. Hydrogen peroxide causes temporary irritation if in contact with the skin and should be washed off.

C5 Reagents

Analytical grade reagents should be used unless otherwise stated.

Silver nitrate is light sensitive and should be protected from light by use of dark brown glass containers or by masking a clear container, and preferably storing in the dark. Both silver nitrate and sodium chloride, if pure, are primary standard substances. The reliability of the method can be improved by checking one against the other in control analyses using either this method or method A.

C5.1 **Water**

The water used for reagent preparation, blank determination and sample pre-treatment should be free of chloride and any interfering agents. Deionized distilled water with a conductivity of less than 20 μ S/cm is suitable or alternatively test by the following method.

Fill two Nessler tubes with 50 ml of the water, to one add 1 ml of 50% V/V of sulphuric acid, mix, then add 1 ml of silver nitrate solution (C5.2), mix and allow to stand for five minutes then examine for turbidity by comparing the two tubes. If there is visually no perceptible turbidity then the level of chloride is less than 0.2 mg/l and the water is suitable for use in the method.

C5.2 **Silver nitrate solution**
(0.0141M – 1 ml is equivalent to 0.50 mg of chloride)
Dissolve 2.395 ± 0.0005g silver nitrate (dried at 105°C to constant weight) in water, transfer to a 1-litre calibrated flask and make up to the mark with water. If properly stored in a brown glass bottle, in the dark, this solution is stable for at least one year.

C5.3 **Sodium chloride solution** (0.0141M, 1.0 ml is equivalent to 0.5 mg Cl^-)
Weight 0.824 ± 0.0005 g sodium chloride (dried to constant weight at 120–250°C) dissolve in approximately 200 ml of water. Transfer to a 1-litre calibrated flask and make up to the mark with water and mix. Stored in a stoppered glass bottle, this solution is stable indefinitely.

C5.4 **Sulphuric acid 50% V/V**

Add slowly with continuous stirring and external cooling 500 ± 10 mls of sulphuric acid (d_{20} 1.84) to 500 ± 10 ml of water in a 2-litre beaker. The solution is stable indefinitely.

C5.5 **Gelatine solution**

Add 2.5 g of refined gelatine (chloride-free) to about 500 ml of water. Heat gently with constant stirring until the gelatine dissolves, cool and store in a refrigerator. This solution should be stable for at least one week. Warm to room temperature before use.

C6 Additional reagents

The following reagents are required for interference removal.

C6.1 **Hydrogen peroxide 30% V/V.**

C6.2 **Sodium hydroxide 1.0M**

Dissolve 40 ± 1 g sodium hydroxide pellets in 1000 ± 20 ml of water contained in a 2-litre beaker, stirring continuously until dissolved. Cool before use. It is advisable to carry out this procedure in a fume cupboard as irritating fumes are released. This solution is stable indefinitely.

C6.3 Litmus paper

C7 Apparatus

All volumetric glassware should be of grade 'A' quality.

C7.1 **Burette**

25 ml capacity graduated in 0.05 ml divisions.

C7.2 **Millivoltmeter**

A millivoltmeter with impedance of not less than 10^{12} ohms capable of resolving potential changes of 0.1 mV. A digital millivoltmeter is preferred.

C7.3 **Mechanical stirrer or magnetic stirrer** with low heat transference, with plastic (not PVC) or glass coated impeller or follower.

C7.4 Reference electrode

Any suitable reference electrode not containing chloride in the salt bridge and preferably of the sleeve type (a mercurous sulphate electrode with a saturated potassium sulphate salt bridge solution was used to obtain the performance characteristics in Section C1).

C7.5 Silver – Silver Chloride Electrode

This electrode is commercially available but may be prepared as follows. The same procedure can be used to renew the coating of AgCl if this is damaged.

C7.5.1 Apparatus

C7.5.1.1 *High purity silver wire (99.9% pure or better)* of approximately 1.5 mm diameter and approximately 14 cm long.

C7.5.1.2 *Auxillary electrode of silver or platinum wire or plate* with a surface area not less than 1 cm^2.

C7.5.1.3 *4–4.5 volt battery.*

C7.5.1.4 *Resistor of approximately 1000 ohms.*

C7.5.1.5 *Fine, grease-free polishing agent* (300 mesh carborundum powder, pumice dust, jeweller's rouge etc).

C7.5.1.6 *A soft polishing pad free from grease and oil* for applying polishing agent.

C7.5.1.7 *50 ml beaker.*

C7.5.2 Reagents

C7.5.2.1 *Approximately 0.1M Hydrochloric acid*

Add carefully with stirring 9 ± 0.5 ml hydrochloric acid (d_{20} 1.18) to 1000 ± 20 ml of water contained in a 2-litre beaker.

C7.5.3 Procedure

Clean the wire vigorously with the polishing agent and wash with water. Take great care not to contact the wire with the skin, which is always oily. Wind the wire into a loose helix about 1 cm diameter and of convenient length for immersion. Connect the auxillary electrode via the resistor to the negative pole of the battery and the silver wire electrode to the positive pole.

Immerse the electrode in the beaker containing 0.1M hydrochloric acid, complete the circuit and carry out the electrolysis for approximately ten minutes. After the electrolysis the silver helix should have a uniform dark grey coating; if it is stained, the electrode was improperly cleaned and the process should be repeated until a satisfactory coating is obtained. The resulting electrode should be stored in a clean and dry condition.

C8 Sample Collection and Preservation

This is dependent on the nature of the sample, but the sample bottles made of glass or plastic must be halide free. No preservative is needed for chloride itself. If prevention of decomposition of other components is necessary, hydrochloric acid, chlorides, and disinfectants containing halogens, silver, or mercury must not be used for preservation of the sample.

