Fluoride in Waters, Effluents, Sludges, Plants and Soils 1982

Methods for the Examination of Waters and Associated Materials

London Her Majesty's Stationery Office £5.85 net

Fluoride in Waters, Effluents, Sludges, Plants and Soils Methods for the Examination of Waters and Associated Materials

Contents

Warning to users 3
About this series 4
About this booklet 5

Part 1: Fluoride in Raw and Potable Waters
Introduction 7
Sample Collection and Preservation 8

Method A: Potentiometric Method (Ion-Selective Electrode) (Recommended Method) 9
A1 Performance Characteristics of the Method 9
A2 Principle 10
A3 Interferences 10
A4 Hazards 11
A5 Reagents 11
A6 Apparatus 12
A7 Analytical Procedure 12
A8 Sources of Error 14

Method B: Eriochrome Cyanine Colorimetric Method (Tentative) 17
B1 Performance Characteristics of the Method 17
B2 Principle 17
B3 Interferences 18
B4 Hazards 19
B5 Reagents 19
B6 Apparatus 20
B7 Analytical Procedure 20
B8 Sources of Error 21

Method C: Lanthanum Alizarin Fluorine Blue Spectrophotometric Method (Tentative) 22
C1 Performance Characteristics of the Method 22
C2 Principle 23
C3 Interferences 23
C4 Hazards 23
C5 Reagents 23
C6 Apparatus 24
C7 Analytical Procedure 25
C8 Sources of Error 26

Method D: Ion-Chromatographic Method (Tentative) 28
D1 Performance Characteristics of the Method 28
D2 Principle 29
D3 Interferences 29
D4 Hazards 29
D5 Reagents 29
D6 Apparatus 30
D7 Analytical Procedure 30
D8 Sources of Error 32

Part 2: Fluoride in Effluents, Sewage, Sewage Sludge, Plant Materials and Soils
Introduction 37
Sampling of Plant Material 37

Method E: Acid Extraction Method (Tentative) 38
E1 Performance Characteristics of the Method 38
E2 Principle 39
E3 Field of Application and Interferences 39
E4 Hazards 39
E5 Reagents 39
E6 Apparatus 40
E7 Sample Collection Preservation and Preparation 41
E8 Analytical Procedure 41
E9 Extension of Method 43

Method F: Alkali Fusion Method (Tentative) 44
F1 Performance Characteristics of the Method 44
F2 Principle 45
F3 Interferences 45
F4 Hazards 45
F5 Reagents 46
F6 Apparatus 47
F7 Sample Collection, Preservation and Preparation 47
F8 Analytical Procedure 47
F9 Change in Concentration Range of the Method 49
F10 Sources of Error 49
F11 Use of Standard Addition or Known Addition Procedures 50

Part 3: Pre-Treatments for Special Samples
Introduction (read this section first if pre-treatment is thought to be necessary) 52

Method G: Pre-Treatment Procedure for Ashing Prior to Separation by Diffusion, Distillation or for Direct Analyses. 53

Method H: Evaporation of Samples to Dryness. 56

Method J: Pre-Treatment Procedure for the Separation of Fluorides by Distillation. 57

Method K: Pre-Treatment and Procedure for the Separation of Fluorides by Diffusion. 63

Method L: Pre-Treatment Procedure for the Separation of Fluorides by Pyrohydrolysis. 66

Section M: Effluent Disposal and Reagent Recovery 69

Section N: Checking the Accuracy of Analytical Results. 72

Section O: Estimation of the Accuracy of Analytical Results Using the Tentative Methods in this Booklet. 73

Address for correspondence 73
References 74
Membership Responsible for this Method 75

London Her Majesty's Stationery Office

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 specification. Specifications for reagents, apparatus and equipment are given in manufacturers' catalogues and various published standards. If contamination is suspected, reagent purity should be checked before use.

There are numerous handbooks on first aid and laboratory safety. 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 Series No 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.

First published 1983

ISBN 0 11 751662 7

About this series

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

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

1.0 General principles of sampling and accuracy of results
3.0 Empirical and physical methods
4.0 Metals and metalloids
5.0 General non-metallic substances
6.0 Organic impurities
7.0 Biological methods
9.0 Radiochemical methods

The actual methods etc. are produced by small 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.

T A DICK
Chairman

L R PITTWELL
Secretary

8 November 1982

About this booklet

The control of fluoride in the water cycle and as a potential pollutant of both water and land may require its determination in a wide variety of materials. No one method is suitable for all types of sample and this booklet therefore provides a number of different methods. It also includes information on sample pre-treatment and separation of fluoride which is not readily available from any one source. The booklet is therefore larger than usual, but the additional information should be useful to analysts in the water industry and elsewhere. The main features of the methods are summarised in the following table (Table 1).

This booklet is divided into three parts:

Part 1: Methods for Fresh and Saline Waters including some sewages and effluents (Methods A to D)

Part 2: Methods for Sewage Sludge and related materials including plant materials and Soils (Methods E and F)

Part 3: Pre-treatments and Separation methods for Special Circumstances (Methods G to L)

Fluorine in aqueous solution usually occurs as a simple ion (F^-), undissociated HF, acid fluorine ion and as complex fluoro-anions of, for example, boron, silicon, phosphorus, aluminium, tin, iron, beryllium etc. Pre-treatment of samples and the use of 'de-complexing' agents converts some but not all of these complex fluoro-anions to fluoride ion. There are also several highly insoluble naturally occurring simple and complex metal fluorides such as fluorite (CaF_2) and fluoroapatite ($Ca_3F(PO_4)_3$). Parts 1 and 2 are intended for routine use and most analyses for fluoride in water and associated materials can be accomplished with these methods (A-F). A note is included in Part 2 dealing with a special problem sometimes encountered when sampling crops for fluoride analysis. Part 3 gives pre-treatments intended for the determination of total fluorine when either the more stable fluorocomplexes or the highly insoluble compounds are present in the sample. A procedure for the recovery of silver is included.

Special attention is directed to the hazards involved in the use of perchloric acid in Methods J and K in Part 3.

Some methods are very sensitive to minor physical and chemical variations in the quality of the materials and apparatus used. Hence several methods mention the actual equipment used for the evaluation tests. This in no way endorses this as superior to other similar equipment. Equivalent apparatus is equally acceptable though it must be understood that the performance characteristics may be slightly different. It is left to the senior supervising analyst to evaluate and choose from the appropriate brands available.

Throughout this booklet fluoride is expressed as F^-.

Table 1 Summary of Methods in this Booklet

Method	Range	Limit of Detection	Main Interference	Special Apparatus	Time Required	Other Comments
Part 1 — Methods for Raw & Potable Waters:-						
	mg/1F	mg/1F				
A. Ion Selective Electrode	0.1–5.0	0.1	Ionic Strength Fluoride complexes	Fluoride Electrode	7 mins per sample	
B. Eriochrome Cyanine Colorimetric	up to 2.0	0.2	Sulphate	—	15 samples per hour	
C. Lanthanum Alizarin Fluorine Blue Spectrophotometric	up to 1.7	0.05	from Aluminium	—	5 samples per hour	Suitable for sea water
D. Ion-Chromatographic Method	above 5	0.01	—	Ion Chromato-graph	Depends on ions present. Typical 5 mins.	

Method	Range	Limit of Detection	Main Interference	Special Apparatus	Time Required	Other Comments
Part 2 — Methods for Sewage Sludge, Plants & Soils:-						
	mg/KgF	mg/KgF				
E. Acid Extraction	4–80 (wet basis)	4 (wet basis)	Fluoride Complexes	Fluoride Electrode	1 hour a single sample	
F. Alkali Fusion	10–1000 (dry basis)	10 (dry basis)	Fluoride Complexes	Fluoride Electrode	2–3 hours per single sample 10samples in 5 hours	
Part 3 — Pre-treatment and Separation:-						
G. Ashing	5mg–0.5gF					
H. Evaporation	—					
J. Distillation	5mg–0.5gF	5mgF	—	Distillation Apparatus	2 hours per sample	Note: Hazard from perchloric acid
K. Diffusion	0.05–200mgF	—	—	Diffusion Cells	overnight procedure	
L. Pyrohydrolysis	10mg+F	—	—	Pyrohydrolysis furnace train	2 hours per sample	

Part 1: Fluoride in Raw and Potable Waters

Introduction

Fluoride occurs naturally in some waters and may be added in controlled amounts to drinking water. Where fluoridation is practised in countries with a temperate climate, a concentration of about 1.0 mg/l is recommended for drinking water by the medical profession as having a beneficial effect in reducing the incidence of dental caries. Excessive amounts of fluoride are harmful, causing mottling of the teeth and deformation of bone structures.

The practice of fluoridating public water supplies calls for the accurate determination of both the natural background levels of fluoride and the concentration after the addition of fluoride, so as to maintain the fluoride between fairly narrow limits (0.8 to 1.2 mg/1 in the United Kindom).

An ion-selective electrode method (Method A) and two colorimetric methods (Method B and C) are given in this part. Methods A and B are primarily intended for the analysis of fresh waters, and are unsuitable for sea water. The high ionic strength of sea water causes problems with Method A and the high sulphate content with Method B. Method C is suitable for sea water, but its use for fresh waters, especially potable waters is restricted due to interference by relatively low levels of aluminium.

None of these methods is free from interferences, and whilst many potable waters can be dealt with directly, others and also polluted waters require a preliminary separation of fluoride to ensure accurate results. Methods for the separation of fluoride are included in this booklet.

Comparative tests using a variety of different waters have been carried out. The results, which are summarised in Table 2 show clearly the effect of large amounts of sulphate interferences with Method B (Eriochrome Cyanine colorimetric) and other minor problems with the Method C (Lanthanum Alizarin Fluorine Blue) which make the recommendation of several methods essential if reliable results are to be obtained on a variety of types of sample. These tests also showed that success with Method A using the ion selective electrode is dependent on the make of electrode. In consequence, whilst the electrode used in these tests is mentioned, this does not imply specific recommendation of this electrode.

Ion chromatography can separate fluoride from most other anions and a recently developed method is included.

Table 2 Comparative Tests of Methods in this Booklet

Method		A(a) (b)	A(a) (c)	B (b)	C (b)	Sulphate Content
Water Sample		mg/1 F	mg/1 F	mg/1 F	mg/1 F	mg/1 SO_4 (g)
Drinking Water:						
Borehole I	(d)	0.12		0.11	0.06	105
Borehole II	(d)	0.12		0.08	0.13	145
Upland Impoundment I	(d)	0.04		0.07	0.05	20
Upland Impoundment II	(d)	0.04		0.06	0.05	
Treated River Water	(d)	0.05		0.07	0.05	

Method		A(a) (b)	(c)	B (b)	C (b)	Sulphate Content mg/1 SO_4 (g)
Water Sample		mg/1 F	mg/1 F	mg/1 F	mg/1 F	
Raw Waters:						
Borehole I	(d)	0.14		0.09	0.14	
Borehole II	(d)	0.11		0.09	0.07	
Borehole III	(d)	0.14		0.10	0.11	
River Water I	(e)	0.39	0.33	0.58	0.34	150
River Water II	(d)	0.26	0.26	0.39	0.15	87
Mine Water:	(e)	0.60		0.61	0.76	85
Other Borehole Waters:						
F3784	(e)	3.22	3.10	4.20	3.00	1,750
F3774	(e)	0.59	0.49	0.60	0.60	197
F3914	(e)	0.14	0.13	0.33	0.11	647
F3794	(e)	0.70	0.60	0.73	0.84(f)	185
Sewage Works Effluent:						
D6851	(e)	0.45	0.34	1.1	0.46	140-150

(a) Orion Fluoride Electrodes
(b) Analysed by University of Liverpool Department of Oceanography
(c) Analysed by Thames Water Authority, Lea Division
(d) Sample provided by North West Water Authority
(e) Sample provided by Thames Water Authority, Lea Division
(f) A precipitate formed on addition of the reagent, this result obtained using only 5 ml of sample
(g) Typical range value, not sample analysis

General Considerations

Sample Collection and Preservation

Samples should be taken in polyethylene bottles which have been washed with 10% v/v hydrochloric acid and thoroughly rinsed with fluoride-free water. No preservative is normally necessary. Analysis should be carried out as soon as reasonably possible.

A Method for the Determination of Fluoride — Potentiometric Method (Ion-Selective Electrode) (Recommended Method)

A1 Performance Characteristics of the Method

(See also Table 1)

A1.1	Substance Determined	Dissolved fluoride including that in certain soluble inorganic complexes
A1.2	Types of Sample	Potable and other non-saline waters
A1.3	Basis of Method	After the addition of a reagent to adjust the pH value and ionic strength and to release fluoride ion from certain complexes, the fluoride ion concentration is measured potentio-metrically with a fluoride-selective electrode.
A1.4	Range of Application	Tested over the range 0.1 to 5.0 mg/1 but can be extended to higher concentrations.
A1.5	Calibration Curve	The electrode potential has a linear relationship to the logarithm of the fluoride concentration down to about 0.1 mg/1

A1.6 Standard Deviation

Sample Type	Concentration of Fluoride found mg/1 F	Total Standard Deviation mg/1 F^-	Degrees of Freedom
Potable Water	0.12	0.001–0.006	2–13
Potable Water spiked with sodium fluoride to 5.0 mg/1 F^-	5.0	0.027–0.16	2–13
Potable Water fluoridated to 1.0 mg/1 F^-	0.96	0.008–0.027	2–13
Water naturally high in fluoride	0.59	0.004–0.021	2.19

A1.7	Limit of Detection	The method is not recommended for the determination of fluoride below the limit of Nernstian response, which is usually about 0.1 mg/1F^- depending on the electrode combination and the purity of the reagents used. Below 0.1 mg/1F^- there is an increasing probability of erratic electrode response.

A1.8	Sensitivity	Theoretically the potential of a chemical sensor changes by 59.16 mV at 25°C for each decade change in fluoride concentration. (The Nernstian constant for univalent ions). In practice the change in e.m.f. per decade change in fluoride concentration above 0.2 mg/1 should not be less than 55 mV at 25°C.
A1.9	Bias	Not known but see Table II and Sections 1.6, 3 and 8.
A1.10	Interferences	Of the other commonly occurring ionic species in water, the electrode responds directly only to the hydroxyl ion. Buffering of the sample normally overcomes this effect. Any chemical species which reduces the concentration of fluoride ions in the sample will interfere (see Section 3).
A1.11	Time required for Analysis	At 1 mg/1, 7 mins per measurement. At lower concentrations of fluoride ions a longer equilibration time may be necessary.

(a) Based on information supplied by the following organisations:

Colne Valley Water Company, South West Water Authority, Laboratory of the Government Chemist, British Steel Corporation and North West Water Authority.

A2 Principle of the Method

The fluoride electrode is chemical sensor in which the detector is a doped single crystal of lanthanum fluoride across which a potential is developed in the presence of fluoride ions. It is normally used with a standard calomel reference electrode and a high impedance millivolt meter or pH meter with expanded millivolt scale.

The electrode responds to the activity rather than the concentration of the fluoride ions and to ensure a constant relationship between activity and concentration, samples and calibration standards must be adjusted to a constant ionic strength. They must also be buffered at a suitable pH value to prevent interference by hydroxide ions and also the formation of unionised HF under acid conditions. The buffer reagent contains metal-complexing agents (de-complexing agents) to release free fluoride ion from certain metal-fluoride complexes, to which the electrode does not respond. Simple fluoro-silicates are rapidly hydrolysed in water and are detected as fluoride by the electrode (1, 2).

A3 Interferences

Of the commonly occurring ionic species (other than fluoride) the electrode responds directly only to hydroxide ions. This effect causes serious error if the hydroxide ion concentration exceeds one tenth of the fluoride ion concentration. Under acidic conditions the formation of HF reduces the concentration of fluoride ions. The ionic strength adjustment reagent is designed to avoid these interferences with all but strongly acid or alkaline samples by maintaining the pH of the sample between pH 5.0 and 6.0.

Polyvalent cations e.g. Ca, Fe and A1 alone or in combination with other species form complexes with fluoride to which the electrode does not respond. The ionic strength adjustment buffer contains trans 1, 2 diaminocyclohexane N,N,N' ,N' – tetra-acetic acid (CDTA) as a decomplexing agent and the effect of certain potentially interfering species on a solution containing 1.00 mg/1 fluoride is shown in Table 3. (Data from NWWA (Hurleston Laboratory)).

Table 3 Effects of other substances on the determination of fluoride with the fluoride-selective electrode

Other Substance	Other Substance added as	Concentration of other substance mg/l	Recovery of fluoride, mg/1F (1.00mg/1F added)
Aluminium	Aluminium Sulphate	1.0	1.00
		2.0	0.98
Silver	Silver nitrate	2.0	1.00
Tin	Stannous chloride	1.0	1.00
Iron	Ferric chloride	2.0	1.00
Calcium	Calcium chloride	100	1.00
	(calculated as $CaCO_3$)	200	1.00
		500	0.97
Permanganate	Potassium permanganate	80	1.00
Chromate	Potassium chromate	100	1.00
Thorium	Thorium nitrate	2.0	0.97
Nitrate	Ammonium nitrate	10	1.00
		100	1.00
Calcium and Phosphate	Calcium chloride (calculated as $CaCO_3$) and Potassium dihydrogon phosphate	250 10	0.98
Calcium + phosphate + Aluminium	Calcium chloride (Calculated as $CaCO_3$ Potassium dihydrogon phosphate Aluminium sulphate	250 10 2.0	0.98
Free Chlorine	Sodium Hypochlorite	2.0	1.00
		10.0	0.97
		50.0	0.94

If the other substance did not interfere the recovery would be expected to lie (95% confidence) between 0.98 and 1.02 mg/1F.

Borates: Divergent statements have appeared in the literature about borate interference. The reactions between fluoride and borate are slow and dependent on temperature and pH. If borates are suspected separation procedures should be carried out (3).

For unknown samples the absence of interference in the direct electrode method must be checked by comparison with determinations of fluoride after separation by diffusion or distillation. Where it is known that interfering species may cause unacceptable errors, the fluoride must be separated prior to determination (see Part 3).