C9 Analytical Procedure

Step	Procedure	Notes
C9.1	Set up the apparatus in accordance with the manufacturer's recommendations. (See notes a and b).	(a) Allow the meter to reach equilibrium. (b) If the electrodes have been standing for an hour or more without use it is advisable to condition them by running through steps C9.2 and C9.3 with a standard solution of chloride.
C9.2	Pipette a suitable aliquot of sample, not over 150ml, containing from 0.1 to 12.5mg Cl^- into a 400ml beaker. Add 15 ± 0.2ml of 50% V/V sulphuric acid and approximately 0.5ml of gelatine solution. Dilute to 150 ± 15ml with water. Immerse the stirrer electrodes and burette tip in the test solution and commence stirring. Allow the meter to stabilize and note the potential of the system in millivolts. (See note c).	(c) Gelatine is added to maintain the silver chloride formed in suspension to prevent it from coating the electrodes.
C9.3	Add a known amount of standard silver nitrate solution to the sample (note d). Wait until the millivoltmeter reading is stable and record the new voltage. Repeat the addition gradually reducing the amount of silver nitrate solution added each time until the additions are of 0.1ml, after which the amount added is kept constant; but allow progressively longer times between additions for the millivolt-meter to stabilize before reading. Continue the additions until a maximum change per unit addition has been observed.	(d) The size of the initial addition is dependent on the chloride content of the sample. If the initial addition is too large, the increment in voltage for each 0.1ml will decrease right from the start. If this happens start again with a fresh sample, with a substantially smaller initially addition. Past experience of similar samples will be a guide to the size of the initial addition.
C9.4	Determine the volume of silver nitrate used at the point at which there is the greatest change in instrument reading per 0.1ml addition of silver nitrate solution.	
C9.5	If the end point cannot be determined by inspection of the data, plot a differential titration curve. Plot the voltage change in millivolts per 0.1 ml increment of silver nitrate solution added against the volume of silver nitrate added, using the average of the burette readings before and after each addition. The maximum point on the curve is the end point. (See notes e, f, and g).	(e) A double differential plot (of gradient of the differential curve against mean titration) can increase accuracy at low levels of chloride. The end point corresponds to the position where the curve crosses the zero line. (f) The end point may be determined by the Gran Plot Method (See Ref 16). (g) Auto-titration. The end point can be readily determined using an automatic titration apparatus. The manufacturer's instructions should be followed. If this is done, tests of accuracy and precision are recommended as the performance characteristics in Section Cl will not apply.
C9.6	Blank determination Repeat the procedure from step C9.2 using water instead of sample. If pretreatment of the sample is necessary, then a blank must be carried through the pretreatment procedure.	
C9.7	Standardization Pipette 10 + 0.02 ml of standard sodium chloride solution into a 400 ml beaker and proceed from step C9.2 to C9.6 substituting the standard sodium chloride solution for the sample.	

C10 Calculation of Results

C10.1 Molarity of silver nitrate $= \frac{10.0 \times 0.0141}{S - B_S}$

Where S = volume in millilitres of the standardization titre of Silver Nitrate Solution, and
B_S is the blank titre without pretreatment.

C10.2 Concentration of Cl^- in mg/1 $= \frac{(A-B) \times M \times 35.45 \times 1000}{D}$

$= \frac{(A-B) \times 500}{D}$ for 0.0141 M Silver nitrate

Where:–

A = Sample titre in millilitres of silver nitrate.
B = Blank titre, inclusive of pretreatment when necessary, in millilitres of silver nitrate.
M = Molarity of silver nitrate solution.
D = Volume in millilitres of sample taken.

C11 Range of Method

The range of the method may be extended by use of a more concentrated silver nitrate solution, by prior quantitative dilution of the sample, by use of a smaller aliquot in step C9.2, or by using a larger capacity burette, whichever is appropriate.

C12 Removal of Interferences

C12.1 *Cyanide, Sulphite, Sulphide, and Polyphosphate.*
Pipette an aliquot of the sample as in Section C9.2 prepare as for titration, but omit the gelatine solution. Boil for 15 minutes, cool, then add the gelatine solution and make up to volume and proceed as from Step C9.3

C12.2 *Chromate, dichromate, cyanoferrate II and cyanoferrate III, thiocyanate, thiosulphate and organic contamination* and any combination of these with the interferents not removed in C12.1 may be removed by following the procedure.

C12.2.1 Pipette an aliquot of sample as in C9.2 up to "into a 400 ml glass beaker" acidify to litmus with 50% V/V sulphuric acid. Boil to remove volatile material adding more sulphuric acid if necessary to maintain acid conditions. Add 3 ml of hydrogen peroxide and boil for fifteen minutes adding water to maintain the volume above 50 ml. Neutralize to litmus with 1.0M sodium hydroxide, add ten drops in excess, simmer for five minutes, filter and thoroughly wash filter and precipitate with hot water until free of chloride, collect the washings with the filtrate. Neutralize with 50% V/V sulphuric acid to litmus.

C12.2.2 To ensure that all hydrogen peroxide has been removed, add a small piece of platinum, preferable with the surface covered with platinum black. Swirl gently and simmer for one minute, cool, remove the platinum, rinsing into the sample with a few drops of water. If the total volume of the filtrate and washings exceed 150ml, reduce the volume below this amount by evaporation prior to cooling. Then proceed as in step C9.2 from 'Add 15 ± 0.2 ml of 50% V/V sulphuric acid'.

C13 Sources of Error

C13.1 See sections C3 and C12 on interference.

C13.2 High titration values may be obtained if the silver nitrate titrant has been exposed to light.

C13.3 The blank value should be regularly checked.

C13.4 A false value will be obtained in the first determination if the electrodes are not conditioned prior to use.

C13.5 When the end point to the titration is approached, sufficient time must be allowed for electrode stabilization after each incremental addition. (This is particularly important if an automated titration system is in use that requires a pre-set rate of titrant addition.

C13.6 The performance of the silver/silver chloride electrode will deteriorate if the dark surface coating of silver chloride is damaged or if the surface becomes coated with silver chloride precipitate. This should not be a problem if the gelatine solution is used as stated in the experimental procedure.

C13.7 False values will be obtained if the reference electrode is not correctly maintained. The electrolyte must be maintained at the correct level.

C14 Accuracy of Results

Analytical Quality Control Procedures are recommended. Suitable procedures are described in References 6–9.

C15 Effluent Disposal and Silver Recovery

In order to recover some of the cost of an expensive reagent, and remove any risk to the environment, silver may be recovered from the wastes. See Section H1. Silver Chloride is a notifiable waste and must not be disposed to land, or water, without consent.

C16 Automation of the Method

Tests at the South West Water Authority Countess Weir Laboratory have shown that the procedure is readily automated.

D Automated Mercuric-Ferric Thiocyanate Colorimetric Method

D1 Performance Characteristics of the Method (9) (i)

D1.1	Substance determined	Soluble chloride.
D1.2	Type of sample (f)	Raw, potable, effluent and waste waters.
D1.3	Basis of method	Chloride reacts with mercury (II) thiocyanate to form a soluble nonionic compound; the thiocyanate ions released react with iron (III) nitrate to form the red iron (III) thiocyanate complex, which is determined colorimetrically. Chloride is determined by calibration. Dialysis is employed to remove interference due to sample colouring and turbidity.
D1.4	Range of application (a) (f)	Up to 200 mg/l.
D1.5	Calibration curve (a) (f)	The calibration is slightly curved.
D1.6 (a) (f)	Total standard deviation	These data were obtained in a within-laboratory analytical quality-control programme (e). (See also Section D10 and Table 5).

Chloride Concentration mg/l Cl^-	Total Standard Deviation mg/l Cl^-	Effective degrees of freedom (h)
0.0 (b)	0.88	approx. 8
20.0 (b)	0.99	8.6
180.0 (b)	3.03	4.8
53.05 (c)	1.21	8.6
76.03 (d)	1.78	8.1

D1.7	Limit of detection (a) (f)	3.4 mg/l with 9 degrees of freedom.
D1.8	Sensitivity (a) (f)	200 mg/l gives an absorbance of approximately 0.38 (using a 15 mm flow-cell).
D1.9	Bias (a) (f)	No bias >5% detected, except when interferences occur (see Sections D1.10 and D3.2).
D1.10	Interferences (a)	Bromide, sulphide, thiocyanate, cyanides including complex cyanides, nitrite, ammonia, and nonionic detergents. (See Section D3).
D1.11	Time required for analysis	The total analytical time for the analysis of 60 samples is approximately 100 minutes. The sample retention time is 7 minutes. (g)

(a) These data were obtained at the Thames Water Authority Lea Division, using a Technicon Auto-Analyser mark II system with a 15 mm flow-cell.
(b) Distilled water spiked with the stated concentration of chloride.
(c) River water.
(d) Same river water spiked with 23.1 mg/l chloride.
(e) Department of the Environment Harmonized Monitoring Programme.
(f) The performance data and the relatively high limit of detection are due to the use of a dialyser. If the samples are sufficiently clean for the dialyser to be omitted, a better performance and lower limit of detection can be obtained. Similarly if the dialyser is operated with counter current flows instead of flowing in the same direction as in Figure 1, different performance data are obtained. See Section D10.
(g) This is dependent on the sample and wash times used which is dependent on the accuracy required and with variations between the different samples. See reference 17.
(h) Fractional degrees of freedom can occur when data with varying degrees of freedom are combined, as from a mixture of inter and intra laboratory tests.
(i) Data from at least 10 laboratories in 8 Water Authorities have been used in proving this method.

D2 Principle

Chloride ions are first dialysed from an acid donor solution into a water receiving stream, and then mixed with acid chloride colour reagent containing mercury (II) thiocyanate. The released thiocyanate ions then react in acid solution with iron (III) nitrate to give a reddish-brown coloured iron (III) thiocyanate complex. The resulting intensity of the stable colour produced is measured at a wavelength of 480 nm.

D3 Interferences and Bias

The effect of other substances on the determination of chloride by this method are listed in Table 2. The data were obtained by the Thames Water Authority Lea Division.

Table 2 Interference test data for the automated mercury-iron thiocyanate method

Substance added	Test Substance Concentration mg/l	Total Chloride Concentration mg/l 0	20	180
		Effect upon the determination of Chloride as mg/l Cl^-		
Ammoniacal Nitrogen	50 (as N)	0	+ 0.3	+ 1.5
	100 (as N)	0	+ 0.5	+ 2.4
	250 (as N)	0	+ 0.4	+ 1.2
	500 (as N)	0	− 2.1	− 29.2
Nitrate Nitrogen	50 (as N)	0	− 1.1	− 1.0
	100 (as N)	0	− 1.3	+ 1.8
	500 (as N)	0	− 0.5	− 7.8
Nitrite Nitrogen	5 (as N)	0	− 0.2	− 2.4
	10 (as N)	0	− 1.0	+ 1.0
	25 (as N)	0	+ 0.4	− 21.0
	50 (as N)	+ 2		
Sulphate	500	0	+ 2.6	+ 1.2
Bicarbonate	500	0	− 0.8	− 4.1
Silicon	20 (as SiO_2)	0	+ 0.4	+ 0.7
	100 (as SiO_2)	+ 1.3	+ 1.4	− 3.1
	200 (as SiO_2)	0	− 0.8	− 20.0
	1000 (as SiO_2)	+ 6		
Orthophosphate	10 (as P)	0	− 0.4	+ 1.3
	50 (as P)	0	− 1.3	− 1.0
	100 (as P)	0	+ 1.2	− 24.5
Boron	50	+ 1.7	+ 1.7	− 8.9
Calcium	500	0	− 0.1	− 5.3
Sodium	137	0	− 0.8	− 4.1
	400	0	− 1.0	+ 1.3

Substance added	Test Substance Concentration mg/l	Total Chloride Concentration mg/l 0	20	180
		Effect upon the determination of Chloride as mg/l Cl^-		
Potassium	30	0	− 1.1	− 1.4
	224	0	+ 2.6	+ 1.2
Cyanide	20	+ 13	+ 12.6	+ 11.2
Thiocyanate	20	+ 19.7	+ 17.9	+ 25.6
Sulphate	20	+ 48.0	+ 49.0	+ 47.1
Perchlorate	20	0	− 1.0	− 2.6
Fluoride	10	0	− 0.4	− 6.4
Fluoride	100	0	+ 0.1	− 5.5
Bromide	10	+ 5.0	+ 5.3	+ 3.0
Bromide	100	+ 48.3	+ 40.2	+ 30.2
Iodide	10	0	− 3.2	− 4.6
	100	+ 4.0	− 0.7	+ 0.2
$F^-/Br^-/I^-$ (in combined solution)	2.0 of each	0	− 1.5	− 3.9
Anionic detergent as Manoxol OT	100	0	−	+ 0.9(a)
Nonionic detergent as Lissapol NX	10	+ 15.6	+ 8.1	+ 9.7

(a) This result at a chloride concentration of 100 mg/l
The results shown are the mean of duplicates.
If there were no interference, then for a 95% confidence level for duplicate samples, the results would be expected to lie within the following ranges:

mg/l Cl^-	
0	±1·24
20	±1·41
180	±4·31

D3.1 **Complex Cyanides**

Many complex cyanides are in equilibrium with cyanide ion. Such cyanides also interfere. Cyanoferrates (II) and (III) form intensely coloured blue and green complexes with iron which also cause interference with the measurement of the liberated thiocyanate.

D3.2 **Recovery Data from Spiked Samples**

Samples of three river waters and a borehole water were spiked with known concentrations of sodium chloride to give a range of samples varying from 20.0 to 90.0 mg/l total Cl^-. No two samples had the same final chloride content. These samples including the initial unspiked samples were used for a within-laboratory analytical quality control programme and the percentage recovery of each spike was calculated. Recoveries ranged from 93.0% to 104.2%, with a mean recovery of 97.8% at a total standard deviation of ± 4.0% with 9 degrees of freedom. One river water gave consistently low recoveries (93.7 ± 0.7%); the others gave no indication of any significant bias.