A4 Hazards

Considerable heat is generated when sodium hydroxide is dissolved in water. Glacial acetic acid must be handled with care and sodium fluoride is a toxic substance.

A5 Reagents

Use only reagents of recognised analytical reagent grade.

A5.1 **Fluroide-free water:** Distilled water or deionized water is normally suitable (see Section A8.11).

A5.2 **5 M Sodium Hydroxide Solution**

Dissolve 20.0 ± 0.5 g sodium hydroxide in water, cool and transfer to a 100 ml calibrated flask and make up to the mark with water. Store the solution in a polyethylene container.

A5.3 **Total Ionic Strength Adjustment Buffer**

To about 500 ml of water in a 1 litre beaker add 58.0 (± 0.5)g of sodium chloride and 57(± 1.0) ml of glacial acetic acid. Stir until the salt is completely dissolved. Add 150 (± 5) ml of 5 M sodium hydroxide solution and 4.0 (± 0.1)g of CDTA (trans 1, 2 diamino-cyclohexane — N,N,N' ,N' — tetra-acetic acid) and continue stirring until all

the solid has dissolved. (Note CDTA does not dissolve readily below pH 4.5). Adjust the pH value to 5.2 with 5 M sodium hydroxide solution.
Transfer to a 1 litre calibrated flask and dilute to the mark with water.

A5.4 **Stock Standard solution of Sodium Fluoride**
1 ml = 1000 μg F (1000 mg/lF^-)

Dry sodium fluoride by heating in an oven at 105°C for 4 hours. Cool in a desiccator. Weigh accurately 2.210 (± 0.001) g of dried sodium fluoride and dissolve in water. Transfer to a 1 litre calibrated flask and dilute to the mark with water. Standard solutions should be stored in screw capped ploye thylene containers which should not be used for any other purpose. This solution is believed to be stable for at least three months.

A5.5 **Dilute Standard solution of Sodium Fluoride**
1 ml = 20 μg F (20 mg/lF^-)

Pipette 20.00 ± 0.02 ml of stock standard sodium fluoride solution into a 1 litre calibrated flask and dilute with water to 1 litre: Transfer to a screw-capped polyethylene bottle. This solution should be freshly prepared daily.

A6 Apparatus

A6.1 **Potential measuring device** : an expanded scale or digital millivolt meter with impedence of not less than 10^{12} ohms capable of resolving potential changes to 0.1 mV or better.

A6.2 **Calomel Reference Electrode**

Note

(i) Fibre type liquid junction reference electrode should be avoided.
(ii) Sleeve type reference electrode (single or double junction) should be used in preference to ceramic frit type reference electrodes.
(iii) The electrode combination (reference and sensor electrodes) should be selected so as to give the best response times and calibration curve (see Section A6.3).
(iv) It is essential that the manufacturer's instructions should be followed concerning the maintenance of the electrode, particularly with respect to the replenishment of the filling solution.

A6.3 **Fluoride ion-selective electrode** containing an appropriately doped lanthanum fluoride detector membrane. The e.m.f. response (on standard solutions) per decade change in fluoride concentration should not be less than 55 mV over the range of F concentrations 0.2 to 200 mg/l. Experience has shown that a preformance less than this may lead to unsatisfactory results; this may be due to mismatching of sensor and reference electrodes, deterioration of the sensor electrode membrane, or poor maintenance of the sensor or reference electrode.

Fluoride electrodes incorporating other detector membranes are available. The analyst should satisfy himself that these electrodes give the required performance set out above.

A6.4 **Magnetic stirrer,** with polypropylene coated stirring bar.

A6.5 **100 ml plastic beakers.**

A7 Analytical Procedure

A7.1 **Warning to users of ion-selective electrodes**

A7.1.1 Ion-selective electrodes, including the fluoride sensor exhibit various instability effects arising both from external and internal sources. For details of these effects readers should refer to Section 8 before carrying out the experimental procedure.

A7.1.2 *Care of fluoride electrode*

The doped lanthanum fluoride membrane is particularly susceptible to damage by mechanical shock and care should be taken to avoid the electrode being struck (e.g. by the magnetic stirrer follower) during use or during storage. The electrode should

be stored according to the manufacturer's instructions. Certain electrode membranes are susceptible to "coating" with certain organic substances e.g. proteinaceous material, tannin, etc. This coating results in a deterioration of electrode performance. Cleaning of the membrane may be effected by gently polishing with a "soft" abrasive — alumina or cigarette ash may be suitable. Care should be taken not to use the fluoride electrode in solutions below about pH 4 or in which the fluoride concentration is greater than 20,000 mg/l.

A7.1.3 *Effect of age on electrode*

Eventually the performance of an electrode may deteriorate with age and the analyst should bear this in mind with electrodes which have been in use for six months to one year depending on intensity of use.

Step	Experimental Procedure	Notes
A7.2	For each batch of samples construct a calibration graph over a range of fluoride concentrations which extend slightly beyond the expected range of fluoride concentrations in the sample (see Notes (a) and (b)). It is suggested that e.m.f. readings are obtained at the following fluoride concentrations.	(a) It is desirable to extend the calibration graph upward from the normal range required for water analysis in order to obtain a more accurate calibration graph in the region of immediate interest and to detect more readily any abnormalities in electrode behaviour.
	(b) Some potential measuring devices can provide a direct read out of F^- activity. Refer to the manufacturer's instructions before using this facility as an alternative to the construction of a calibration graph. If a direct readout instrument is used it is still necessary to make frequent and regular checks that the electrode gives a Nernstian response (see Section A6.3)	
	Measure the volumes of standard solution accurately by pipette into calibrated flasks of appropriate sizes and dilute to the mark with water. Use the 20 mg/l calibration standard (see Section A5.5) as the standard solution for the lower concentrations and prepare these standard solutions freshly for each calibration graph, starting with the standard solution of sodium fluoride (A5.4) (see Note (c)). Standards and samples must be analysed at the same temperature (see Note (d)).	(c) Whilst it is preferable to construct a new calibration graph for each batch of samples it may be found sufficient in practice the check the calibration graphs at three points, e.g. 20, 1 and 0.20 mg/l.
		(d) It is essential that sample, buffer and calibration standards are at the same temperature (± 0.5°C) and for convenience the temperature of measurement should be at or about room temperature. Standing the solutions in a water bath maintained at the desired temperature prior to analysis is recommended (see Section A8.3).
A7.3	Pipette 25.00 ± 0.02 ml of the lowest concentration calibration standard (A7.2) and 25.00 ± 0.02 ml of buffer into a clean dry 100 ml plastic beaker (see note (e)). Allow the mixture to stand for at least 10 minutes for the de-complexing of interfering substances to be complete and the temperature to stabilise.	(e) A change in buffer solution during a batch of analyses must be avoided. Before starting the analysis of samples ensure that sufficient buffer solution from one batch is available for both calibration standards and samples.
A7.4	Place the magnetic follower in the beaker and put on to the platform of the magnetic stirrer (see Note (f)). Switch on the stirrer and adjust the stirring rate so that the liquid is thoroughly mixed but no vortex or air bubbles are formed. Maintain the same stirring rate for both samples and standards.	(f) It is desirable that some form of thermal insulation is provided between sample beaker and the magnetic stirrer.

F mg/l	Volume of Standard Solution Required ml		Final Volume of Solution ml
	1000 mg/l	20 mg/l	
200	20		100
20	20		1000
2		10	100
1		5	100
0.50		25	1000
0.20		5	500
0.10		5	1000

Step	Experimental Procedure	Notes
A7.5	Insert the electrodes into the solution taking care to avoid the entrapment of air bubbles under the electrodes.	
A7.6	Allow the system to achieve equilibrium for 4 minutes and switch off magnetic stirrer (see Note (g)).	(g) This avoids the interference by stirring potentials at the time the e.m.f. is measured.
A7.7	Take the e.m.f. reading after one minute to the nearest 0.1 mV. Repeat after a further minute and, if these two readings differ by 0.5 mV or more, repeat the e.m.f. readings at one minute intervals until consecutive readings differ by not more than 0.5 mV. If the electrode has not reached a steady e.m.f. after 5 minutes, resume stirring and repeat step A7.6 and A7.7 until a steady reading is obtained (see Note (h)).	(h) Investigate cause if the time to reach a steady reading is excessive (see Section A.8).
A7.8	Lift electrodes out of the solution, wash with water. Dry on absorbent tissue and store as directed by the manufacturer.	
A7.9	Remove sample beaker from stirrer, remove stirrer follower and repeat procedure A7.3 — A7.9 with each calibration standard in ascending order of concentration (see Notes (i) and (j)).	(i) Sample beakers should be washed thoroughly immediately after use with water and dried in a warm oven. (j) Calibration standards and samples may be analysed within the same batch so that the electrode system is subjected to an ascending order of concentration during the construction of the calibration curve and analysis of samples.
A7.10	Carry out sample analysis by repeating the procedure described under A7.3–A7.9 pipetting 25.00 ± 0.02 ml of sample in place of the calibration standards	
A7.11	Plot a graph on semi-log paper of e.m.f. in millivolts (linear scale) against fluoride concentration (logarithmic scale) of the calibration standards, and having obtained the e.m.f. of the sample, use this to obtain the fluoride concentration.	

A8 Sources or Error

A8.1 Presence of Interfering Species

The presence of species which either complex with the fluoride ion or which affect the electrode membrane may cause interference with this method (see Sections A3 and A7.1.2). If it is suspected that interfering species are present, separate the fluoride prior to analysis (see Part 3 of this booklet).

A8.2 Electrode Drift

The e.m.f. of the electrode system may not be constant due to a number of factors:

1. Damaged or deteriorated electrode membrane — investigate and replace electrode if necessary.
2. Dirty electrode membrane — clean by polishing with suitable abrasive (see Section A7.1.2).
3. Poorly maintained reference electrode — investigate and remedy or replace as necessary.
4. Presence of borates in sample — separate fluoride (see Part 3 of this booklet).
5. Poor electrode-meter electrical connections or malfunctioning meter.

A8.3 Inadequate Control of Temperature

It is essential that standards and samples should be at the same temperature (± 0.5°C) when measurements of e.m.f. are made. A temperature-controlled bath may be necessary.

A8.4 Inadequate Control of the ionic strength of the sample solution

The electrode system measures the e.m.f. arising from the activity of the fluoride ion (a_F) in solution. The activity of the fluoride ion is related to the concentration [F^-] by the expression

$a_F = f \times [F^-]$ where f is the activity co-efficient which approaches unity at infinite dilution.

For dilute solutions of electrolytes the activity co-efficient is the same in all solutions of the same ionic strength. Hence, should the ionic strength of the solution vary, the activity of the fluoride ion will vary correspondingly. The total ionic strength adjustment buffer is designed to adjust the ionic strength of the sample to a constant value. Unacceptable variations in the ionic strength of the buffered sample may arise if samples of very high ionic strength are examined.

A8.5 Inadequate Control of sample solution pH

The optimum pH for the determination of fluoride using a fluoride electrode is between pH 5.2 and 5.8. Highly acid or alkaline sample solutions may cause the pH of the buffered sample to deviate from this range. Below pH 5.0, an increasing proportion of the fluoride is associated as HF. Under alkaline conditions, the fluoride electrode is sensitive to hydroxyl ions.

A8.6 Changes in Stirring (streaming) Potential

The motion of a magnetic stirrer follower generates stirring or streaming potentials, which vary according to the speed of stirring. These potentials may be several millivolts. It is important that stirrer speeds are kept constant throughout the equilibration stage and that the stirrer is switched off before taking readings (see Section A7.6).

A8.7 Changes in Liquid Junction Potentials

A liquid junction potential is that potential which arise at the interface of two different solutions i.e. solutions of different electrolytes or solutions of different concentration of the same electrolyte. The most probable sources of error arising from changes in the liquid junction potential are those associated with the reference electrode — especially when the KCl internal filling solution is allowed to become undersaturated.

A8.8 Changes in external electrostatic forces

The fluoride electrode is normally encased in a polymeric material designed to screen the electrode system from changes in electro-static forces. If these changes are large or if the casing of the electrode has deteriorated, changes in the detected e.m.f. may be induced by changes in the external electrostatic forces.

A8.9 Changes in external illumination

With some electrodes the e.m.f. is susceptible to changes in external illumination. It is desirable that the e.m.f. of the sample and standard solutions are determined under the same illumination.

A8.10 Electrode memory effects

The e.m.f. of the fluoride electrode is determined by the diffusion of fluoride ions through the lanthanum fluoride crystal membrane which has an inherent "memory".

If an electrode has been in contact with a solution of relatively high fluoride concentration, the effect of this higher fluoride concentration may persist (the "memory effect") when the electrode is immersed in a solution of lower fluoride concentration, thus leading to erroneous results. Both samples and standards should therefore be examined if possible in ascending order of concentration and if a high

fluoride concentration must be measured, the electrode must be allowed to reach equilibrium conditions either in a blank solution, or in a solution of low fluoride concentration before any further e.m.f. readings are taken at lower fluoride levels.

An "electrode memory" effect is probably indicated when duplicate readings on aliquots of the same sample solution differ by more than 0.5 mV.

A8.11 **Fluoride Contamination of the water used for the preparation of the standard solution**

Any fluoride present in components used for preparing the buffer solutions will be present in both standard solutions and samples for analysis. This will increase the lower limit down to which the log-linear response is maintained but should not cause any bias in the results. Fluoride in the water used for preparing standard solutions will lead to a negative bias in the results.

If the concentrations of interest are well within the log-linear part of the calibration curve the concentration of fluoride in the distilled water used is negligible compared with the concentrations of interest. In particular, provided that the log-linear response is maintained down to a concentration not more than 0.2 mg/l then the concentration of fluoride in the water used can be ignored. Any change in this limit should be investigated since it may be due to significant contamination of the water and/or reagents with fluoride.

B Method for the Determination of Fluoride — Eriochrome Cyanine Colorimetric Method (Tentative)

B1 Performance Characteristics of the Method

(See also Table 1)

B1.1	Substance Determined	Fluorine present at F^- or in such complexes as are broken down to liberate F^- under the conditions used.
B1.2	Type of Sample	Most non-saline waters.
B1.3	Basis of Method	The bleaching of the colour of the Eriochrome cyanine R-zirconium complex by fluoride ions.
B1.4	Range of Application (a)	Up to 2mg/l in a 15 ml sample.
B1.5	Calibration Curve (a)	Not linear
B1.6	Standard Deviation (a)	15 ml aliquots of standard solutions:-

Concentration mg	Mean absorbance	Total s.d as mg/lF^-*
0	0.449	0.04
0.33	0.368	0.04
0.67	0.289	0.04
1.0	0.211	0.03
1.33	0.143	0.05
2.0	0.060	0.08

*10 degrees of freedom in each case

B1.7	Limit of Detection (a)	0.2 mg/l F using a 15 ml sample.
B1.8	Sensitivity (a)	0.016 absorbance per μg F^- below 15 μg of F^-; 0.008 absorbance per μg F^- at 25 μg of F^-. See Section 1.6 for calibration data.
B1.9	Bias	Bias less than 5% (see Section 8) in the absence of interfering species.
B1.10	Interferences	See Section B3
B1.11	Time requires for Analysis	15–10 samples and standards per hour

(a) These data were obtained from NWWA (Workington Laboratory) and the Laboratory of the Government Chemist.

B2 Principle

When standard amounts of solutions of zirconium oxychloride in hydrochloric acid and ericochrome cyanine R are added to aqueous solutions containing fluoride ions a zirconium-fluoride complex is preferentially formed. The resulting decrease in the intensity of the colour of the residual zirconium-eriochrome cyanine R complex is directly related to the concentration of fluoride ion present (References 4–7).

B3 Interferences

B3.1 Interferences may be of three types:-

(a) metal ions (eg zirconium and hafnium) that give a colour with eriochrome cyanine R at the acidity used; none of the common metals form coloured complexes.

(b) cations, eg iron (III) and aluminium (III) which form stronger complexes with fluoride and therefore give low results.

(c) anions, eg. phosphate, sulphate, citrate and tartrate which form complexes with zirconium in competition with eriochrome cyanine R and so give high results.

(d) coloured or turbid samples may give low results.

(e) Residual chlorine and other oxidizing or reducing agents may react with Eriochrome Cyanine R (see Section B7.1).

B3.2 The effect of other ions on the determination of fluoride in waters is shown below (from Reference 3):-

Table 4

Interference	Concentration mg/l	Recovery mg/l F^- at 0.2 mg/l	Recovery mg/l F^- at 1.0 mg/l
PO_4^{3-}	6	0.26	1.07
	10	0.23	1.07
	20	1.4	1.33
$(NaPO)_{36}$ (hexameta)	1	0.23	1.09
	2	0.32	1.09
	5	0.8	1.8
HCO^-_3	500	0.17	1.09
	1000	0.12	1.11
SO_4^{2-}	50	0.29	1.08
	200(a)	0.23	1.05
	500(a)	0.46	1.31
Fe^{3+}	10	0.13	1.09
	50	0.00	0.83
Al^{3+}	0.5	0.23	1.01
	2	0.17	1.01
	20	0.00	0.85
Ca^{2+}	200	0.32	1.1
	500	0.45	1.33
Al^{3+} B (borax)	1 + 1	0.24	1.06
	10 + 10	0.19	0.77
Al^{3+} HCO_3^-	20 + 100	0.09	0.82
95% confidence limits for no interfering effect.		0.14-0.26	0.94–1.06

(a) Interference by SO_4^{2-} >200 mg/l can be reduced by adding more barium chloride.

B4 Hazards

Sodium hydroxide is a caustic alkali and considerable heat is produced when it dissolves in water.

The acid zirconium reagent, barium chloride and sodium fluoride are toxic substances.

B5 Reagents

All reagents should be kept in glass bottles unless stated otherwise. Analytical reagent grade reagents are suitable unless otherwise stated.

B5.1 **Fluoride-free water.**

Distilled water or deionized water is normally suitable (see Section B8.1).

B5.2 **Sodium Fluoride (standard solution) 1 ml = 100 μg F^-.**

Pipette 10.00 ± 0.02 ml of stock standard solution of sodium fluoride (Method A,A5.4) into a 100 ml calibrated flask and dilute to 100 ml with water. Transfer immediately to screw-capped polyethylene bottle(s) for storage. This solution is stable for at least 1 month.

B5.3 **Dilute standard solution of sodium Fluoride** 1 ml = 5 μg F^-

Pipette 5.00 ± 0.02 ml of standard solution of sodium fluoride (B5.2) into a 100 ml calibrated flask and dilute to 100 ml with water. This solution must be prepared immediately before use.

B5.4 **Zirconyl Chloride agent.**

Dissolve 200 ± 5 mg of zirconyl chloride ($ZrOCl_2.8H_20$) in not more than 10 ml of water, add 700 ± 20 ml of concentrated hydrochloric acid (d_{20} 1.18) and dilute with water to one litre in a calibrated flask. Keep for 24 hours before use, it is then stable for at least a year. The solid reagent $ZrOCl_2.\ 8H_20$ readily hydrolyses in air to lose HCl and so changes its composition. The solid reagent should therefore be fresh or should be kept in a tightly sealed bottle.

B5.5 **Eriochrome cyanine R.** (C.I No 43820 Mordant Blue 3)

Most samples of Eriochrome cyanine R contain large amounts (about 40%) of sodium sulphate or chloride. A uniform pure product may be obtained from almost any commercial sample of eriochrome cyanine R by the following procedure (4).

Dissolve 4 ± 0.5 g of the material in 60 ± 2 ml of water and add with stirring 40 ± 2 ml of concentrated hydrochloric acid (d_{20} 1.18) to liberate the free acid. Filter off the precipitated free acid on a Buchner funnel and wash it with 6M hydrochloric acid. Dry in a dessicator containing sodium hydroxide pellets to remove excess hydrochloric acid.

B5.6 **Eriochrome cyanine R reagent.**

Dissolve 1.00 ± 0.05 g of purified Eriochrome cyanine R in water, add 2.0 ± 0.2 ml of concentrated hydrochloric acid (d_{20}.1.18) and dilute with water to 1 litre.
The solution is stable for at least 6 months out of direct sunlight.

B5.7 **0.4M Sodium Hydroxide.**

Dissolve 1.6 ± 0.1 g of sodium hydroxide, in about 5ml of water, dilute with water to 100 ± 0.5ml and store in a screw-capped polyethylene bottle.

B5.8 **Barium Chloride.**

Dissolve 50 ± 1 g of $BaCl_2.\ 2H_20$ in water and dilute to 1 litre.

B5.9 **Agar-Agar**

Suspend 1.0 ± 0.1 g of agar-agar in 50 ± 10 ml of water, pour into 450 ± 50 ml of boiling water; stir to dissolve, cool. Some grades of agar may gel at this strength in which case, heat the gel gently and dilute with water to 1 litre. Reject and prepare freshly if this reagent shows any sign of biological growth.

B5.10 **Hydrochloric acid (8.2M)**

Dilute 700 ± 20 ml of hydrochloric acid (d_{20} 1.18) with water to 1 litre.

B6 Apparatus

B6.1 **A spectrophotometer or a photoelectric colorimeter** with a filter having maximum transmission at about 540 nm.

B6.2 **Normal Laboratory Glassware**

All glassware used for this method must be washed first with the zirconyl chloride reagent and then thoroughly with water to remove all zirconium ions. It should be reserved solely for this method.

B7 Analytical Procedure

Step	Procedure	Notes
B7.1	If the sample contains residual chlorine remove by purging with nitrogen gas or by boiling and cooling to room temperature.	
B7.2	Measure accurately by pipette an aliquot of not more than 15 ml of sample containing up to 30 μg of fluoride (see Note(a)) transfer to a 25 ml calibrated flask.	(a) If necessary the sample can be diluted with water first to bring the sample within the range of the method, or smaller aliquots of the sample may be used.
B7.3	Add 1.0 ± 0.1 ml of 0.4M sodium hydroxide (B5.7) to a flask and mix (see Note (b)).	(b) This is intended to break up fluoride complexes with Al^{3+} to AlO_2^- and to precipitate Fe^{3+} as Fe $(OH)_3$. It is presumed that on addition of the zirconyl chloride reagent all the free F^- reacts with Zr ions before the Al^{3-} of Fe^{3+} can be liberated.
B7.4	Transfer by pipette 2.00 ± 0.01 ml (see note (c)) of zirconyl chloride reagent (B5.4) into the flask and mix.	(c) The volumes of reagent must be added reproducibly.
B7.5	Add 0.5 ± 0.1 ml of barium chloride solution (B5.8) to the flask.	
B7.6	Add 0.5 ± 0.1 ml of agar-agar (B5.9) to the flask.	
B7.7	Transfer by pipette 1.00 ± 0.01 ml see note (c)) of eriochrome cyanine R reagent (B5.5) into the flask, mix and dilute to the mark (see Note (d)).	(d) If a precipitate or turbidity remains, centrifuge until clear.
B7.8	Transfer the solution to a 1 cm path length cell and measure the absorbance at 540 nm against a reference solution prepared by pipetting 2.00 ± 0.01 ml of 8.2M hydrochloric acid (B5.10) and 1.00 ± 00.1 ml of eriochrome cyanine R reagent (B5.5) into 15 ml of water in a 25 ml calibrated flask and diluting to the mark (see Notes(e) and (g)).	(e) If a filter instrument is used then absorbance readings will be less than those using a spectrophotometer; 2cm cells may then be used. Colour development is almost instantaneous and the colour is stable in clean glassware.
B7.9	Calibration standards With each batch of samples run a set of standards through the same procedure used for the samples using suitable volumes of dilute fluoride standard solutions (B5.3) containing 0,5,10,20 and 30 μg of fluoride. Plot a calibration graph (see Note (f)).	(f) The calibration graph is non-linear. (g) Cells used for reference and sample should match to ± 0.002A when both are filled with distilled water. Before inserting them in the cell-holder wipe them carefully with absorbent tissue to ensure that they are free from smears and finger marks. They should always be placed in the same position in the cell holder with the same face towards the light source. The reference and sample cells should not be interchanged.

Step	Procedure	Notes
B7.10	**Calculation of results**	
	Evaluate the number of μg of F^- corresponding to the absorbance obtained in B7.7 by using the calibration graph obtained in B7.8. Calculate the concentration in the original sample by dividing the mass of fluoride by the volume of sample taken.	
	Read off from the calibration curve the weight of fluoride (W μg) corresponding to the absorbance from V ml of sample taken for analysis. Calculate the fluoride concentration from	
	$C = \frac{W}{V}$ mg/l.	

B8 Sources of Error

B8.1 Contamination by fluoride

Common sources of contamination by fluoride are tap water (especially if fluoridated) and air intakes which can on occasions contain appreciable quantities of fluoride if there is atmospheric pollution either from industrial sources or from the use of hydrofluoric acid elsewhere in the building. Tea is rich in fluoride but damages fluoride electrodes.

If the water used in the preparation of standards contains fluoride the calibration curve will be displaced in the direction of the absorbance axis and consequently the results will be falsely low. The purity of the water may be checked in the following way:

(a) To each of two 250 ml stainless steel or platinium beakers or basins, add 150 ± 5 ml of water and, by pipette. 1.00 ± 0.02 ml of 0.4M sodium hydroxide (B5.7)

(b) Cover the beakers with clean watch glasses and heat on the hot plate until the volume of the liquid has been reduced to between 10 and 15 ml.

(c) Transfer the residual liquid to a 25 ml calibrated flask and treat as a sample but omitting step B.7.3.

(d) From the calibartion graph, evaluate the amount of fluoride contained in the concentrated water. This should not exceed the limit of detection of the method, i.e. 3 μg from 150 ml of water.

(e) If the limit in (d) is exceeded check that the sodium hydroxide is not the source of fluoride by preparing a solution containing 40 ml of 0.4M sodium hydroxide (B5.7) in 1 litre of the same water used in (a) to (c) and treat this as a sample, using 15 ml and omitting step B7.3.

(f) If the amount of fluoride found in (e) is less than that found in (d) the water must contain fluoride and an alternative source of fluoride-free water obtained.

(g) If the amount of fluoride found in (e) is equal to or greater than that found in (d) the sodium hydroxide must contain fluoride. A purer source of sodium hydroxide should be obtained.

C Method for the Determination of Fluoride — Lanthanum Alizarin Fluorine Blue Spectrophotometric Method (Tentative)

C1 Performance Characteristics of the Method

(See also Table 1)

C1.1	Substance Determined	Dissolved fluorine present as the fluoride ion.
C1.2	Type of Sample	Sea water, estuarine water and non-saline waters containing acceptable levels of interfering elements (see Section C3)
C1.3	Basis of Method	Reaction of fluoride in acetone solution with the chelate of lanthanum with alizarin fluorine blue complexone at an apparent pH of 4.5 in acetate buffered medium, followed by spectrophoto-metric measurement of the blue ternary complex at 622 nm.
C1.4	Range of Application (a)	Up to 1.7 mg/l on a 15 ml sample. (b)
C1.5	Calibration Curve	Linear up to 1.7 mg/l. (b)
C1.6	Standard Deviation (within batch)	Using 15 ml samples:

Sample Type	Mean concentration found mg/l F^-	Standard Deviation mg/l F^-	Degrees of freedom
Sea Water(b)	1.27	0.01	8
Sea Water(c)	1.11	0.026	9
Standard Solution(c)	0.094	0.010	9
Standard Solution(c)	1.325	0.029	9
Standard Solution 1 mg/l(b)		0.007	8

C1.7	Limit of Detection	0.05 mg/l F^-
C1.8	Sensitivity	1 mg/l gives an absorbance of approximately 0.370 (b)
C1.9	Bias	Not known
C1.10	Interferences	Metal ions which form stable complexes with fluoride, particularly iron and aluminium (see Section C3)
C1.11	Time required for Analysis	Typical times for the analysis of 10 samples are:

Operator time	1.5 hours
Total time	2.0 hours

(a) Range can be increased by reduction in the volume of sample taken.

(b) Data obtained in the Department of Oceanography, University of Liverpool.

(c) Information from North West Water Authority (Broughton Laboratory).

C2 Principle

The method described is based on a modification by Greenhalgh and Riley of a technique developed by Belcher, Leonard and West (References 8 & 9). Fluoride in the sample is allowed to react at an apparent pH 4.5 with the red chelate formed between lanthanum and alizarin fluorine blue. The absorbance of the resulting blue ternary complex is measured at 622 nm. The reaction is carried out in 16% v/v acetone medium which stabilizes the colour and increases its intensity.

C3 Interferences

The effect of other substances on the determination of fluoride by the method is shown in Table 5. Residual chlorine may interfere and should be removed (see Section C7.2.1). The data were obtained in the Oceanography Department of the University of Liverpool. (Reference 8).

C4 Hazards

Perchloric acid is a potentially hazardous compound. Care must be taken to avoid spillage; if this does occur, the affected area should be swabbed thoroughly with water, all liquid wiped up and all swabs washed very thoroughly, even if then discarded. Spills on clothing should be treated similarly. Considerable heat is evolved when sodium hydroxide dissolves in water.

C5 Reagents

Analytical reagent grade chemicals should be used whenever possible.

C5.1 Fluoride-free water

Distilled water or deionized water is normally suitable (see Section C8.4).

Table 5 Effects of Other Substances on the Determination of Fluoride by the Lanthanum Alizarin Fluorine Blue Method

Other substance	Other substance added as	Concentration of other substance mg/l	Effect* in mg/l F^- of other substance at a fluoride concentration of 1.333 mg/l
Aluminium	ammonium alum	0.033	−0.013
Aluminium	ammonium alum	0.166	−0.050
Aluminium	ammonium alum	0.532	−0.210
Barium	chloride	0.13	−0.011
Boron	boric acid	33.3	0.00
Bromide	potassium salt	83	+0.01
Calcium	perchlorate	560	−0.013
Cobalt	chloride	0.66	+0.074
Copper	sulphate	0.66	+0.045
di-Na EDTA		13.2	−0.140
Iodide	potassium salt	0.13	0.00
Phosphate (as P)	potassium dihydrogen salt	660	−0.01
Iron (III)	ammonium alum	0.066	+0.006
Iron (III)	ammonium alum	3.33	−0.051
Magnesium	perchlorate	845	−0.113
Magnesium	perchlorate	1,690	−0.201
Nickel	nitrate	0.666	+0.061
Nitrate (as N)	potassium salt	0.666	−0.004
Nitrite (as N)	sodium salt	0.666	−0.003
Silicate (as SiO_2)	sodium salt	0.340	−0.009
Sulphate (as SO_4^{2-})	sodium salt	1,765	−0.013
Sulphate (as SO_4^{2-})	sodium salt	3,510	−0.040
Uranium		6.66	+0.026
Zinc	sulphate	0.666	+0.010

* If the other substance did not interfere the effect would be expected to lie (95% Confidence) between 0 ± 0.04 mg/l at 1.33 mgl/l fluoride F^-.

C5.2 **Ammonia solution** (d_{20} = 0.890)

C5.3 **Ammonium acetate** (4% m/v)

Dissolve 4.0 ± 0.1 g of ammonium acetate in water and dilute to 100 ± 2 ml.

C5.4 **Sodium acetate** (anhydrous)

C5.5 **Acetic acid** (6M)

Dilute 346 ± 10 ml of glacial acetic acid to 1 litre in a calibrated flask.

C5.6 **Acetone**

C5.7 **Alizarin fluorine blue**

(1, 2-dihydroxyanthraquinonyl-3-methylamine-N, N-diacetic acid).

C5.8 **Hydrochloric acid** (2M)

Dilute 18 ± 1 ml of hydrochloric acid (d_{20} 1.18) to 100 ± 2 ml with water.

C5.9 **Lanthanum chloride solution**

Dissolve 0.816 ± 0.005 g of lanthanum oxide in 2M hydrochloric acid and dilute to 50.0 ± 0.5 ml with the same acid

C5.10 **Mixed reagent**

Dissolve 0.0479 ± 0.0005 g of alizarin fluorine blue in a mixture of 0.10 ± 0.01 ml of ammonia (C5.2) and 5.0 ± 0.5 ml of 4% ammonium acetate solution (C5.3). Filter the solution through a small filter paper into a 200 ml calibrated flask containing 8.2 ± 0.2 g of sodium acetate (C5.4) and 6.0 ± 0.2 ml of acetic acid (C5.5) dissolved in the minimum volume of water. Wash the filter with a few ml of water. Add 100 ± 5 ml of acetone slowly with swirling and then pipette in 2.5 ml of lanthanum chloride solution (C5.9). Dilute to 200 ml with water and mix well. Store the reagent in a well-stoppered flask, it is stable for a least one week.

C5.11 **Sodium hydroxide** (0.1M)

Dissolve 4.0 ± 0.2 g of sodium hydroxide in water and dilute to 1000 ± 20 ml with water.

C5.12 **Perchloric acid** (0.1M)

Dilute 5.0 ± 0.1 ml of 60% m/m perchloric acid to 500 ± 10 ml with water.

Standard fluoride solutions

C5.13 **Solution A**

1 ml is equivalent to 0.1 mg F^-. Dissolve 0.2210 + 0.0002 g of sodium fluoride (dried for 4 hours at 105°C) in about 50 ml of water containing 1 ml of 0.1M sodium hydroxide in a 1 litre calibrated flask and dilute to volume with water. Stored in a polyethylene bottle, this solution is stable for at least one month.

C5.14 **Solution B**

1 ml is equivalent to 2 μg F^-. Dilute 10.00 + 0.02 ml of Solution A with water to 500 ml in a calibrated flask. This solution should be freshly prepared before use.

C6 Apparatus

C6.1 **Glassware**

If possible, apparatus should be reserved solely for fluoride determinations. Before and after use glassware should be well washed with water.

C6.2 **Spectrophotometer**

A prism or grating spectrophotometer capable of operating at 622 nm is required. A filter instrument is not suitable for this method.

Step	Experimental Procedure	Notes
C7.1	Preparation of blank solution A blank solution (which is itself coloured and has a substantial absorbance at 622 nm) must be included with each batch of samples. Pipette 15.0 ± 0.5 ml of water into a 25 ml calibrated flask, and add 0.40 + 0.02 ml of 6M acetic acid (C5.5). With a burette add 8.00 + 0.02 ml of the mixed reagent (C5.10) and then dilute to volume with water (Note (a))	(a) A quality control containing 1 mg/l fluoride should be run with each batch of samples (see Section N)
	Analysis of samples	
C7.2	C7.2.1 If the sample contains suspended matter filter through a retentive filter paper (Note(b)) or a 0.45 μm membrane filter. If residual chlorine is present remove by purging with nitrogen gas or by boiling and cooling to room temperature.	(b) 'Ashless' grades of filter papers should not be used as these may contain traces of the fluoride used in their preparation.
C7.2.2	Check the pH of the sample, if it lies within the range 5.0 to 8.5 proceed to Step C7.2.3. If not, pipette 15.0 ml of the sample into a 50 ml beaker and titrate it to within the above range with either 0.1M sodium hydroxide (C5.11) or 0.1M perchloric acid (C5.12) as appropriate. Note the volume of reagent required (Note (c)).	(c) For a 15 ml sample aliquot this must not exceed 1 ml.
C7.2.3	Pipette an aliquot of up to 15.0 ml of the sample containing preferably not more than 20 μg F^- into a 25 ml calibrated flask and if necessary adjust it to pH 5.0 – 8.5 by addition of the necessary amount acid or alkali found in Step C7.2.2 (Note (d)).	(d) If samples of less than 15 ml are taken the volume of acid or alkali must be reduced accordingly.
C7.2.4	Dilute to 15.0 ± 1.0 ml with water and add 0.40 ± 0.02 ml of 6M acetic acid (C5.5) (Note (e)).	(e) For sea and estuarine waters use (0.4 – 0.02 x) + 0.02 ml of 6M acetic acid where x is the chloride concentration in g/l.
C7.2.5	With a burette add 8.00 ± 0.02 ml of the mixed reagent (5.10), dilute to volume with water, and mix well (Note (f)). Allow to stand for at least 30 min. (Note (g)).	(f) The solution at this stage should have an apparent pH of 4.50 ± 0.3 (g) Colour development in non-saline medium is complete in 10 min, but requires 25 min in sea water. Once formed, the colour is stable for at least 6 hours in subdued light.
C7.2.6	Set up the spectrophotometer (Section C6.2) according to the manufacturer's instructions. The wavelength scale of the instrument should be checked to ensure its accuracy. This can be most readily achieved using didymium glass filters which are supplied by most manufacturers. The method used for measuring absorbance should be rigorously controlled to ensure satisfactory precision. Adjust the absorbance of the instrument to zero with the blank solution (Section C7.1) in the reference cell (See Note (h)). Measure the absorbance (A_s) of the solution at 622 nm using a 10 mm cell. Re-check the zero absorbance.	(h) Cells used for reference and sample should match to + 0.002 A when both are filled with distilled water. Before inserting them in the cell-holder wipe them carefully with absorbent tissue to ensure that they are free from smears and fingermarks. They should always be placed in the same position in the cell holder with the same face towards the light source. The reference and sample cells should not be interchanged.