D4 Hazards

D4.1 The precautions given in the essay review on continuous flow anlaysis (17) should be observed.

D4.2 Nitric acid and iron (III) nitrate are corrosive. Eye protection and gloves should be worn when handling them, and any spillages washed away with copious quantities of cold water. Mercury (II) thiocyanate is toxic and should be handled with caution, care must be taken not to inhale or ingest dust. The solid should not be heated as it decomposes. Methanol is a fairly volatile and flammable solvent and should be handled with care in the fume cupboard, ensuring that no naked flames are in the vicinity.

D4.3 It is thought that mercury (II) thiocyanate may react with methanol and concentrated nitric acid to form mercury fulminate. Although this procedure uses dilute nitric acid in the chloride colour reagent, the solution should be kept cool when mixed and stored in a cool place when not in use.

D5 Reagents and Standards

Analytical reagent grade chemicals are used except where stated to the contrary. Provided the actual bottles themselves do not contain or absorb halide, either glass or plastic bottles may be used for reagent storage.

D5.1 Water

Distilled or deionized water is suitable. (50 ml of water in a 50 ml Nessler Cylinder should not give any opalescence when a few drops of silver nitrate solution (A5.2) followed by one drop of N/10 nitric acid are added to it; alternatively the specific conductance should be below 20 μS/cm).

The wash water should contain about 0.2 ml per litre of a wetting agent. Evaluate wetting agents for freedom from interference prior to use.

D5.2 Nitric acid solution 7.9M

Cautiously add with stirring and cooling 125 ± 1 ml water to 500 ± 2 ml concentrated nitric acid (d_{20} 1.42). Carefully boil the solution for 15 minutes to remove nitrous acid and allow to cool. Dilute the clear solution to 1 litre with water and mix.

D5.3 Nitric acid solution 0.75M

Dilute 95.0 ± 0.5 ml of the 7.9M nitric acid solution (D5.2) to 1 litre with water, and mix.

D5.4 Iron (III) nitrate stock solution

Dissolve 202 ± 0.5 g iron III nitrate in 500 ± 5 ml water in a 1 litre beaker. Carefully add 63.0 ± 0.5 ml of 7.9M nitric acid solution (D5.2) and mix. Transfer to a 1 litre calibrated flask, and make up to the mark with water. This solution is stable for at least 8 weeks.

D5.5 Mercury (II) thiocyanate solution

Dissolve 4.17 ± 0.01 g mercury (II) thiocyanate in methanol and dilute to 1 litre in a calibrated flask with methanol. Mix thoroughly, and filter the solution. Store in an amber-glass bottle. This solution is stable for at least 8 weeks.

D5.6 Chloride colour reagent

Mix 150 ± 1 ml iron (III) nitrate stock solution (D5.4) with 150 ± 1 ml mercury (II) thicyanate stock solution (D5.5) in a 1 litre calibrated flask. Dilute to the mark with water. Cool solution during preparation. This solution is stable for at least 4 weeks.

D5.7 Stock standard chloride solution 1 ml contains 1 mg chloride

Weigh 1.6484 = 0.0005 g sodium chloride, (dried to constant weight at 120–250°C) and dissolve in approximately 200 ml of water. Transfer quantitatively to a 1 litre calibrated flask and made up to the mark with water and mix. Stored in a stoppered glass bottle, this solution is stable indefinitely.

D5.8 Calibration standard chloride solutions

Prepare a series of standard chloride solutions containing 10, 20, 30, 40, 50, 80, 100, 150 and 200 mg/l by adding, 2.5, 5.0, 7.5, 10.0, 12.5, 20.0, 25.0, 37.5, and 50.0 ml of the stock solution (D5.7) to 250 ml calibrated flasks using a burette. Make up to the mark with water and mix. These solutions are stable for at least 4 weeks.

D6 Sample collection and Preservation

This is dependent on the nature of the sample, but the sample bottles, made of glass or plastic, must be halide free. No preservative is needed for chloride itself. If prevention of decomposition of other components is necessary, hydrochloric acid, chlorides, and disinfectants containing halogens, mercury, or silver must not be used for preservation of the sample.

D7 Apparatus

The following apparatus, shown diagrammatically in Figure 1, is required:

Sample presentation unit (sampler)
Multi-channel peristaltic pump with air inlet valve attachment
Analytical cartridge including pump-tubes, mixing coils and a 3″ dialyser with a cellophane dialysis membrane. The donor and recipient streams flow in the same direction.
Colorimeter incorporating a 15 mm path length flow-cell (Detector Unit)
Single-pen recorder output, or printer unit. (Recording Unit).

D8 Analytical Procedure

Step	Experimental Procedure	Notes
D8.1	Starting Operation. Arrange the apparatus as depicted in the flow diagram (Fig 1) (notes a and b.)	(a) Follow the manufacturer's general operating instructions (b) See reference 17.
D8.2	Place the reagent tubes in the respective reagent bottles with the sample probe in the wash water container. Start pump (note c). Switch on recording and detector units. Allow at least 30 minutes for the equipment to warm up (note d).	(c) With a newly-constructed manifold, pump-test to ensure hydraulic continuity. Check that bubbles do not accumulate in the flow-cell, and eliminate any problem before proceeding to the next step. (d) As the reaction is sensitive to temperature, every effort should be made to ensure that sample and standard temperatures are the same throughout the analysis.
D8.3	Initial Sensitivity Setting When a satisfactory base-line has been obtained with water for 15 minutes, aspirate a 200 mg/l standard solution through the sample line for about 3 minutes. Adjust the baseline response to about 2 per cent full scale (note e). Return sample probe to rest position (note f).	(e) An elevated baseline allows for any negative drift that may occur. (f) Remove traces of standard solution from probe, before replacing it.
	After a period of about 7 minutes from the beginning of step D8.3, a positive response appears on the chart. Adjust the response to give a reading at about 90 per cent of full scale (note g).	(g) A setting 10 per cent less than full scale allows for any increase of sensitivity that may occur.
D8.4	Analysis of samples Arrange the standards, blanks and samples on the turntable and start the sampler with the sampling rate set at 60 samples per hour (notes h and i).	(h) The samples and standards can be loaded on the turntable during the initial setting up period (steps 8.2 and 8.3). (i) Alternative loading arrangements are given in reference 17.