Step	Experimental Procedure	Notes
C7.3	Preparation of Calibration Curve	
	Into a series of 25 ml calibrated flasks pipette 1.0 ± 0.01, 2.5 ± 0.01, 5.0 ± 0.01 and 10.0 ± 0.01 ml of standard fluoride solution B (C5.14). Adjust the volume to 14–15 ml with water. Add 0.4 ± 0.02 ml of 6M acetic acid (Section C.5) followed by 8.00 ± 0.02 ml of the mixed reagent (Section C5.10). Dilute to volume with water and mix well. Carry out Step C7.2.6, after 30–180 min. Plot the absorbances obtained against the amounts of fluoride added, 2.0, 5.0, 10.0 and 20.0 μg F. A calibration standard using 10 ml of standard fluoride solution B should be run with each batch of samples. The calibration curve should be checked at regular intervals; it should be linear up to 1.7 mg/l fluoride.	
C7.4	Calculation of results	
	Read off from the calibration curve the weight of fluoride (W μg) corresponding to the absorbance A_s arising from V ml of sample taken for analysis. Calculate the fluoride concentration C in the original sample from $C = \frac{W}{V}$ μg/ml For sea and esturaine samples C must be multiplied by the factor (1 + 0.0011 S) (where S is the salinity in g/kg) (Reference 5) in order to allow for suppression of the absorbance by the major ions.	

C8 Sources of Error

C8.1 Contamination by fluoride

Contamination may arise from both tap water (particularly if fluoridated) and air which may, be polluted with fluoride originating either from industrial activity or from the use of fluorine compounds in the laboratory, or in other parts of the building.

C8.2 Failure to adjust the pH before the addition of the reagent

Serious error will occur if the pH of the sample does not lie within the range 5.0 — 8.5 when the mixed reagent is added.

C8.3 Presence of interfering elements

Serious errors can result from the presence of interfering elements, particularly aluminium. If unacceptable levels of these are present (see Section C3), fluoride must be separated by a suitable procedure (see Part 3). Corresponding blanks must also be run.

C8.4 Presence of fluoride in the water used for the preparation of standards and blanks and for the dilution of samples

If the water used to prepare standards and blanks contains fluoride, the results will be falsely low.

The purity of the water may be checked in the following way:

(a) Using a measuring cylinder transfer 50 ± 2 ml and 150 ± 2 ml of the water to two 250 ml stainless steel or platinum beakers or basins.

(b) With a pipette add 1.00 ± 0.02 ml of 0.1M sodium hydroxide solution (C5.11) to each.

(c) Cover each beaker with a watch glass and heat them on a hot plate until the volume of solution has been reduced to 5–10 ml. Do not allow to become dry.

(d) After cooling, quantitatively transfer the residual liquid to 25 ml calibrated flasks, add 1.00 ± 0.02 ml of 0.1M perchloric acid (C5.12).

(e) Carry out steps C7.2.4 to C7.4.

(f) The difference between the two amounts of fluoride found in this way is the amount of fluoride present in 100 ml of the water. If this difference is statistically significant, it can be used to correct the results or preferably an alternative source of water obtained.

D Method for the Determination of Fluoride — Ion Chromatographic Method (Tentative)

Introduction

The pK value of hydrogen fluoride is low enough for the fluoride ion to be detected and measured by ion-chromatography using conductimetric detection after a suppressor column (References 10 and 11). With most eluants used in ion-chromatography, fluoride has a short retention time, usually emerging just before chloride. The fluoride peak is therefore sharp and the sensitivity of the method quite high. Fluoride can be determined down to about 0.01 mg/litre. Further details of ion-chromatographic methods generally will be found in a review published in this series — Ion Chromatography in the Analysis of Water.

D1 Performance Characteristics of the Method (no comparative results available).

D1.1	Substance Determined.	Dissolved fluoride.
D1.2	Types of Sample.	Potable and saline waters.
D1.3	Basis of Method.	Separation from other anions by ion-chromatography followed by a suppressor column and conductivity detector.
D1.4	Range of Application.	Tested over the range 0.01 to 5 mg/l, but can be extended to higher concentrations.
D1.5	Calibration Curve.	Linear relationships between peak height/area of the fluoride peak and concentration over the range 0.01 to 5 mg/l.
D1.6	Standard Deviation. (a)	Sample type and concentration mg/l F^- / Within batch relative Standard Deviation * % / Degrees of Freedom Distilled water spiked with sodium fluoride:- 0.1 — 1.2 — 9 5.0 — 1.2 — 9 * Based on measurement of peak height.
D1.7	Limit of Detection.	0.01 mg/l
D1.8	Bias.	Not known but see sections D3 and 8.
D1.9	Interferences	In some eluent systems formate, acetate, chloroacetate and relatively high levels of carbonate give peaks with a similar retention time. Changing eluent to one based on borate ions gives no recorded interference. **Note**: Glycolate & pyruvate ions are reported to be eluted close to fluoride ions.
D1.10	Time required for Analysis	Dependent on the presence, or absence of other ionic species being eluted from the chromatographic column. The analysis of a solution containing only fluoride ions is completed within 3–5 minutes.

Note(a): Information from I.C.I. Organics Division using a Dionex Model 16 Ion Chromatograph.

D2 Principle of the Method

Ion Chromatography is a form of High Pressure Liquid Chromatography (HPLC) where the separation of ions is carried out on a specially prepared ion exchange resin which has excellent separating properties, but only limited ion exchange capacity. Detection of the ionic species being eluted from the separator column is carried out by monitoring the electrical conductivity in a micro cell. Thus the response for a given ion will depend on its ionic conductivity and order of elution from the column. Since the best eluents are weak solutions of strong electrolytes e.g. Na_2CO_3, it is necessary to pass the eluent from the separator through a suppressor column to remove the strong conducting cations eg Na^+, K^+. (References 10, 11).

Note: Single column ion chromatography can be used for the measurement, but to reduce the conductivity of the eluent to make detection of the emerging ions possible it is necessary to use weak electrolytes with inferior separation characteristics. Methods can be based on single column ion-chromatography provided the required separation and sensitivity criteria are satisfied.

D3 Interferences

A number of relatively common ions are eluted from the ion exchange column close to the fluoride peak when using a standard eluent eg 0.003M $NaHCO_3$/0.0024M Na_2CO_3. These are formate, acetate, chloroacetates and high levels of carbonate. Due to poor peak resolution, 1000mg/l HCO_3^- gives a 10% negative bias for fluoride present at a concentration of 1mg/l. Alternative eluent systems will resolve all these species from the fluoride peak, but the analysis time is increased. (See Fig. 4). In well characterised waters the fastest eluting system possible should be chosen in the absence of interfering ions.

Cations which normally interfere with other techniques for the detection and measurement of fluoride do not interfere. Levels of iron and aluminium, up to 10mg/l have no effect on the measurement. Calcium and magnesium and anions such as sulphate and phosphate appear to have no interference on fluoride.

D4 Hazards

Considerable heat is generated when sodium hydroxide dissolves in water. Sodium fluoride is a toxic substance. Hazards associated with HPLC such as leakage of electrolyte are most likely to occur with "home made" apparatus than the commercially available equipment.

D5 Reagents

Use only reagents of recognised analytical purity.

D5.1 **Fluoride-free water:** Distilled or deionized water is normally suitable. If not available, limited amounts can be obtained by collecting the final eluent from the suppressor column. Injection of 100 µl of the water onto an ion chromatograph set to a high sensitivity range will be the ultimate test for water suitability.

D5.2 **Standard eluent solution** (0.003M $NaHCO_3$, 0.0024 M Na_2CO_3).

Dissolve sodium bicarbonate, 1.018 (±0.002)g $NaHCO_3$ and 1.008(±0.002)g anhydrous sodium carbonate, Na_2CO_3 in 4 (±0.01) litres fluoride-free water (D5.1).

D5.3 **Standard "S2 Type" eluent solutions** (0.003M Na_2CO_3, 0.002M NaOH).

Dissolve 1.272 (±0.002)g anhydrous sodium carbonate, Na_2CO_3 and 0.820 (±0.002)g sodium hydroxide NaOH in 4(±0.01) litres fluoride-free water (D5.1).

D5.4 **Borate Eluent (0.005M $Na_2B_40_7$. $10H_20$).**

Use: Borate eluent greatly increases the retention times of $C1^-$and NO_2^-. Separation of simple organic compounds, such as short chain carboxylic acids (formate, acetate, pyruvate, etc) can be accomplished with this eluent without $C1^-$ interference.

Dissolve 7.628(±0.005)g$Na_2B_40_7$. $10H_20$ in 4(±0.01) litres fluoride-free water.

D5.5 **Dilute Standard solution of Sodium Fluoride.**

1ml = 50 µg F^-

Pipette 50 ml of stock standard sodium fluoride solution (Section A, A5.4) into a 1 litre calibrated flask and dilute with water to 1 litre: Transfer to a screw-capped polyethylene bottle. This solution should be freshly prepared daily.

Note: More dilute standards can be prepared by further dilutions of A5.4 but care must be taken at low levels of F^- to use the appropriate fluoride-free water for dilution.

D5.6 **Chromatographic Check Standard**

This is a mixture of common ions and is usually purchased from the instrument supplier or prepared shortly before use. The compostion is:

Fluoride,	3 mg/l F^-	
Chloride,	4 mg/l Cl^-	
Nitrite,	10 mg/l NO_2^-	Figs. 1 and 2 are typical chromatograms for this mixture.
Phosphate,	50 mg/l $PO^3{}_4^-$	
Bromide,	10 mg/l Br−	Fig. 3 is a chromatogram of a typical water containing no fluoride.
Nitrate,	30 mg/l NO_3^-	
Sulphate,	50 mg/l SO_4^{2-}	

D6. Apparatus

D6.1 **Ion Chromatograph** fitted with a separator column capable of resolving fluoride ions from adjacent common anionic species, suppressor column and conductivity detector. Either a commercially manufactured unit or one based on available HPLC components will be suitable.

Note: Operating parameters are given for a Dionex Model 16 Ion Chromatograph.

D6.2 **Flat bed potentiometric recorder** – either single pen or dual pen operation.

D6.3 **Integrator**

Peak areas can be measured manually but use of an integrator is convenient for the analysis of large numbers of samples.

D6.4 **Sample injection loop**

A volume of 100 µl will be adequate to obtain the detection limits quoted in D1.7. In the Dionex equipment, samples are introduced by means of a 10ml plastic disposable syringe purchased from any medical supply house. The loop is flushed and filled with the test solution via the syringe before injection onto the ion exchange column.

D7 Analytical Procedure

D7.1 **Precautions on the care of the packed columns of the ion chromatograph**

D7.1.1 Any technique in the development stages of application suffers from a multiplicity of information and new modifications. Ion chromatography is no exception to this so that any comments at a given state in time tend to apply to the technique as the present state of the art. The chromatographic columns are the critical feature of the technique so that precautions must be taken to maintain them in their effective condition. The manufacturers' instructions will guide the user on column use and regeneration etc.

D7.1.2 **Separator Column**

This is based on a specially manufactured ion exchange resin of low exchange capacity, but exceptionally good separation characteristics. The useful life and effectiveness of this column will largely depend on the type of samples injected onto the ion chromatograph and the treatment to which the column has been subjected. In general the examination of waters containing considerable amounts of organic matter appreciably shortens the column life. The columns can be partially reconditioned by a number of recommended treatments, but they are seldom returned to their original state.

D7.1.3 **Pre-Column**

This is not an essential feature of the ion chromatograph, but can be added to serve two important roles.

(i) Removal of strongly retained ions and particulate matter, thereby protecting the expensive separator columns.

(ii) Concentration of low levels of ions before elution and measurement on the main separator column.

Analysis of good quality potable water will not necessitate the use of a pre-column.

D7.1.4 **Suppressor Column**

Used only in dual column ion chromatographic equipment and particularly suited for the measurement of trace levels of ions. This column is necessary to achieve a high sensitivity with conductivity detection. It is a high capacity cation exchanger in the

hydrogen form and functions by removing the highly conducting cations in the eluent and converting the sample anions into the corresponding acids. This column has a finite capacity and must be regenerated at intervals depending on the total volume and type of eluent being used. The recently developed "fibre" type suppressors are continuously regenerated.

D7.1.5 **Ageing of columns**

Both pre-columns and separator columns will change their characteristics on ageing. Some material is irreversibly absorbed on the ion exchange material and will contribute to reduced resolution. Additionally, the active ion exchange coating of the resin will be progressively removed with a reduction in retention time and resolution. The high price of the pre-packed columns makes regular replacement expensive since at the present time there is no manufacturer who is prepared to market a suitable resin so that column packing can be carried out in the individual laboratories.

Suppressor columns have a long life and only need replacing infrequently.

Step	Experimental Procedure	Notes
D7.2	Preparation of Calibration Curve For each concentration range of interest, construct a calibration graph of fluoride concentration against peak height or peak areas.	
D7.3	Measure by pipette suitable volumes of dilute standard solution of sodium fluoride (D5.5) into a series of volumetric flasks. Dilute each flask to the mark with water (note (a)) and rinse. At least five standards should be taken and the concentrations to be measured should lie between the top and bottom standards. The range covered by the standards is preferably not more than one decade.	(a) At low fluoride levels very high quality water is necessary to prepare the standards (see D5.1).
D7.4	Switch the Ion-Chromatograph on and allow to reach equilibrium with the chosen eluent (D5.2 and D5.3) pumping at the rate of 3 ml/minute. Check for general performance and resolution by running the chromatographic check standard (D5.7) (see Figs. 1 & 2).	
D7.5	Set the attenuation range of the conductivity cell so that the highest fluoride standard is on the scale of the recorder.	
D7.6	Inject into the fixed volume loop of the ion chromatograph by means of a syringe each of the prepared standards from D7.3 and a water blank and transfer the fixed volume (say 100 µl) in the injection loop onto the column (note (b) and (c)). Measure the peak heights or peak areas and plot a graph of peak height or area against fluoride concentration (notes (d) & (e)).	(b) Injections can be made directly onto the column but the precision may be adversely affected. (c) The blank response should be negligible. If not repeat the standardisation using a better quality water for blanks and standards.
D7.7	Analysis of Samples Repeat the procedure in D7.6 using the same injection loop with the samples. Allow the ions in each sample to be completely eluted before injecting the next sample on the column (note (f)). Samples and standards should be analysed at the same temperature (see Section D8.3). Include a standard fluoride solution as a control standard after every fifth sample injection in batches of samples to check that the instrument sensitivity is unchanged.	(d) An integrator may be used to measure peak area or manual triangulation for peaks which do not tail. (e) One the linearity of the calibration has been established over the range of interest it will be sufficient to re-calibrate with a single standard.

Step	Experimental Procedure	Notes
D7.8	Measure the height or area of the peak due to fluoride ion and read the corresponding fluoride concentration from the calibration graph.	(f) For standards containing only fluoride ions, injections can be made every 3–5 minutes, but for samples of unknown composition it may be necessary to wait 20 minutes before a further sample is injected. (See Figs 1 & 2).
D7.9	Regeneration of the Suppressor Column Regenerate the suppressor column by acid washing following the procedure given in the manufacturing instructions. The analyst should establish the regeneration interval for each ion-chromatographic appartus. (see notes (g) and (h)).	(g) A wash with water followed by treatment with N sulphuric acid, and a final wash with water will usually be sufficient. (h) "Fibre" type suppressors are continuously regenerated.

D8 Sources of Error

D8.1 **Presence of Interfering Species**

The method is generally free from interference due to the complexing of fluoride ion by other species (see Section D.3). But the behaviour of fluoroborates is uncertain and should be checked if suspected to be present. Any pre-treatment of samples should avoid introducing high concentrations of other ions (eg chloride).

D8.2 **Chromatographic Interferences**

The only possible anionic interferences observed are those eluting from the column at approximately the same time as fluoride ion. These are formate, acetate, chloroacetate and carbonate at high concentrations (see figure 4). All these anions can be resolved from the fluoride peak by changing the eluent to 0.005M $Na_2B_4O_7$. 10 H_2O solution (see figure 4).

D8.3 **Change in Retention Time due to Temperature Drift**

Unless the chromatographic column temperature is controlled a change in retention time occurs when ambient temperature rises, or falls. This will not only affect the position of the eluting peaks, but will change the relationship between peak height and weight of fluoride ion. In this case peak areas should be used with frequent calibration checks.

D8.4 The document refers to the present state of the art of ion chromatography. No doubt changes in technique, chromatographic materials, equipment etc., will take place over the next few years requiring modification to Method D.

Fig.1 : DIONEX S1 TYPE COLUMN

250×10mm.

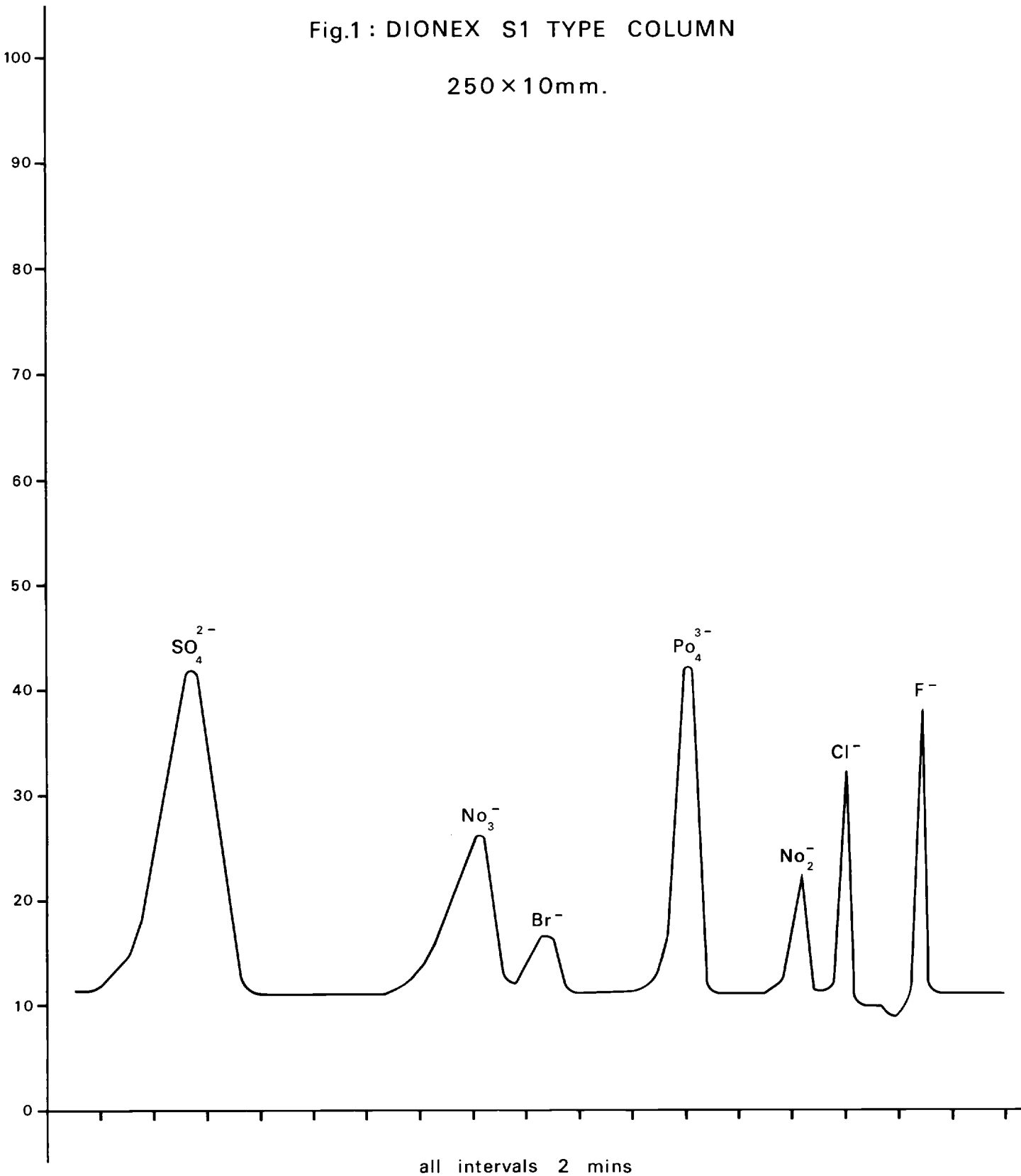


Fig.2 : DIONEX S2 TYPE COLUMN

0·003M Na_2CO_3 / 0·002M NaOH

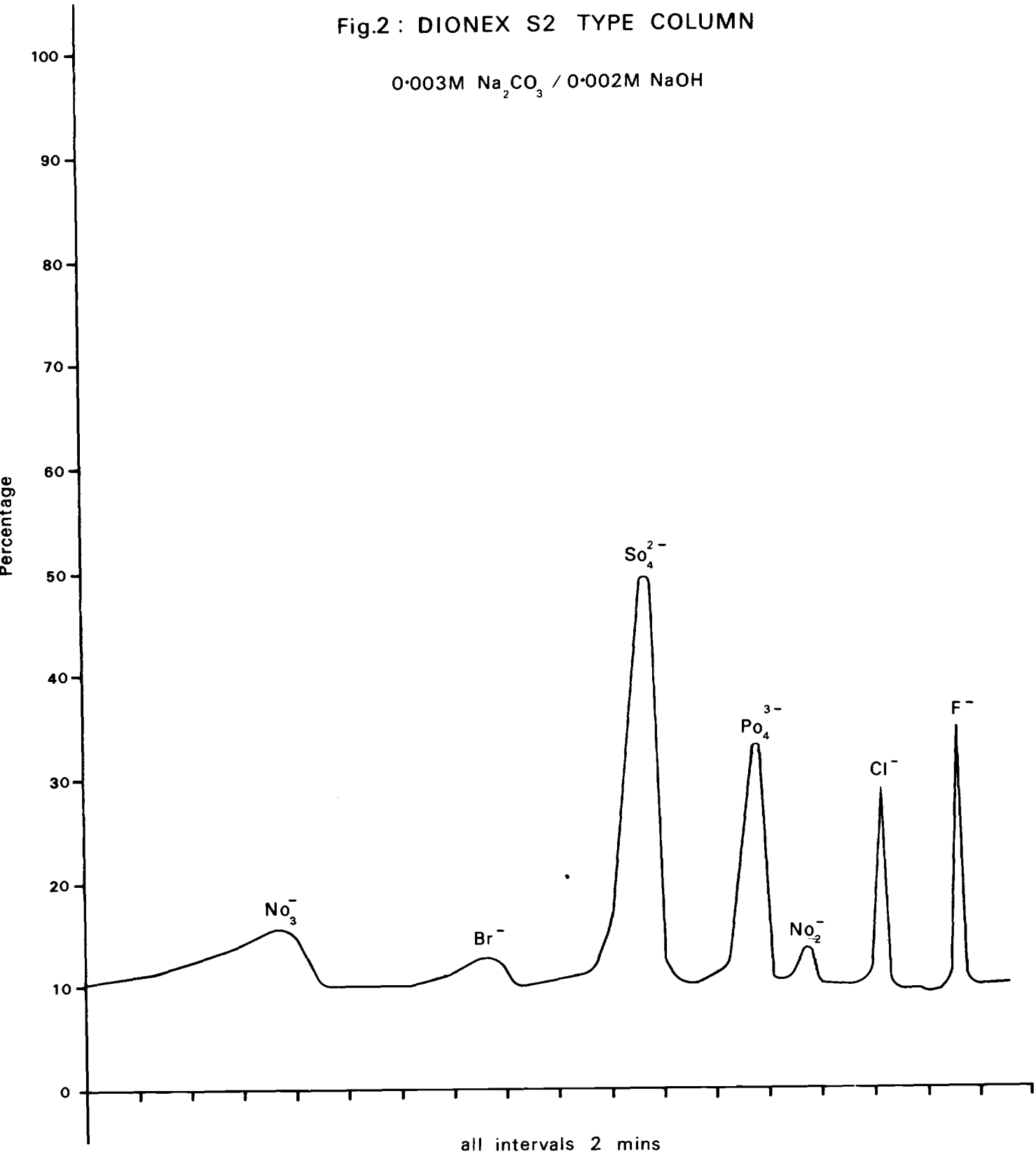
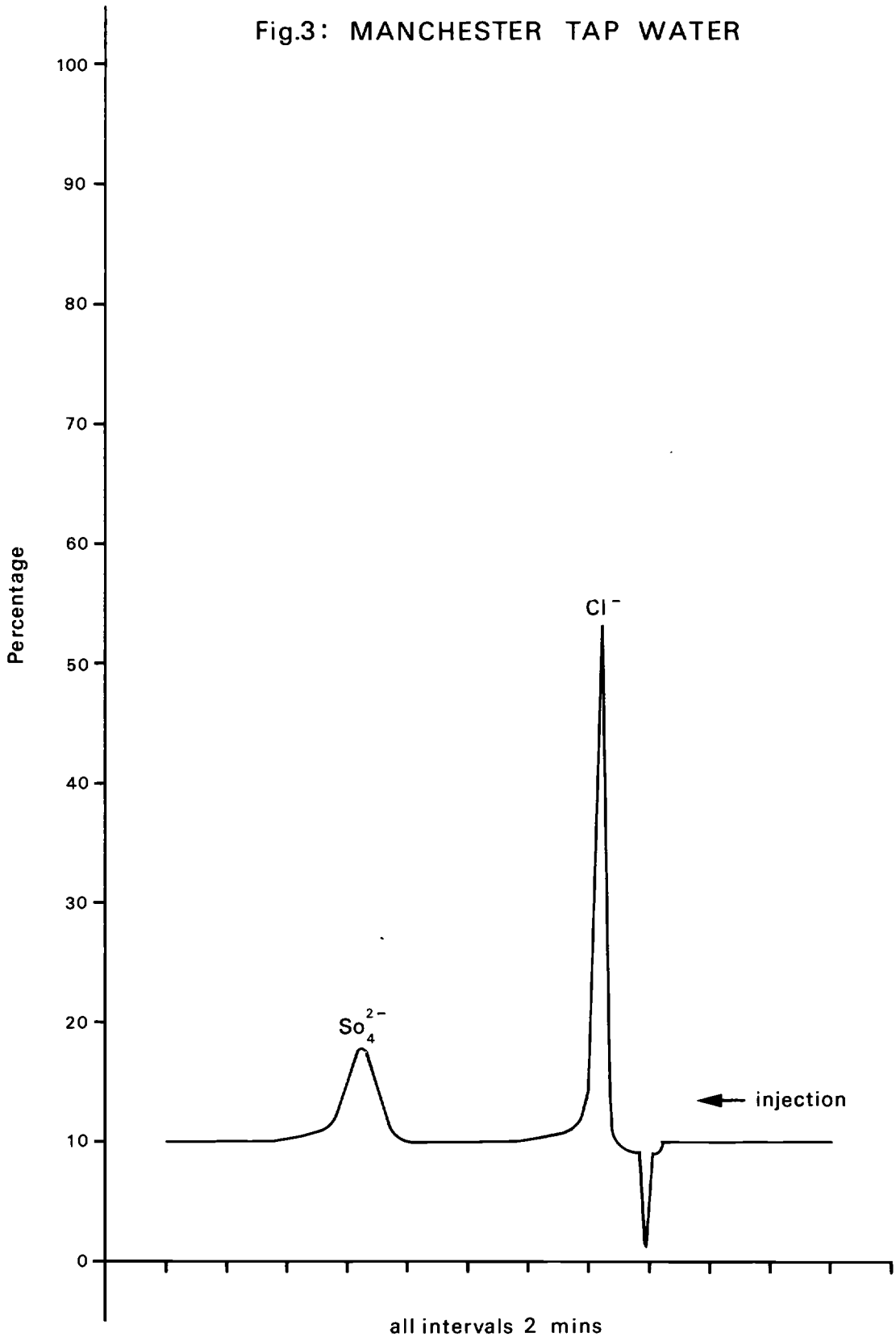


Fig.3: MANCHESTER TAP WATER



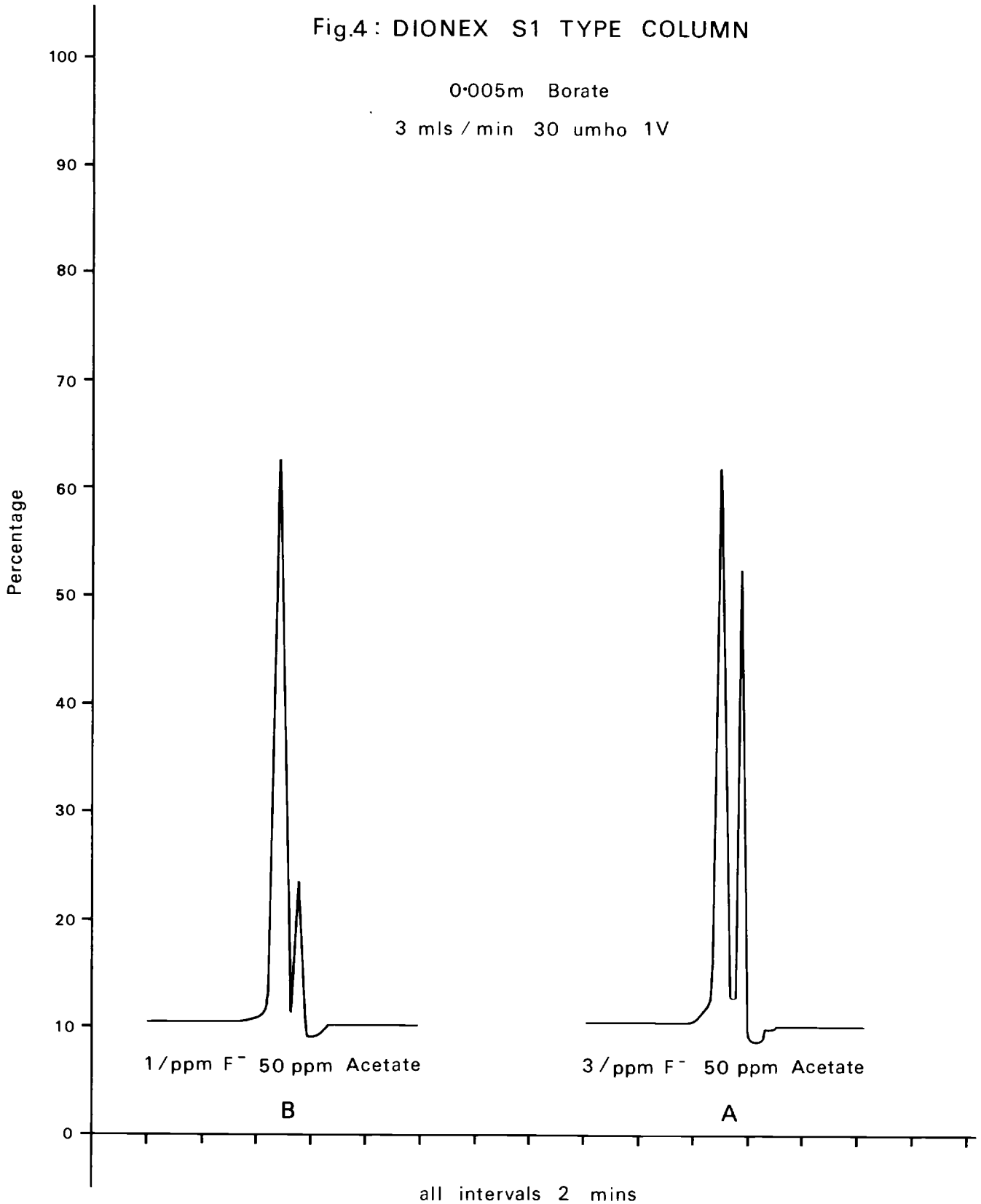


Fig.4 : DIONEX S1 TYPE COLUMN
0·005m Borate
3 mls / min 30 umho 1V
100
90
80
70
60
50
40
30
20
10
0
Percentage
1/ppm F⁻ 50 ppm Acetate
B
3/ppm F⁻ 50 ppm Acetate
A
all intervals 2 mins

Part 2: Fluoride in Effluents, Sewage, Sewage Sludge, Plant Materials and Soils

Introduction

Fluoride is likely to be present in many industrial effluents and where such effluents are discharged to sewer and the sludge from the receiving works is disposed of by application to agricultural land, fluoride may need to be determined not only in the sewage sludge, but also in soil and crops.

Certain industrial effluents can be analysed directly by the methods given in Part one, but sewage, sewage sludge, plant materials and soils require more or less extensive pre-treatment before any method for fluoride can be applied.

Because of the relatively large errors associated with sampling grossly non-uniform materials such as sewage sludge, the use of a precise but lengthy method of analysis may not be warranted, whereas a method allowing reasonable throughput at moderate cost for screening at background fluoride levels and above would be preferred (12).

The two methods given in this part of the booklet are primarily intended for the analysis of sewage sludge, but can be easily adapted for other materials. Method E, based on acid extraction of the sample is the simplest and most rapid. It does not respond to all forms of fluorine but experience indicates that it determines those forms which are likely to have any direct or indirect toxic effects on plants and/or animals. Method F, an alkali-fusion method, determines total fluorine and should be used whenever this is the required determinand.

Where the nature of the industrial processes from which fluoride containing effluents are derived give cause to doubt the validity of the simple acid-extraction method the analyst is strongly advised to use the alkali-fusion method. It should also be noted that the chemical forms of fluoride may change between the point of discharge of the effluent and the separation of sludge at the sewage treatment works.

Sampling of Plant Materials

When sampling plant materials for fluoride analysis, consideration must be given to why the analysis is being made. If the problem is only concerned with the uptake of fluoride by plants, the procedure given in The Sampling and Initial Preparation of Sewage and Waterworks Sludges, Soils, Sediments and Plant Materials Prior to Analysis 1977 should be used (18). If on the other hand, the problem concerns grazing and ingestion, consideration must be given to deposits on the plants from aerial fallout, spraying, etc. Such material may not need washing and care may be needed to avoid undue loss of dust. Consideration should also be given as to whether or not the animal concerned consumes soil with the plant.