Step	Analytical Procedure	Notes
	Suggested position number on turntable / Solution 1–9 Calibration standards in ascending order of concentration 10 blank (note j) 11 Calibration standard (note k) 12–21 samples (note l) 22 blank 23 Calibration standard 24–33 samples 34 blank 35 Calibration standard Repeat the sequence 12–35 until all the samples have been analysed (note m). If it is thought necessary, repeat the calibration standards 1–9 at the conclusion of the run of samples.	(j) Use the same water as used to prepare the calibration standards. (k) The 150 mg/l standard is used to check variation in sensitivity. (l) A quality control standard should be included in one batch as a check on the system. See reference 7. The standard solution used should be different from that used for the calibration standards, but should be stored under identical conditions. (m) If cross-contamination is seen to occur (incomplete peak separation), either separate the samples by blanks and reanalyse them, or reanalyse with increased wash time.
D8.5	When the last sample or standard has been analysed and the final baseline is obtained, and all the responses have been registered on the recording unit, switch off this unit.	
D8.6	Shut-down Procedure Remove reagent lines, wipe dry with a tissue, and transfer to a beaker of deionized water and allow to pump though for 15 minutes. (note n)	(n) Pumping water through the system and shutting-down with water in the dialyser prolongs the life of the dialyser membrane, and also removes reagent and sample solutions from the tubing.
D8.7	Switch off pump and detector units.	
D8.8	Check all pump tubes for wear, replace any worn tubes with new flow-rated tubes.	
D8.9	Calculation of Results Plot a calibration curve of measurement unit responses (y axis) against concentration (x axis) of the calibration standard solutions. (notes o and p).	(o) Providing that the responses due to the blanks and calibration standards are acceptably close to their respective initial values. If not refer to reference 17 for a suggested alternative procedure to obtain calibration curves.
D8.10	Using the calibration curve convert the measurement unit responses due to the samples into the concentrations of chloride in the samples. (note p). The results are expressed as mg/l Cl^-.	(p) The measurement unit responses of the samples must first be corrected for any baseline and sensitivity changes.

D9 Extending the Range of the Method Upwards

Samples with a chloride concentration in excess of 200 mg/l should be diluted accordingly, and subjected to re-analysis. The result, corrected for blank and sensitivity, should then be multiplied by the dilution factor to obtain the chloride concentration in the sample.

D10 Extending the range of the Method Downwards

For very clean water samples, it may be possible to dispense with the dialyser; this greatly improves the sensitivity of the method. Samples may also be concentrated by evaporation and making up to a known volume. For samples not amenable to such treatment, some improvement in sensitivity can be gained by operating the dialyser with counter current flows, though this affects the linearity of the calibration curve for concentrations close to the limit of detection. To eliminate this, add a known amount (eg 100 mg/l) of chloride as sodium chloride when running both samples and standards, this extra chloride being added to the nitric acid stream. Typical performance characteristics for counter current dialyser operation are given in Table 3.

Table 3 Performance Characteristics for use of a Counter Current Dialyser (compare with Section D1.4, D1.6 and D1.7. All other data are similar to that with the Parallel Flow Dialyser shown in Figure 1).

(i) Range of Application up to 300 mg/l.
(ii) Total Standard Deviation (a).

Sample	Chloride concentration (mg/l)	Total Standard deviation (mg)	Degrees of freedom	Recovery of spike %
Distilled water	0	0.48(b)	22	
Sodium chloride	30	0.46	12	
in distilled	198	0.81	6	
water	270	1.52	14	
		1.59	9	
		1.25	6	
River water	40.8	0.38	14	
Spiked river water (c)	137.1	0.85	19	99.0
Sewage final effluent	65.4	1.02	4	
Spiked sewage final effluent (c)	209.3	3.67	4	97.9
Treated borehole water	19.6	0.52	9	
Spiked treated borehole water (c)	212.3	1.35	6	98.4

(a) These data were obtained by the Anglian Water Authority, Regional Standards Laboratory, Cambridge. Sample and wash times were 120s and 12s respectively. The Calibration Standards used were 300, 250, 200, 150, 100, 50 and 25 mg/l Cl^-. 100 mg/l Cl^- was added to the nitric acid stream (see Figure 1) and the concentration read out was adjusted so as to correct automatically.
(b) Within batch standard deviation.
(c) The preceding sample spiked with sodium chloride.

(iii) Limit of Detection 1.36 mg/l with 22 degrees of freedom.

Note if the 100 mg/l chloride addition were omitted, the calibration curve is slightly dished below 50 mg/l (see Figure 2).

D11 Checking the Accuracy of Analytical Results

As there are many factors which can adversely affect the performance of the method, it is advisable to carry out experimental tests to check the sources of inaccuracy. Periodically, a series of replicate standards and samples should be analysed to obtain data on mean and standard deviations. In addition an analytical quality control standard should be analysed in duplicate at least once a day and the responses entered on an appropriate control chart. The control standard used in this method corresponding to 0.9C is 180 mg/l where C equals the highest working standard. See also references 6–9.

The use of analytical quality control, and construction of control charts is discussed in reference 7.

D12 Effluent Disposal and Mercury Recovery

In order to avoid risk to the Environment, eg sewage treatment works, watercourses and the sea, and also to recover an expensive reagent, wastes containing mercury should be treated to remove mercury. See Section H2. Mercuric compounds are notifiable wastes and must not be disposed of to land or water without consent.