E Method for the Determination of Fluoride in Sewage Sludge: Acid Extraction Method (Tentative)

E1 Performance Characteristics of the Method

E1.1	Substance Determined	Acid-extractable fluoride.
E1.2	Type of Sample	Sewage sludge.
E1.3	Basis of Method	Addition of dilute sulphuric acid and citrate ions to release fluoride ions which are measured potentiometrically with a fluoride-selective electrode.
E1.4	Range of application (a)	4–80 mg/Kg on a wet basis corresponding to about 100–1500 mg/Kg of dry solids. This range may be extended by taking appropriate aliquots of the extracts and diluting. See Section E8.9 Note (g)
E1.5	Calibration Graph (a)	Log-linear (see Method A Section A1.5)
E1.6	Standard Deviation (a)	
E1.7	Limit of Detection (a)	4 mg/Kg on a wet basis. This limit has not been calculated on a statistical basis (see also Part 1, Method A, Section A1.7).
E1.8	Sensitivity	About 58 mv per decade change in fluoride concentration (see also Part 1, Method A, Section A1.8).
E1.9	Bias	Negative bias will be observed for most sludges due to failure of the treatment to release fluoride ions from all fluroine-containing compounds and complexes. The estent of bias will vary but in many cases will not be significant. The recoveries of added fluoride in E1.6 were as follows:-

Sample	Fluoride mg/Kg Wet basis	Total Standard Deviation mg/Kg Wet Basis
Sludge	15	0.6
Spiked sludge (b)	24	0.7
Spiked sludge (b)	44	1.3
Spiked sludge (b) (c)	115	3.8
Spiked sludge (b) (d)	1000	19

Each estimate has at least 8 degrees of freedom

		Spiking Concentrations mg/Kg wet basis	% Recovery and 95% confidence limits
		10	95 ± 6
		30	97 ± 3
		100	99 ± 2
		1000	101 ± 1
E1.10	Interferences (a)	High concentrations of aluminium interfere (see Section E.3).	
E1.11	Time required for Analysis (a)	Total analytical time for one sample is about one hour, but the time per sample is substantially less for large batches.	

(a) These data were obtained at the Water Research Centre, Stevenage Laboratory.

(b) Sludge spiked with sodium fluoride.

(c) Procedure included a 5 ml – 25 ml dilution.

(d) Procedure included a 1 ml – 25 ml dilution.

E2 Principle of the Method

The sample is treated in a standardized arbitrary manner with solutions of sulphuric acid, sodium citrate and potassium chloride. The fluoride ions released are measured potentiometrically with a fluoride-selective electrode, by reference to a calibration curve obtained by treating standard solutions of sodium fluoride in a similar manner. (Refs 17 and 19).

E3 Field of Application and Interferences

E3.1 Many soluble and insoluble simple and complex fluorides show complete release of fluoride and are determined quantitatively. (See also (Section E9).

E3.2 Some insoluble fluorides may show only partial release of soluble ionic fluoride. Recovery may be improved by extended treatment (see Section E.9).

E3.3 Some complex fluorides may show little or no release of soluble ionic fluoride. Recovery may be improved by extended treatment.

E3.4 Some complex fluorides, particularly when bound inside mineral grains, eg micas, clays, do not respond.

E3.5 Although some organofluorine compounds may respond, it should be assumed that they do not.

E3.6 Aluminium may cause negative interference, the magnitude of which depends on the concentration of aluminium and fluoride and other complexing ions or ligands which may be present. Tests using sodium fluoride and aluminium sulphate indicate that for sample extracts diluted to contain 0.2 to 2 mg F/1 and less than 25 mg A1/1 (corresponding to 1000 mg A1/Kg wet basis using 25 ml of extract) in the final solution, the interference may be negligible. The analyst should confirm this by his own tests for samples likely to contain appreciable concentrations of aluminium.

E4 Hazards

Poisonous gases may be emitted from the sample on acidification, if not before. All operations should be carried out in a fume cupboard. Hydrogen sulphide is highly toxic at low concentrations and also paralyses the sense of smell. Sewage sludge may contain pathogenic organisms.

Much heat is produced when concentrated sulphuric acid is diluted with water. Acid must be added to the water in a vessel which can be kept cool.

E5 Reagents

Analytical reagent grade chemicals should be used unless otherwise stated.

E5.1 **Water**

Distilled or deionized water is usually suitable (see also Part 1, Method A, Section A8.11).

E5.2 **1M Sulphuric Acid**

Add slowly and cautiously with continuous stirring 56 ± 1 ml concentrated sulphuric acid (d_{20} 1.84) to about 800 ml water in a 2l beaker surrounded by cold water. Allow to cool and dilute to 1 litre in a measuring cylinder.

E5.3 **0.1M Sulphuric Acid**

Dilute 100 ± 1 ml 1M sulphuric acid to 1 litre with water in a measuring cylinder.

E5.4 **16%m/v Sodium citrate**

Dissolve 160 ± 1g tri-sodium citrate dihydrate in water and dilute to 1 litre with water in measuring cylinder.

E5.5 **15%m/v Potassium Chloride**

Dissolve 150 ± 1g potassium chloride in water and dilute to 1 litre with water in a measuring cylinder.

Combined Reagents:

Several combinations of water and reagents E5.3, E5.4 and E5.5 will be found useful, bearing in mind that the final solution to be measured contains water and these three reagents in the ratio 1:1:1:1. It is easy to adapt the solutions to enable just one solution addition to be made instead of four. The following will be found useful:-

E.5.6 **Reagent A — Diluent for Calibration Standards**

Mix equal parts of 0.1M Sulphuric acid (E5.3), 16% m/v Sodium citrate (E5.4) and 15% m/v Potassium chloride (E5.5)

E5.7 **Reagent B — Sample Buffer Mixture**

Mix equal parts of water, 16% m/v Sodium citrate (E5.4) and 15% m/v Potassium chloride (E5.5).

E5.8 **Reagent C — Dilution Mixture**

Mix equal parts of water, 0.1M Sulphuric acid (E5.3), 16% m/v Sodium citrate (E5.4) and 15% m/v Potassium chloride (E5.5).

E5.9 **Stock Standard Solution of Sodium Fluoride**

1 ml = 1000 μg F^- (see Part 1, Method A, Section A5.4).

E5.10 **Standard Solution of Sodium Fluoride**

1 ml = 10 μg F^-. Dilute 10.00 ± 0.02 ml of stock standard solution of sodium fluoride (E5.9) to 1 litre with water in a calibrated flask. This solution should be freshly prepared.

E5.11 **Storage Solution**

1 ml contains about 2 μg F^-. Dilute 2.0 ± 0.1 of stock standard solution of sodium fluoride (E5.9) to 1 litre with water in a measuring cylinder.

E6 Apparatus

As for Method A, Part 1, Section A6 and the following:

E6.1 100 ml screw-capped plastic bottles, including some polypropylene bottles.

E7 Sample Collection Preservation and Preparation

The procedures described in "Methods for the Examination of Waters and associated materials" (this series of booklets) should be followed. (Ref 18). Fluoride is reasonably stable, but samples should be collected in plastic bottles, stored in a refrigerator at 4°C and the analysis carried out within one week.

For most routine purposes the use of the wet sludge is adequate, although for results on a dry basis, a separate determination of total solids will be required. For more accurate work or for longer storage it may be preferable to dry and grind the sample and reconstitute a known weight in 10 ml water when required.

E8 Procedure

Step	Procedure	Notes
	Calibration procedure	
E8.1	Ensure that the electrodes and meter are in good operating condition before proceeding with the calibration. Checks should be carried out in accordance with the manufacturers instructions (Notes (a) and (b)).	(a) See also Part 1, Method A, Sections A6.2, A7.1 and A7.2. (b) A recorder attached to the millivolt meter though not essential, assists in observing the rate of response, when equilibrium is reached, any invalid negative signals and provides a permanent record.
E8.2	Transfer 1.00 ± 0.01, 2.00 ± 0.01, 5.00 ± 0.02 and 20.00 ± 0.03 ml of standard solution of sodium fluoride (E5.10) to 100 ml calibrated flasks. Add 75 ± 1 ml of Reagent A — diluent for calibration standards (E5.6) and dilute with water to 100 ml. These solutions contain 0.1, 0.2, 0.5 and 2.0 μg F^- per ml respectively (Note (c)).	(c) These solutions are preferably freshly prepared but tests have shown them to be stable for at least 1 week, if stored in plastic bottles in a cool dark place.
E8.3	Proceed as in Method A (Part 1) Section A7.4 to A7.9 for each calibration standard and note the readings in millivolts. (Note (d)).	(d) It is essential that samples and standards are at the same temperature within 0.5°C when e.m.f. readings are taken.
E8.4	Using semilogarithmic paper plot the mV readings on the linear axis against the concentrations on the log-axis. A straight line should be obtained with a slope of about 58 mV per decade change in concentration (Notes (e) and (f)).	(e) If the calibration standard readings do not form a reasonably straight line, more standards should be run and the analyst can then assess whether to proceed with analysis using a graph which is slightly curved at the lower concentrations or to investigate the problem (instrumental or contamination). (f) If the decade change is less than 55 mV between 0.2 and 2 ug/ml, or the electrode response is slow or unstable it is unwise to proceed with analysis until the cause is found (see Part I, Method A, Sections A6.8, A8.9 and A8.11).
	Analysis of Samples	
E8.5	Weigh a 100 ml plastic bottle, add 10.00 ± 0.5 ml well-mixed wet sludge, re-weigh and calculate the weight of wet sludge taken. Record this weight Wg to the nearest 0.1g (Note (g)).	(g) Dried samples may be used, in which case transfer about 0.5g, accurately weighed, to a 100 ml plastic bottle, add 10.0 ± 0.1 ml water and proceed to Step E8.6.
E8.6	Add 10 ± 0.1ml 1M sulphuric acid (E5.2) secure the cap and shake the bottle. Shake occasionally during the next 15 minutes.	
E8.7	Add 80 + 1 ml water, shake and allow to stand for 15 minutes.	

Step	Procedure	Notes
E8.8	Transfer a suitable volume V (not exceeding 25 ml) (Note (h)) to another 100 ml plastic bottle, add (25-V)ml 0.1M sulphuric acid (E5.3) and 75 ± 1 ml Reagent B — Sample Buffer mixture (E5.7). Shake and allow to stand for 15 minutes.	(h) The following table may assist in selecting suitable volumes:-

Expected concentration on original wet sludge mg/kg F^-	Volume V to be taken ml
0 – 40	25 + 0.25
40 – 100	10 + 0.11
100 – 300	5 + 0.05
200 – 1,000	2 + 0.02
500 – 2,000	1 + 0.01

E8.9	Transfer the contents of the bottle to a plastic beaker. Insert the electrodes, stir gently and allow the system to reach a steady reading (up to 4 minutes). Take the reading, remove the electrodes, wash with water, and blot dry. (Note (i) and (j)).	(i) Samples and standards must be at the same temperature when readings are taken. See Note (d) to Section A7.2 in Part I, Method A. (j) Any readings indicating a final concentration above 2 μg/ml should be repeated using a smaller aliquot of the extract or diluted with Reagent C — Dilution mixture (E5.8).
E8.10	On completion of a batch of measurements, rinse the electrodes with water. Store in accordance with the manufacturer's instructions or in a 2 ug/ml F^- solution (Storage Solution — E5.11) (Note (k)).	(k) Manufacturers recommend that the fluoride electrode is not left in contact with solutions containing citrate which slowly attacks the crystal membrane. There may be some advantage in storing for short periods in a standard solution of fluoride or for longer periods storing dry after rinsing with the standard solution followed by water. The presence of fluoride without citrate should 'rejuventate' the crystal membrane. Operators should not be alarmed if the signal from a standard fluoride 2 μg/ml in water is not the same as the 2 ug/ml calibration standard (the ionic stengths are quite different).
	From the mV reading in step E8.9 and the calibration graph (E8.4) determine the concentration of fluoride in the final solution from E8.8. Let this be A μg/ml.	
	Calculation of results	
E8.12	Calculate the concentration of fluoride in the original wet sludge from:- F^- in wet sludge $= \frac{A \times 10{,}000}{Wg \times V}$ mg/Kg	
	If the measured solution was diluted as in Note (i), include the appropriate factor in the calculation.	
	If necessary convert the result to a dry solids basis using the appropriate factor obtained from the total solids determination.	

Step	Procedure	Notes
	CALIBRATION BY STANDARD ADDITIONS	
E8.13	Unless the sample has been shown not to contain substances likely to interfere, it is recommended that calibration by standard addition is carried out in addition to the procedure in step E8.9 which relies on comparison of sample readings with a calibration curve based on standard solutions (Note (1)).	(l) A Gran's plot method of standard addition is described in Section F11.

E9 Extension of the Method

Most inorganic fluorine compounds which are availabe to biological processes are likely to be measured by the method as described in Section E8. However, it is known that some compounds, e.g. fluoroborates and fluorophosphates do not respond, and additional treatment is required if they are to be included in the response. The follow extension is recommended in these cases. (Ref 19)

E9.1 Proceed as in Step E8.6 but use 100 ml polypropylene bottles.

E9.2 Add 10.0 ± 0.1 ml 1M sulphuric acid (E5.2), secure the cap and shake the bottle. Loosen but do not remove the cap and place the bottle on a steam bath for 30 minutes, swirling occasionally. Allow to cool to room temperature.

E9.3 Proceed as in Section 8, Steps E8.7 to E8.13.

F Method for Total Fluorine in Sewage Sludge and Related Materials (Tentative)

F1 Performance Characteristics of the Method

F1.1	Substance Determined	Total fluorine
F1.2	Type of Sample	Dried ground sewage sludge and other similar agricultural materials.
F1.3	Basis of Method	Total fluorine is converted to fluoride ions following potassium hydroxide fusion of a pre-ashed sample. The resultant melt is incorporated into a citrate buffer and the fluoride ion concentration is determined potentiometrically, using a fluoride-selective electrode by means of standard additions.
F1.4	Range of Application	10 — 1000 mg F/kg based on 0.5 g dried sample. The range can be extended upwards by the use of suitable aliquots.
F1.5	Calibration Curve	A standard addition technique is used to determine the concentration of F in the sample, however, the success of the procedure is dependent on the linear relationship of the electrode potential to the logarithm of the fluoride concentration over the range of 1 to 1000 mg/1.
F1.6	Standard Deviation	

F^- Conc.	Total Standard Deviation	Degrees of Freedom
% m/m	% m/m	
1.55	0.09	28

F1.7	Limit of Detection	Based on a sample of 0.5 g sewage sludge the practical limit of detection of the Grans' Plot method of calculation is 10 mgF/Kg. This limit has not been calculated on a statistical basis. (See also Part 1 Method A. Section A1.7). The majority of sewage sludges examined so far contain fluoride in the range 100 — 1000 mg F/kg dry matter. (15)
F1.8	Sensitivity	Electrode response approximately 58 mV per decade change in fluoride concentration.

F1.9 Bias	Bias may arise from the presence of interfering species. Recovery of fluoride from a certified fluoride standard — Basic Slag BSC 382 — over 95 percent. Recovery of soluble (NaF) and insoluble (CaF_2) forms of fluoride added to domestic sewage sludge and Standard Kale was found to be over 95 percent (14).
F1.10 Interferences	High levels of Al^{3+} Ca^{2+} Fe^{3+} Mg^{2+} PO_4^{3-} may interfere with the release of fluoride. (See Section F3)
F1.11 Time of Analysis (a)	Approximately 20 minutes for determination overall i.e. 10 mins for the preparation and 10 mins for the analysis including four standard additions and construction of the Gran's Plot (see Note (a)). A batch of 10 samples would take approximately 3 hours Operator time and 5 hours Total time allowing for cooling between stages (See Note (b)).

(a) Although there are other methods available for calculating the fluoride concentration from the standard additions procedure e.g. ADDFIT computer programme and a programme calculator model these do not give the same visual check on the results nor are they as simple to use as the Gran's Plot paper method recommended (Refs 16 and 17).

(b) The data quoted were obtained at the Polytechnic Wolverhampton and S.T.W.A. Coalport Analytical Laboratory Telford.

F2 Principle

A sample of dried, ground sewage sludge is gently ashed to remove organic matter and the residue fused with potassium hydroxide.

The resulting melt is extracted, neutralised with dilute acid and incorporated with a sodium citrate/citric acid buffer at pH 5.8 ± 0.2 to eliminate complex formation and also to adjust the ionic strength of the digest and aid suppression of the major interferences e.g. hydroxyl ion and certain polyvalent cations.

The fluoride activity is determined in the resultant prepared solution using a fluoride selective electrode together with a standard addition procedure. The sample concentration is calculated with the aid of pre-calibrated Gran's Plot paper (Refs 14, 15 and 17).

F3 Interferences

The major interferences likely to occur in sewage sludges are Al^{3+}, Ca^{2+}, Fe^{3+}, Mg^{2+}, PO_4^{3-}. The effects of these ions on the response of the fluoride selective electrode in citrate buffer are given below.

F4 Hazards

F4.1 Harmful fumes may be emitted during the ashing and fusion procedures thus these operations together with extraction and neutralization of the melt must be carried out in a fume cupboard.

F4.2 Potassium hydroxide in pellet form is extremely caustic. Eye, face and hand protection is required together with extreme care whilst handling the fused product.

F4.3 Considerable heat may be generated on neutralisation of the fusion product with 50% mineral acid and extreme caution is needed.

F4.4 Sodium fluoride is toxic.

Table 6

Other Substance	Other Substance added as	Concentration of other Substance	Effect in mg/l F^- of other Substance mg/kg		
			Fluoride 50	Level 200	(mg/kg) 5000
Aluminium	Aluminium sulphate	500	−2	−7	+200
		2,000	−3	−8	+233
		5,000	−3	−8	−400
Iron	ferric nitrate	2,000	−1.3	−3	+210
		20,000	−1.3	+11	−150
Phosphate	Potassium dihydrogen phosphate	80,000	+0.7	+9	+250
Calcium	Calcium chloride	100,000	+1.7	+8	——
Magnesium	magnesium sulphate	20,000	+1.7	+9	+250
			+2	+10	+400

95% confidence limits if the other substance did not interfere.

The above Data were reported by the Yorkshire Water Authority (17).

F4.5 Concentrated hydrochloric acid is extremely corrosive.

F4.6 The handling of nickel crucibles using a micro-burner requires suitable tongs in good condition and special vigilance is needed to avoid skin burns from accidentally touching hot equipment.

F5 Reagents

All reagents and Standards should be kept in polypropylene bottles unless otherwise stated. Analytical Reagent Grade chemicals are suitable unless otherwise specified.

F5.1 **Water**

Distilled or deionized water is usually suitable (see also Part I, Method A, Section A8.11).

F5.2 **Molar Sodium Citrate Buffer**

Dissolve 294 ± 2 g of Tri-Sodium Citrate in approximately 1 litre of distilled water. Add citric acid in small quantities with stirring until the pH reaches 5.8 ± 0.2.

F5.3 **50% V/V Hydrochloric Acid.**

Dilute 50 ± 1 ml of hydrochloric acid (d_{20} 1.18) with water to 100 ml in a measuring cylinder.