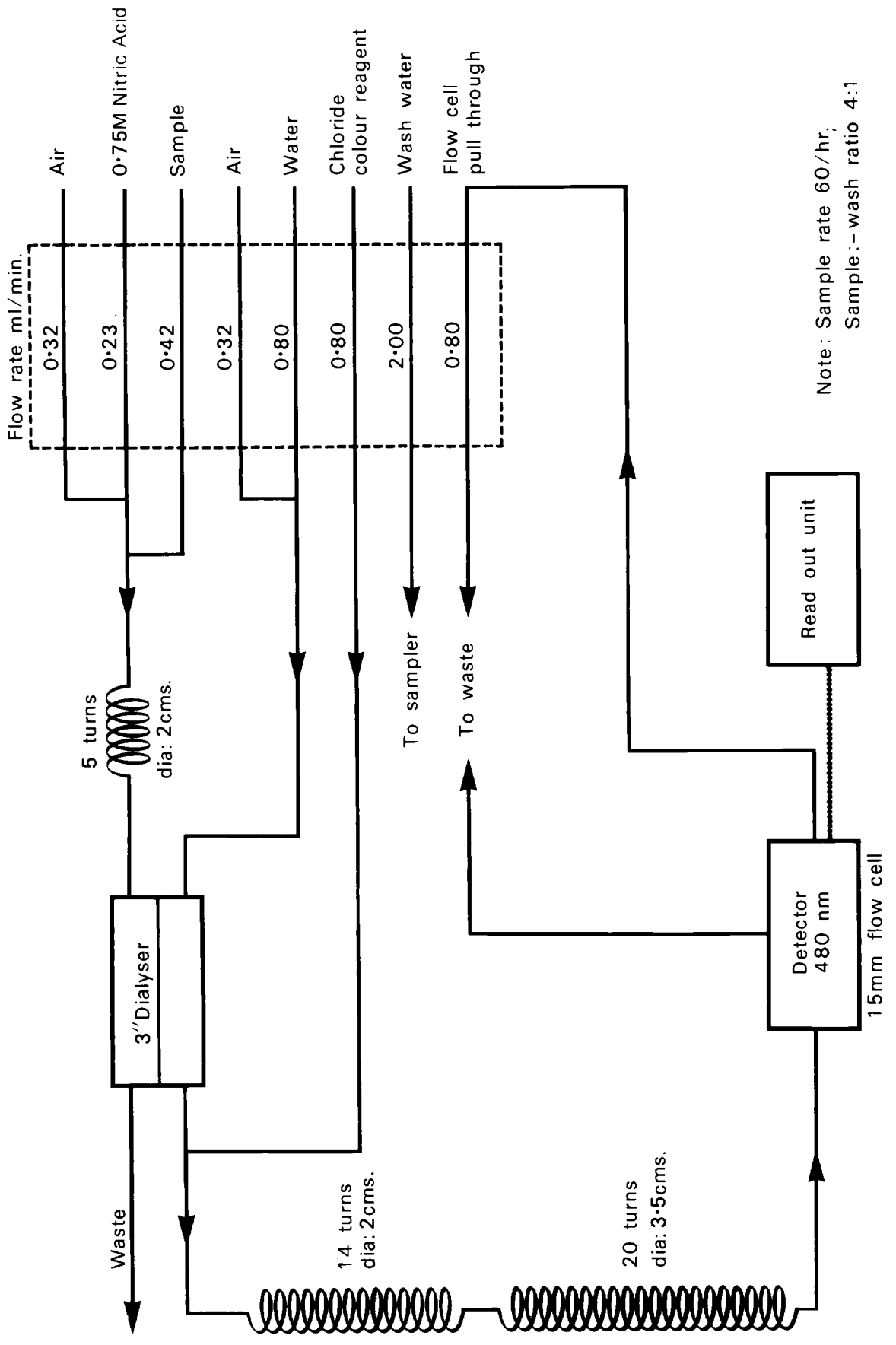

Fig.1 CHLORIDE IN WATER (0–200 mg/l)

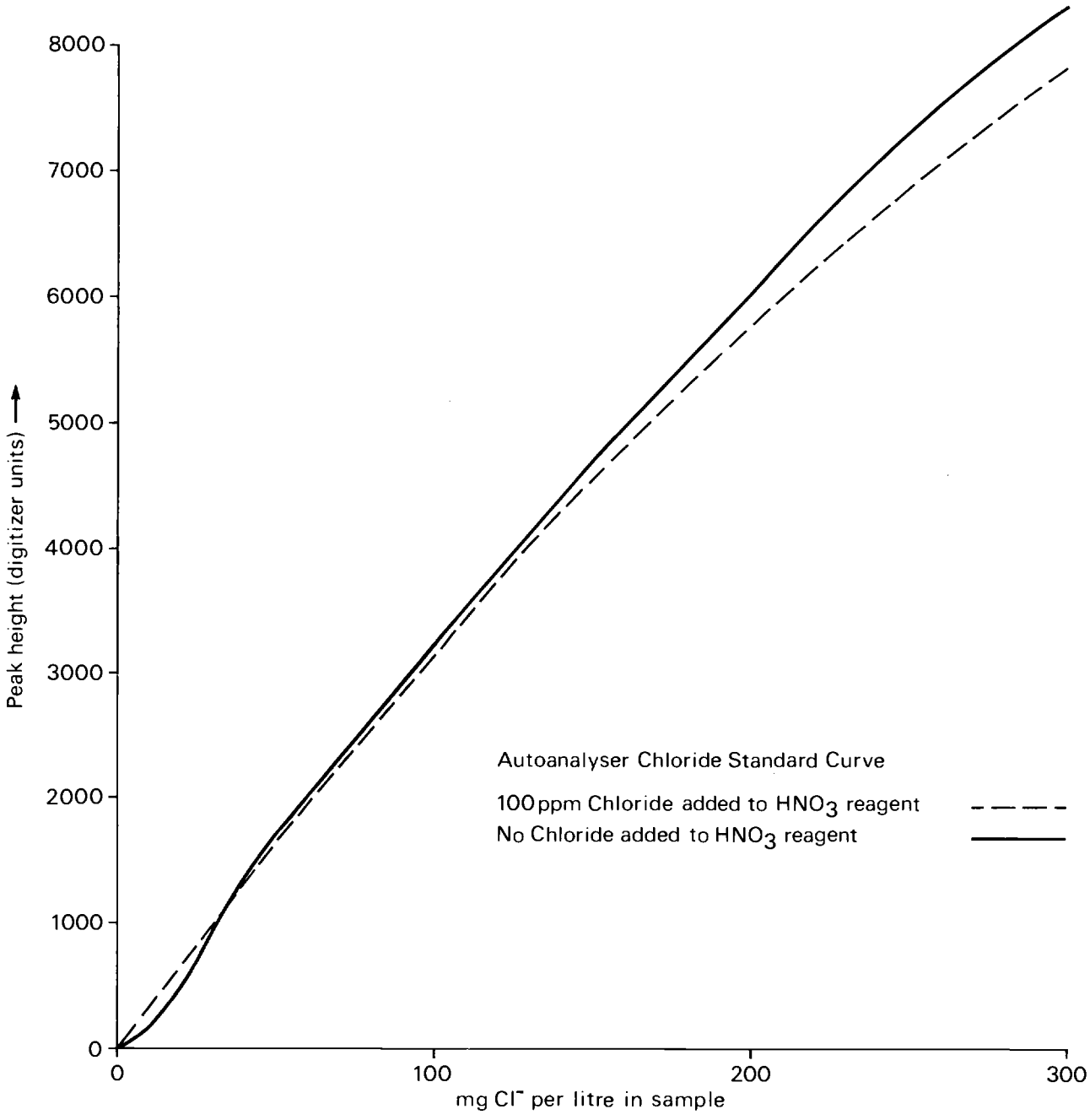

FIG. 2 COUNTER CURRENT DIALYSER RESPONSE CURVES

E Note on the Chloride ion Selective Electrode

E1 Use

The chloride ion-selective electrode is used for rapid and control analyses especially of rivers and other relatively clean waters, where it is inconvenient to bring all the samples to the laboratory, when a continuous monitor of chloride concentration is required, and also as a finish to certain special analyses which stoichiometrically generate relatively pure solutions of a soluble chloride or hydrochloric acid for subsequent quantification.