F5.4 **Stock Fluoride Solution 1 ml Contains 1000 μg F**

See Part 1, Method A, Section A5.4.

F5.5 **Standard Fluoride Solution 1 ml Contains 100 μg F**

Dilute 10.0 ± 0.05 ml of stock solution F5.4 to 100 ml with water in graduated flask. Prepare freshly each week.

F5.6 **Standard Fluoride Solution 1 ml Contains 10μg F**

Dilute 10.00 ± 0.05 ml of standard solution F5.5 to 100 ml with water in a graduated flask. Prepare freshly each week.

F5.7 Potassium hydroxide pellets.

F6 Apparatus

As for method A, Part I, Section A6 and the following:

F6.1 Polypropylene beakers 100 ml.

F6.2 Polypropylene volumetric flasks 50 ml and 100 ml.

F6.3 Nickel Crucibles nominal size 15 ml.

F6.4 Wide range pH Test papers.

F7 Sample Collection Preservation and Preparation

F7.1 The procedures given in Methods for the Examination of Waters and Associated Materials should be followed (Ref 18)

F7.2 Sludge samples should be collected in plastic containers and stored in a refrigerator at 4°C prior to analysis.

F7.3 A suitable quantity of wet sludge or cake corresponding to around 10 g of dry matter is fan-oven dried at 60 — 80°C followed by grinding using a laboratory size hammer mill with a 1 mm sieve.

F8 Analytical Procedure

Step	Procedure	Notes
	The electrodes and pH/millivoltmeter are used in accordance with the manufacturers instructions.	
	Read Section 4 on hazards before starting this procedure.	
F8.1	Dry Ashing and Fusion of Samples	
F8.1.1	Weigh 0.500 ± 0.004 g of the dried ground sludge sample into a nickel crucible (Note (a)).	(a) The size of the nickel crucible used should allow for easy manipulation during the ashing and fusion stage.
F8.1.2	Gently ignite the Sample using a microburner until the bulk of the organic material is removed. Allow the crucible and contents to cool.	
F8.1.3	Fuse the resultant ash with 1.0 ± 0.1g potassium hydioxide (F5.7) using only just sufficient heat to produce a liquid melt. As soon as the ash has dissolved or dispersed, stop heating and allow the crucible to cool. (Note (b)).	(b) With a little experience the operator can observe when the melt has fully incorporated the ashed sample. The use of a low flame and cessation of heating when a suitable melt is obtained is necessary to avoid losses of fluoride (See Section F.10).
F8.1.4	Extract the cooled melt and transfer to a 100ml polypropylene beaker with small successive quantities of deionized distilled water incorporating sufficient hydrochloric acid (50% V/V)) (F5.3) to give approximate neutrality using a pH Test paper strip (F6.8) as indicator. (2 – 2.5 ml was found to be a typical volume). Incorporate 25.0 ± 0.2 ml of the citrate buffer (F5.2) at the rinsing and transfer stage using a glass rod and wash bottle jet to remove the last traces of melt from the crucible.	
F8.1.5	Cool to room temperature and transfer all rinses and buffer to a 50 ml volumetric flask and make up to volume with water.	

Step	Procedure	Notes
	Calibration Procedure for the Fluoride Electrode (Note (c))	
F8.2		(c) The Gran's Plot paper is constructed on the basis of a slope factor of 58 mV per decade. The slope adjustment control facility of the meter should be used to ensure that the slope factor is as close as possible to this value. See also Part 1, Method A, Section A8.9 regarding the effect of light on electrode response.
	Prepare buffered standard solutions as follows (Note (d)).	(d) The calibration is carried out in the same strength citrate buffer as used throughout the analytical procedure i.e. 50% V/V of molar sodium citrate pH 5.8 ± 0.2
F8.2.1	100 μg/ml F. Transfer 5.00 ± 0.05 ml of 1000 μg/ml F solution (F5.4) to a 50 ml volumetric flask add 25.0 ± 0.2 ml of citrate buffer (F5.1) and make up to volume with water.	
F8.2.2	10 μg/ml F. Transfer 5.00 ± 0.05 ml of 100 μg/ml F solution (F5.5) to a 50 ml volumetric flask. Add 25.0 ± 0.2 ml of citrate buffer (F5.2) and make up to volume with water.	
F8.2.3	1 μg/ml F. Transfer 5.00 ± 0.05 ml of 10 ug/ml F solution (F5.6) to a 50 ml volumetric flask. Add 25.0 ± 0.2 ml of citrate buffer (F5.2) and make up to volume with water.	
F8.2.4	Transfer completely without rinsing the 50 ml prepared buffered 1 μg/ml standard into a polypropylene beaker. Proceed as in Method A (Part 1) Section A7.4 to A7.8 and note the reading in millivolts (Note (e)).	(e) During calibration the initial readings may take a few minutes to stabilise if the electrode has been stored dry or in distilled water previously.
F8.2.5	Repeat the procedure with the 10 μg/ml F and 100 μg/ml F prepared buffered standards in ascending order (Note (f)).	(f) It is essential that all prepared solutions are at the same temperature ± 0.5°C and for convenience room temperature is preferred.
F8.2.6	Plot a graph on semi log paper of EMF (mV) (on the linear vertical scale) against fluoride concentration (μg/ml) (on horizontal log scale) and use this to check the electrode slope.	
F8.3	**Sample Analysis using the Standard Addition Technique**	
F8.3.1	Transfer the 50 ml prepared buffered sample from step F8.1.5 to a polypropylene beaker and carry out step F8.2.4 to determine the initial EMF potential E_0 mV (Note (g)).	(k) For samples likely to contain fluoride at levels in excess of 1000 mg/kg a dilution procedure is necessary as described in Section 9.
F8.3.2	Add 1.0 ± 0.01 ml of 100 μg/ml standard fluoride solution (F5.4) and after equilibrium conditions are observed note the new EMF (mV) reading.	
F8.3.3	Repeat Step 8.3.2 a further 3 times and record the equilibrium mV potential each time E_2, E_3, E_4 (Note (h)).	(h) Steps F8.3.2 and F8.3.3 are required to enable a Gran's Plot to be constructed.

Step	Procedure	Notes
F8.3.4	On completion of a sample run the electrodes should be thoroughly rinsed in water and stored according to the manufacturers instructions (Note (i)).	(i) Manufacturers recommend that the fluoride electrode is not left in contact with citrate, which slowly attacks the crystal membrane and affects performance. Therefore it is advisable to keep contact with the buffer solution to a reasonable minimum. The electrode may be stored for short periods in a distilled water standard or for longer periods stored dry after rinsing in a distilled water standard and distilled water (the presence of fluoride without citrate should 'rejuvenate' the LaF_3 crystal). (See E8.11 Note (k)).
F8.3.5	Plot the mV potentials E_0 to E_4 versus the volume of standard fluoride solution added on 10% corrected Gran's Plot paper (Note (j)). Hence determine the fluoride concentration A μg/ml F in the prepared buffered sample.	(j) Orion Research Gran's Plot (Cat No. 90–00–90 is suitable. See also Section F11.
F8.4	Calculation If 0.500 ± 0.004 g of dried ground sludge was taken and incorporated into a final volume of 50 ml using a volumetric flask, i.e. 10 g of original sample per litre, then the fluoride concentration on the original dried sludge sample is:- 100 A mg per kg F on dry matter (Note (k)).	(k) For samples likely to contain fluoride at levels in excess of 1000 mg/kg a dilution procedure is necessary as described in Section 9.

F9 Change in Concentration Range of Method

F9.1 The procedures adopted provide for a rapid screening of sewage sludges containing up to 1000 mg/kg F^- on dry matter. For samples with a higher fluoride content make the extract from Step F8.1.4 (without buffer) to 50 ml with water in a volumetric flask. Transfer a suitable aliquot to another 50 ml volumetric flask, add 25.0 (± 0.20) ml citrate buffer (F5.2) and dilute to 50 ml with water.

Using this buffered aliquot proceed as in Step F8.3.

The concentration of fluoride in the original sample is given by:-

$$100\ A \times \frac{50}{B}\ \text{mg/kg}\ F^-\ \text{on dry matter.}$$

Where B is the volume (in ml) of the aliquot taken.

F10 Sources of Error

F10.1 The method is not intended for determining fluoride at low levels of detection or for high accuracy, however, it might be desirable to reserve plasticware solely for this purpose and carry out checks from time to time with a fluoride standard such as Basic Slag BSC 382/1, together with blank determinations.

No additive is used to prevent loss of fluoride in the ashing and fusion procedures. If there is reason to suspect that loss of fluoride by volatilization may cause unacceptable errors, the analyst should refer to Part 3 (Section G) for alternative methods.

F10.2 For samples of unknown composition especially where industrial contamination exists, the effect of complexing by unsuspected agents may not be fully realised. The use of a relatively high citrate buffer concentration (15% V/V), together with a standard addition technique, should allow for excessive levels of most of the known interferences. Some workers have reported on the limitations of the concept of Standard Addition as a technique in greater detail. (8).

F10.3 Fluoride contamination of samples during ashing has been reported from the use of muffle furnaces (refractory linings). The use of a simple microburner technique should avoid any such problems with the method described.

F10.4 The electrode response may alter gradually and exhibit non-linearity in the required range. Regular calibration over the range 1–1000 mg/kg F is therefore advisable.

In this method the potential (emf) generated by the electrode in a prepared sample is recorded before and after the addition of a known concentration of fluoride.

F11 Use of Standard Addition or Known Addition Procedures

The change in potential ($\triangle E$) can be expressed as follows, derived from a simplified form of the Nernst equation assuming that the known addition causes no change in activity coefficients or the fraction of total fluoride present in the free ionic form:-

$$\triangle E = S \log \frac{VC + V'C'}{C(V + V')}$$

Where S = Slope factor (about 58 mv per decade)

V ml = Original volume of prepared buffered sample

C mg/l = Original concentration of prepared buffered sample

V′ ml = Volume of standard fluoride solution added

C′ mg/l = Concentration of standard fluoride solution added

Re-arrangement of this equation gives the following:-

$$C = \frac{V'C'}{V\left[\left\{\text{antilog}\left(\frac{\triangle E}{S}\right)\right\} \times \left\{1 + \frac{V'}{V}\right\} - 1\right]}$$

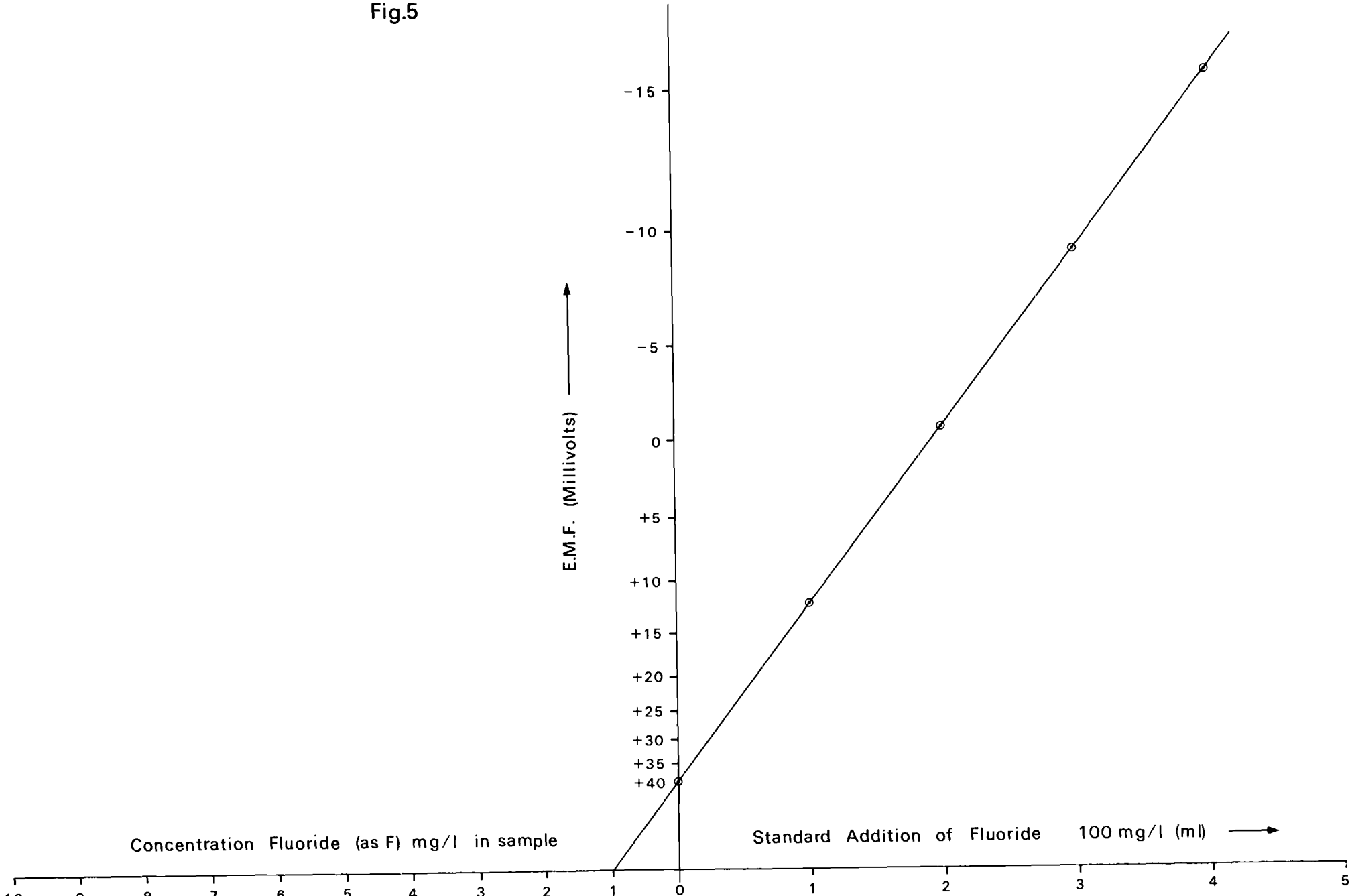
Calculations based on this equation can be simplified by the use of Gran's Plot paper.

Use of Gran's Plot Paper

The potentials obtained in procedure step 8.3 may be plotted directly on Gran's Plot paper (obtainable from Orion Research Inc. Ref. 90-00-90). This is semi-antilog paper with the antilog axis skewed to compensate for the 10% overall increase in volume caused by the standard additions. The slope term S is incorporated in the antilog scale. (58 mV per decade change in fluoride concentration for the Orion 90–00–90 paper). It is important that the electrode response complies with this condition, otherwise errors in the slope intercept will be introduced.

The millivolt reading corresponding to the highest fluoride concentration (E4) must be assigned to the divisions at the top of the vertical axis. Each major division must be plotted as 5 mV. The concentration should be scaled according to the strength of the fluoride solution used for the standard additions. An example of a typical plot is given in Figure 5.

Fig.5


-15
-10
-5
0
+5
+10
+15
+20
+25
+30
+35
+40
E.M.F. (Millivolts)
Concentration Fluoride (as F) mg/l in sample
Standard Addition of Fluoride 100 mg/l (ml)
10
9
8
7
6
5
4
3
2
1
0
1
2
3
4
5

Part 3: Pretreatments for Special Samples

Introduction

Some waters and effluents cannot be analysed directly for total fluoride by the methods given in Part 1 of this booklet. The fluoride is too strongly bound to the central atom of a complex ion for more than a trace to be detected. Some solid samples and sludges may contain highly insoluble fluoride. It may also be desirable to remove large quantities of organic matter prior to starting the anylysis. There is also the risk of losing fluoride as a volatile fluoride formed by over-heating some of the fluoro-complexes already mentioned.

The pretreatments which follow, used, if necessary, in suitable combination are intended for the analysis of total fluoride when one or more of the above problems occur. Although tested thoroughly, test data cannot be given for all possibilities and the analyst is recommended to evaluate the proposed scheme of analysis prior to use.

Pretreatment G, Ashing, is intended for the removal of large amounts of organic matter prior to further separation of fluoride by distillation or diffusion, but in favourable circumstances, the ash may be soluble in water, or in other ways suitable for direct analysis by any of the Methods A to E above. Under no circumstances should samples containing organic matter be directly subjected to Pretreatment J, Distillation or K, Diffusion because of the risk of an explosive reaction between organic matter and perchloric acid.

Pretreatment H, an evaporation procedure, is given, for use when there is a risk of fluoride loss from complex fluorides by overheating.

Pretreatments J, K and L are based on the volatilization of hydrofluoric acid and silicon tetrafluoride. The Diffusion procedure K is the mildest. The distillation procedure given as Pretreatment J is the one which, in the experience of Panel members has proved the most reliable and given the best recoveries of fluoride. However, it has the disadvantage of using perchloric acid which requires careful handling and specially made fume cupboards. Most, but not all, fluorides can be decomposed by this method. It is possible to extend this method to even more insoluble samples but only at increased risk, Method L has therefore been given as a means of analysing such samples. Some perfluoro-organic compounds will not react to any of these pretreatments, but it is unlikely that they would need to be analysed for fluoride. For such compounds organic analytical methods such as the oxygen flask method are more appropriate (20. and 27.)

X-ray Fluorescence Spectrophotometry cannot be used for fluoride, but occasionally DC arc band emission spectra have been used as have direct X-ray emission and some of the rare related techniques. See reference 20 but Section 3.8.1 and also Chapter 5.

G Pre-Treatment Procedure for Ashing Prior to Separation by Diffusion, Distillation or for Direct Analysis

G1 Purpose

The procedure is designed to effect the removal of organic and other volatile material from fluoride-containing samples prior to fluoride separation and determination.

G2 Types of Sample

1. Potable and other non-saline waters.
2. Sewage and sludges.

G3 Basis of the Method

Organic matter is removed by ignition at 600°C in the presence of a suitable magnesium salt to prevent loss of fluorine by volatilisation. The fluorine is retained as magnesium fluoride.

G4 Range of Application

Given suitable care and attention to detail the method is capable of removal of organic material from samples containing 5 μg to 0.5 g fluorine.

G5 Efficiency of Separation

Ignition at 600°C for 15 minutes will remove more than 95% of most organic matter (see Section G11).