There are two types of chloride electrode, one using a solid state membrane, the other a liquid ion-exchange membrane. In addition, the solid state electrode is manufactured in two important variations using silver chloride and mercurous chloride. (Chloride electrodes should not be confused with the chlorine electrode which is usually a redox electrode).

E2 Limit of Detection and Range

The limit of detection varies with electrode and technique from <0.001 mg/l to 0.05 mg/l. The range for 10% coefficient of variation is about 0.2 to 350 mg/l.

E3 Interferences and Poisons

Solid State electrode:–	Liquid Ion-exchange electrode:–
Bromide, iodide, sulphide, thiosulphate, cyanide, reducing agents, ammonia.	Perchlorate, nitrate, sulphate, bromide, iodide

The solid state electrode type has the better stability, if not poisoned.
Some forms of organic matter can damage both types of electrode.

E4 Sample Type

All types of electrode can be used for most clean waters and solutions, but the different susceptibility to interference precludes the use of solid state electrodes with many sewage and sewage effluents samples. Before use check for absence of the appropriate interferents.

E5 Analytical Procedure

The electrodes are calibrated against standard chloride solutions. Full calibration is only required if the electrode is used below the limit of Nernstian response. As the response from these electrodes is also dependent on pH, ionic strength and temperature, samples and standards should have similar pH and ionic strength values and be at the same temperature.

Some chloride electrodes can be used over the pH range 2.3–7.8. Mercury I Chloride (calomel) type electrodes must not be used at a pH value above 3. Silver Chloride type electrodes are often used with an ammonium acetate buffer at a pH value of 4.7 or with a citrate buffer at a pH value between 2.5–2.8. Ionic strength and pH are adjusted by addition of a suitable buffer solution.

The reference electrodes must either not contain chloride, or be a double bridge type, otherwise it can contaminate the sample.

For additional information and references see references 23 and 24.

F Note on the Silver Coulometric Determination of Chloride

F1 Principle

Chloride ions in an acid-buffered solution are titrated with silver ions generated in situ by the passing of a known, constant current through silver electrodes. The end-point of the titration can be detected by monitoring the conductivity of the solution which changes rapidly with the formation of free silver ions when all the chloride ions have been precipitated out of solution as silver chloride. As the current is kept constant the concentration of chloride ions can be directly related to the time of current flow (see refs 21 and 22).

F2 Use

Instruments based on this principle are commercially available and can be used by operators with the minimum of training for the laboratory determination of chloride.

F3 Range

Typical ranges of application quoted are 10–300 mg/l Cl.

F4 Interferences

The presence of other halides, sulphides or other substances reacting with silver ions in an acid medium will lead to falsely high results. Fouling of electrode surfaces can cause erratic results.

F5 Calculation of Results

1 ampere second is equivalent to 0.3674 mg of chloride. If fouling is suspected, also compare with standard chloride solutions.

G Note on the use of Ion Chromatography

Ion chromatography can be used to determine chloride in the presence of bromide, iodide and many other anions. The range of the method is very dependent on the size of the sample aliquot injected, the concentrations of other anions in the sample which elute close to chloride, and whether a concentrator column is used. If the other anions do not overlap, a 1 ml aliquot will give a limit of detection down to 20 μg/1, but a limit of detection of <1 μg/1 can be achieved using a concentrator column. For further details see the essay review 'Ion Chromatography in the Analysis of Water Samples', also published in this series (18).

H Effluent Disposal and reagent Recovery

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

H1 Silver

H1.1 Removal of silver

Place 40 ml of hydrochloric acid (d_{20} 1.18) in a Winchester bottle and add the spent test solutions including precipitates to the acid. When the Winchester is full, allow the silver chloride precipitate to settle overnight. Decant the supernatant liquid into a beaker, and discard the liquid. Wash the settled precipitate with water, by decantation, until the washings are no longer strongly acid.

H1.2 Silver Recover

Silver chloride can be dried, and stored until sufficient has accumulated to make it worth selling back to precious metal refiners. The minimum amounts purchased are not excessive. Precious Metal Dealers are listed in Trade Directories such as the latest edition of Kompass (19). Alternatively, one of the variants of the following procedure may be used. The silver chloride is first converted to crude silver by reduction with an aluminium-silver couple. The crude silver is dissolved in nitric acid to form crude silver nitrate, which can be crystallized out, converted to solid silver sulphate for use in COD determinations (ref 29), or further purified by electrolysis to silver metal which can be redissolved in nitric acid and a purer grade of silver nitrate obtained.

H1.2.1 *Reduction to Crude silver*

H1.2.1.1 *Apparatus*

Face shield
5-litre plastic beaker
Stirrer with propeller attachment
1-litre Buchner flasks
11 cm diameter Hartley funnel
Glass fibre filters, 11 cm diameter, retaining particles over 1 μm with a rapid rate of filtration
1-litre Erlenmeyer flasks
Hot plate
Shallow PTFE coated baking tray
Vacuum desiccator
This apparatus is required for the whole of Section H1.2. A few additional items are listed in the appropriate sections.

H1.2.1.2 *Reagents*

Silver chloride slurry
Aluminium foil, cut into approximately 2 cm squares
Hydrochloric acid d_{20} 1.18
Industrial methylated spirit.
Nitric acid d_{20} 1.42
Silver powder retained from the procedure, or precipitated from a silver nitrate solution by copper wire.
Sodium sulphate decahyydrate
Sulphuric acid solution 10% V/V

H1.2.1.3 *Hazards*

Silver salts stain the skin brown. Although no permanent harm is likely to be caused by splashes in the eye, face shields should be used when there is risk of splashing. Vacuum filters and desiccators may implode, such filtration and drying should always be done inside a safety screen and face shields and gloves used.

H1.2.1.4 *Procedure*

WEARING A FACE SHIELD, wash and filter at the pump enough silver chloride slurry to give about 300 g of moist cake, the weight of water retained by the solid being relatively small.

Suspend the caked solid in about 2.5 litres of water in a 5-litre plastic beaker and stir, taking care to avoid splashing.

Add about 1 g silver powder and 30 g aluminium foil. Stir continuously for about 3 hours and allow to stand overnight.

If an aluminium hydroxide floc forms, dissolve by adding the minimum of hydrochloric acid d_{20} 1.18.

Filter the deposited silver powder at the pump through a GF/C filter (or equivalent) and wash with water. Discard the filtrate.

H1.2.2 *Formation of Silver Nitrate*

The same procedure is used either for the crude silver obtained in step H1.2.1.4 or for the purer silver obtained from step H1.2.4.

H1.2.2.1 *Solution Procedure*

Distribute the filtered residue from step H1.2.1.4 into 1-litre erlenmeyer flasks and add about 30 ml water to each. Add the minimum of nitric acid to dissolve the silver completely, but there will be a small residue of aluminium foil and silver chloride. Boil the contents of the flasks in the fume cupboard until brown fumes cease to be evolved, and cool.

Dilute each flask with 200 ml water and filter at the pump through glass fibre filters into litre Buchner flasks. Store the residue on the filter in a suitable container for future recovery.

If solid silver nitrate is required, proceed with step H1.2.2.2. If solid silver sulphate is required proceed with Section H1.2.3. If silver nitrate solution is required dilute as required.

H1.2.2.2 *Crystallization Procedure*

Transfer the silver nitrate solution to a wide form 1-litre beaker and cautiously evaporate the solution on a hot plate to about 100 ml. Cover and cool in a dust-free dark place to crystallize, finishing at about 4°C in a refrigerator. Filter off the crystals rapidly, using a glass fibre filter and suction. Suck dry and complete the drying in a vacuum desiccator.

The filtrate may be saved and added to future evaporated batches. Silver nitrate has an exceptionally high solubility in water which varies considerably with temperature (9.52 Kg/l at 100°C and 1.2 Kg/l at 0°C), hence filtrates still contain relatively large amounts of silver.

H1.2.3 *Formation of Silver Sulphate*

H1.2.3.1 *Additional Reagents*

Sulphuric Acid 10% V/V. Measure out 100 ml of sulphuric acid d_{20} 1.84 and pour slowly with stirring and cooling into 800 ml of water in a 2-litre beaker. Cool and make up to 1-litre with water in a measuring cylinder. Store in a glass bottle.

H1.2.3.2 *Procedure*

Transfer the solution from step H1.2.2.1 or the filtrate from steps H1.2.2.2 into one or more 1-litre erlenmeyer flasks and add about 120 g sodium sulphate decahydrate to each.

Bring to the boil with stirring and allow to cool at room temperature with occasional stirring. Leave in the refrigerator overnight for more complete precipitation of silver sulphate.

Filter all the precipitated silver sulphate at the pump through a CF/C filter, collecting the filtrate in a litre Buchner flask and wash each Hartley funnel with three 25 ml portions of sulphuric acid solution 10% V/V. DO NOT DISCARD THE FILTRATE.

Return the filtrate and washings into the silver residue bottle to reprecipitate as silver chloride the silver which has not been converted to silver sulphate.

Wash each full Hartley funnel of silver sulphate with three 25 ml portions of industrial methylated spirit and dry rapidly at the pump. Discard the filtrate.

Spread the silver sulphate onto a shallow PTFE coated tray and air-dry at room temperature, preferably in the dark, and ensuring that no organic matter falls onto the powder.

H1.2.4 *Preparation of Silver Crystals*

Compact the crude silver from step H1.2.1.4 with a suitable central electrical connection of silver wire to form an anode. Set up, in a fumehood, an electrolytic cell with this anode and a sheet silver cathode. Make up an electrolyte which is approximately

2% V/V nitric acid (d_{20} 1.42),
2–5% m/V silver nitrate,
the balance being water

Electrolyse at a cathode potential of 0.8 volts. The deposit should be granular and, after switching off the current may be scraped off, washed with water and dried. Having a warm but not boiling electrolyte is reported to improve the cell performance.

When the anode is too frail for further use, shut down the cell. Spent electrolyte may contain impurities from the anode. This should be treated as in Section H1.1 above.

The residual anode can then be redissolved in nitric acid to form silver nitrate as in Section H1.2.2 above.

H1.2.5 *Efficiency data for steps H1.2.1, H1.2.2 (except step H1.2.2.2) and H1.2.3*

(a) If required, the recovery may be stopped at the silver metal stage and the silver stored as dry metal powder, contaminated with a small amount of aluminium foil and silver chloride.
(b) It has been shown that about 95% silver chloride is converted to silver metal.
(c) It has also been shown that about 70% silver metal is converted to silver sulphate. The remaining 30% can be recycled for recovery in future batches.
(d) An assay (reference 1) of 99% was obtained on portions of recovered silver sulphate.
(e) The COD blank value obtained using a 1% W/V solution of recovered silver sulphate in sulphuric acid d_{20} 1.84 by the standard procedure (reference 29) was satisfactory.

Data supplied by North West Water Authority, Workington Laboratory.

H1.2.6 *Warning. Do not attempt to reduce ammoniacal solutions of silver salts.*

Silver azide, a highly unstable explosive, can be formed and many accidents have been so caused.

H2.1 Removal of mercury

Add between 1 and 3 g of stock ferrous sulphide to the collected liquid in a large beaker. Allow to stand at least 24 hours, occasionally swirling or stirring the solution to disperse the hydrogen sulphide, and finally allow the precipitated mercuric sulphide to settle. Decant the supernatant liquid. Wash the settled precipitate with water by decantation until free of hydrogen sulphide.

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

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

H2.2 Mercury recovery

Metal refiners and recoverers may possibly accept mercury sulphide for recovery, for further information see a trade directory such as the appropriate section of Kompass (19). See also Ref 20. The sections which follow give ways in which laboratories may recover mercury for re-use. The first and apparently simplest method is fraught with technical problems and hazards. It is only mentioned as a warning.

H2.2.1 *Unless personel already experienced in the method are available do not attempt to recover mercury from the sulphide in the laboratory by heating it in a stream of air with or without the addition of sodium carbonate. The metal is very volatile and is difficult to condense into a pool of liquid.* It can be recovered as nitrate using the procedure outlined below.

H2.2.2 *Procedure*

Decant off the excess liquid from the mercury sulphide and wash the solid residue with dilute hydrochloric acid in a fume cupboard to remove any un-reacted ferrous sulphide. Filter off the mercury sulphide and transfer it to a suitable large beaker, add concentrated hydrochloric to more than cover the mercury sulphide. Then add potassium chlorate a crystal at a time and warm, but do not boil until all the sulphide has dissolved. Cool this colution, dilute with water and pour slowly with stirring into excess approximately 2N sodium hydroxide solution. The precipitate should be yellow. If a reddish-brown precipitate starts to form, add more sodium hydroxide. Filter off the yellow precipitate (Note a), wash to remove excess sodium hydroxide, then dissolve in a slight excess of concentrated nitric acid and allow to crystallize in a dessicator over quicklime. The crystals are mercuric nitrate hemihydrate. The liquor can be kept for further evaporation.

(a) This filtrate and washings will contain traces of dissolved mercury salts. It should be acidified and treated with ferrous sulphide in a fume cupboard as in Section H2.1.

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