G6 Precision

Data from this technique on its own is not available. Coupled with a suitable separation and/or detection procedure, total standard deviation should be better than 0.03 mg/lF at fluorine concentrations in the range 0.05 – 1.0 mg/l.

G7 Bias

Not known (see Section G9).

G8 Time Required for the Procedure

The operator time should not exceed 30 minutes but the total analytical time is dependent on the evaporation stage and the volume or wet weight of the sample taken.

G9 Recovery of Fluorine

G9.1 The ashing procedure may not completely pyrolyse keratinous proteins and hence fluorine may not be released.

G9.2 Carbon-fluorine bonds in some compounds are stable to temperatures in excess of 600°C. Fluorine contained within organofluorine compounds may not be released by this technique. Some organo-fluorine compounds are volatile.

G9.3 Alkali metal fluroides are volatile and in the presence of excessive amounts of alkali metal ions fluorine may be lost even in the presence of the magnesium salt.

G9.4 Fluoroborates, fluorophosphates, fluorosilicates and similar compounds can evolve volatile fluorides such as BF_3, PF_5, SiF_4.

G9.5 For most waters and waste waters, the ashing procedure coupled with a recommended separation step prior to fluoride determination should give complete fluorine recovery. In case of doubt or when the circumstances listed above are known to apply, the results obtained by the ashing procedure may be compared with those obtained by the pyrohydrolysis (Method L) or the oxygen flask techniques.

G10 Hazards

There are no special hazards with this method, but if organic material is not fully removed, hazards may arise in later procedures.

Suitable protective clothing and eye protection must be worn.

G11 Apparatus

G11.1 **Muffle furnace**

Rated at 800°C or above with temperature control capable of regulating the temperature within a range of ± 25°C. Refractory linings of muffle furnaces may contain fluorine and are therefore a potential source of contamination of samples.

G11.2 **Platinum Ware**

(a) for liquid samples, beakers or basins of up to e.g. 200 ml capacity.

(b) for solid samples, 20 ml covered crucible.

(c) Platinum tipped tongs. It is not desirable for platinum ware to come into contact with other metals.

G11.2.1 *Care of Platinum Ware*

Platinum ware should not be used with any of the following:-

(a) Aqua Regia or mixtures of hydrochloric acid with oxidizing agents.

(b) Samples which contain lead, zinc, tin, bismuth, gold, silver or copper in metallic state or base metals generally.

(c) Fused alkali oxides, peroxides and hydroxides.

(d) Embrittlement occurs on heating in contact with phosphorus, arsenic, antimony, selenium and tellurium.

Other substances may damage platinum at higher temperatures than recommended in this method.

G11.2.2 *Cleaning of Platinum Ware*

After use, platinum ware should be washed with hot concentrated hydrochloric acid (HAZARD) washed with water, dried and polished (if necessary) with a suitable abrasive, e.g. pumice or silver sand.

G11.3 **Porcelain stands, sintered alumina dishes or fused silica sheets** on which to stand hot platinum apparatus.

G12 Reagents

G12.1 **Water**

should be distilled and deionised.

G12.2 **Magnesium acetate solution**

Dissolve 75 ± 5 g magnesium acetate Mg $(CH_3CO_2)_2$ (low fluoride content) in 800 ml water and make up to 1 litre.

N.B. This is a likely source of high blank values. This solution is stable for at least one month if stored in a glass or polyethylene bottle.

G13 Procedure

Step	Procedure	Notes
	Liquid Samples	
G13.1	Pipette a suitable volume of sample containing not more than 200 µgF into a clean platinum basin and add 10.0 ± 0.1 ml of magnesium acetate solution (G12.2). Evaporate carefully to dryness (see Note (a)).	(a) The use of an infra-red lamp is suggested in order to inhibit "spitting" during the evaporation.

Step	Procedure	Notes
G13.2	**Solid Samples** Place a suitable amount of solid sample containing not more than 200 μgF in a platinum crucible. Add 10.0 ± 0.1 ml of magnesium acetate (G12.2), mix thoroughly and evaporate carefully to dryness (see Note (a)).	
G13.3	Break up any encrusted residue and carefully scrape down the dish sides to free the adhering residue. Heat gently over a burner taking care to prevent inflaming and finally heat at 600°C in a muffle furnace for 15 minutes. Cool, preferably in a desiccator (see Note (b)).	(b) In the presence of lithium and other alkali metal ions, fluoride may be volatilised at low temperatures.
G13.4	Stir the residue with a few ml of water, re-evaporate and repeat the ashing until visible signs of carbon disappear (see Note (C)).	(c) It is important to remove all carbon prior to progressing to the fluoride separation stage.
G14	**Blank Procedure** Carry out a reagent blank determination using 10.0 ± 0.1 ml magnesium acetate solution (G12.2) through Section G15.	
G15	For samples requiring further separation proceed to Section J12 of the distillation procedure or Section K15 of the diffusion procedure.	
G16	For samples not requiring futher separation determine the fluoride content of the sample using an appropriate method.	

H Evaporation of Samples to Dryness

(Note the distillation procedure (J) has its own evaporation section)

H1 Purpose The procedure is designed to allow for evaporation to dryness without loss of volatile fluoride.

H2 Types of sample Aqueous samples and slurries.

H3 Basis of the method The sample is evaporated in alkaline solution at a maximum temperature of 110°C.

H4 Range of Application The range of fluoride concentrations acceptable for this technique is dependent on the sample size taken but can be as low as 1 μg/l (for 5 l or larger sample) and as high as almost saturated.

H5 Procedure

Step	Procedure	Notes
H5.1	Into a borosilicate glass beaker of convenient volume, measure out a suitable volume of sample, sufficient to give an amount of fluoride within the range of the chosen method.	
H5.2	Using a pH meter (or phenolphthalein indicator if the distillation technique is not to follow), adjust the pH to a value above 8 using a few drops of sodium hydroxide solution (B5.7) or other convenient strength.	
H5.3	Gently evaporate the sample almost to dryness (Note (a)). If a completely dry sample is not required, stop evaporation before solid separates. It is usually more convenient to transfer the sample to the container used in the next procedure at this point than to proceed to dryness in the original beaker. Thorough rinsing with several small portions of water should be used to ensure that no fluoride is lost during this transfer.	(a) This step either requires constant supervision or should be carried out with the hot plate set as for step H5.4.
H5.4	If required, complete the evaporation using a hot plate which is not hotter than 110°C (Note (b)).	(b) If the sample is overheated, there is risk of some fluoro-complexes pyrolysing with loss of fluoride.
H5.5	Either proceed with the next pretreatment or with the chosen analytical method.	

J Pretreatment Procedure for the Separation of Fluorides by Distillation

J1 Purpose

The procedure is designed to separate fluorine from samples in which it is in complex form or in which there are elements likely to cause interference in direct determination.

J2 Type of Sample

(a) Aqueous non-saline samples containing excessive quantities of interfering inorganic substances. See under performance characteristics of appropriate analytical method.

(b) Sludges and samples containing organic matter (these samples should only be treated after the removel of organic matter by ashing — see Pretreatment procedure G).

J3 Basis of the Method

Steam distillation at elevated temperature of fluorides as fluorosilicic acid from aqueous or solid samples in a perchloric acid medium followed by the determination of the fluoride in the distillate by a suitable method.

J4 Range of Application

Given suitable care and attention to detail, and also suitably conditioned apparatus, this technique is capable of separating fluorine in the range 5 μg to 0.5 g. The normal range is 5 – 300 μg F for which the apparatus must be specially prepared, conditioned and reserved for use in this concentration range only.

J5 Precision and Limit of Detection

No specific data are available on the precision of this method. The apparatus used and the familiarity of the operator with the separation technique are significant factors in the production of reliable results. The smallest amount which can be separated by a skilled analyst using conditioned apparatus is 5 μg F. The method may not give reliable results if used occasionally by analysts inexperienced in its use.

J6 Bias

Any bias is likely to be negative. Providing adequate care is given to the separation this method can recover more than 95% of the fluorine from the sample.

J7 Efficiency of Separation

Chloride and other halides will co-distil if not removed by addition of silver perchlorate (see reference 23).

Certain fluorine-containing minerals (e.g. apatites and fluorites) may require prolonged distillation in order to release all of the fluoride).

J8 Principle

J8.1 The method described is the Willard-Winter distillation technique. The fluoride present is separated as fluorosilicic acid by steam distillation from perchloric acid at 130 – 140°C. The distillate is maintained alkaline to prevent loss of fluoride (see references 21, 22 and 23).

J8.2 All samples containing organic material or other volatiles will require pre-treatment to remove the organics which would present a hazard. This pre-treatment is normally carried out by ashing (see Pretreatment Procedure G).

J9 Hazards

This separation involves the use of percholoric acid. GREAT CARE MUST BE TAKEN TO ENSURE THAT ALL ORGANIC MATERIAL HAS BEEN REMOVED FROM THE SAMPLE BY MEANS OF A SUITABLE ASHING TECHNIQUE. The hazards associated with the handling of perchloric acid and the precautions to be taken in dealing with spillages etc., must be borne in mind. A metal (preferably stainless steel) spillage containment tray of suitable volume must be used. Perchloric acid may spontaneously ignite organic matter. If possible test a small portion of the sample before proceeding. A safety screen should be used. A special

hazard exists from contamination of wooden structures with perchloric acid. Fume cupboards in which perchloric acid is used must conform to British Standard 3202 (Reference 26).

Hazards also exist from the sodium hydroxide and sulphuric acid used in conditioning the apparatus.

Sodium fluoride is toxic, care must be taken when handling the solid material. All pipetting operations on solutions containing sodium fluoride must be carried out using a safety pipette.

A full length plastic reinforced apron with quick release fastening and a full face visor must be used during the distillation procedure. Use of suitable safety screens to protect both the operator and other laboratory workers is recommended.

There is a possibility of HF being formed during the distillation process. Care should be taken to avoid the distillate having any contact with the skin. Should this occur, immediate washing will minimise the burn. HF has an anaesthetising effect on the skin and the analyst may not be aware of the injury for some considerable time. First Aid treatment with magnesium oxide/glycerol paste will reduce the extent of the injury and medical advice must be obtained immediately.

Distillation flasks will eventually become fragile as a result of attack by HF and perchloric acid. Flasks should therefore be inspected for soundness before use.

Silver salts are toxic if ingested in large amounts. They temporarily stain the skin brown.

J10 Reagents

All reagents shall be of analytical reagent grade. Water must be distilled and deionised or double distilled from quartz vessels. All reagents (except perchloric acid and perchlorates) shall be stored in polyethylene bottles.

J10.1 Perchloric Acid 60% m/m.

J10.2 **Silver perchlorate solution 1000 g/l.** Dissolve 100 ± 1 g silver perchlorate in about 50 ml water. Dilute to 100 ± 5 ml with water.

J10.3 **Perchloric acid approximately 0.1M.** Add 10 ± 0.5 ml 60% perchloric acid (J10.1) to 1000 ± 10 ml water, mix well.

J10.4 **Sodium hydroxide approximately 0.1M.** Dissolve 4.0 ± 0.1 g sodium hydroxide in 1000 ± 10 ml water, mix well.

J10.5 **Sodium hydroxide solution approximately 50% m/v.** Dissolve 50 ± 5 g sodium hydroxide in 100 ± 10 ml water. HAZARD — this operation generates substantial quantities of heat, use a suitable spillage container. Store in a polypropylene container.

Add the sodium hydroxide slowly to the water stirring continuously (preferably using magnetic stirring). This operation also generates a fine mist which is hazardous, carry out the dissolution in a fume cupboard, using the minimum practicable sash opening.

J10.6 **Phenolphthalein solution 0.5% m/v.** Dissolve 1.0 ± 0.1 g phenolphthalein in 100 ± 10 ml ethanol or industrial methylated spirits. Add 100 ± 10 ml water with stirring. Add 0.1 M sodium hydroxide dropwise with stirring until a faint permanent pink colour is obtained.

J11 Apparatus

J11.1 **Steam Generator**

This can conveniently consist of a 5 litre round bottomed flask suitably insulated to reduce heat loss. Heating may be carried out either by gas or electricity. The generator must be fitted with a pressure relief tube system and with a vent valve.

The output of the generator is preferably connected to the distillation equipment directly by glass to glass joints, or in the case of multiple determination via a suitable glass manifold system. If rubber or plastic tube connections are used the length of tube exposed to the steam must be kept to a minimum.

The water (see Section J10) in the generator should be fluroide-free and must be kept alkaline to phenolphthalein (see Section J10.6) by the addition of 0.1 M sodium hydroxide solution (see Section J10.4) whenever the generator is recharged.

J11.2 **Distillation Unit**

This Unit must be constructed of borosilicate glassware and shall comprise typically of:

(a) 100 ml round bottom two neck distilation flask with ground glass sockets heated by an electric heating mantle fitted with a regulation device to facilitate the control of temperature.

(b) A means of introducing steam. This inlet shall be fitted with a tube drawn down to a 1 mm delivery jet extending to within 2 mm of the bottom of the distillation flask.

(c) Splash head designed to prevent the carry over of acid splashes.

(d) Thermometer 0–150°C mounted in a thermometer pocket which extends below the level of the liquid in the flask. Sufficient concentrated sulphuric acid should be placed in the thermometer pocket to ensure good thermal contact.

(e) Bend fitting to the outlet of the splash head connecting to:

(f) Vertically mounted double wall condenser and delivery tube.

All joints in the glassware shall be cone and socket type and shall be held firm by spring fittings or other suitable means. The joints must under no circumstances be lubricated with grease or similar organic material. Lubrication may be achieved using drops of 60% m/m perchloric acid on the distillation flask joints.

The apparatus described above may be constructed from any suitable commercially available borosilicate glassware providing the main principles of the design are adhered to. Fig. 6 shows a typical arrangement of apparatus which has been shown to be suitable for the distillation.

J11.3 **Conditioning of the Apparatus**

Prior to using the equipment, carefully wash all glassware with 50% sodium hydroxide solution (see Section 10.5) (HAZARD from sodium hydroxide burns. Wear appropriate protection). Wash well with water.

Add about 20 ml concentrated sulphuric acid to flask and heat until the acid fumes. (HAZARD : use appropriate protective clothing and screens). Cool to room temperature, reject the sulphuric acid. Wash well with water.

Before using new apparatus for analysis, check the recovery by following the separation procedure with prepared standard solutions of sodium fluoride of appropriate concentration (see relevant analytical method). The recovery obtained should be at least 95%. Failure to achieve this recovery is usually associated with ill-fitting glass joints or with insufficiently conditioned apparatus. Examine the fluoride content of the distillate and repeat if necessary until suitable and consistent recovery is obtained.

Apparatus should be reserved for this purpose only and used for no other purpose. Once apparatus has been conditioned, it should normally be stored assembled. If the apparatus is used only occasionally, the conditioning check, (by running a standard fluoride solution) must be carried out before use and the apparatus should be reconditioned if necessary.

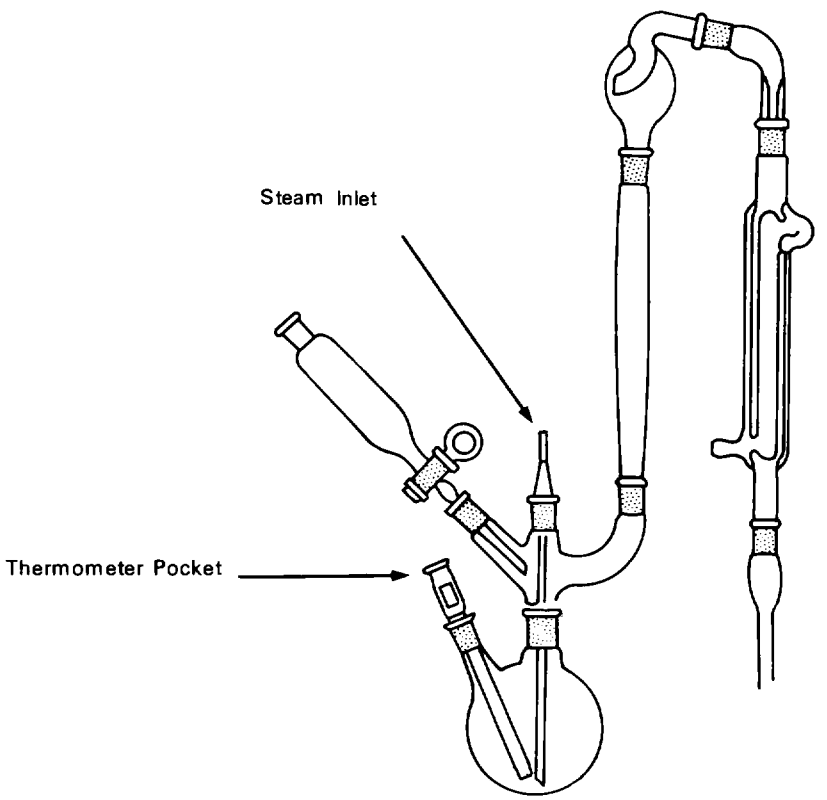
Separation Procedure Read Section 9 on hazards before starting this procedure.

Step	Procedure	Notes
J12	Samples ashed to remove organics prior to separation	
J12.1	Add a few drops of water to the platinum crucible containing the ashed sample. Add dropwise 60% perchloric acid (J10.1) until any effervescence has ceased.	

Step	Procedure	Notes
J12.2	Cover with lid and allow to stand for a few minutes.	
J12.3	Transfer the contents of the crucible quantitatively to the distillation flask, taking care to include any material on the underside of the crucible lid. Wash the crucible lid well with water and add the washings to the flask (see Note (a)). Add a few glass beads. Proceed to step J14.	(a) Keep total volume of acid and water used at this stage to less than 25 ml.
J13	Samples not ashed.	
J13.1	Transfer to distilation flask by pipette or other suitable means an aliquot of sample containing not more than 200 μg F.	
J13.2	Add a few glass beads and 3.0 ± 0.5 ml 0.1 M sodium hydroxide solution (J10.4). (See Note (b)).	(b) Addition of sodium hydroxide and step J13.3 may be omitted if aliquot volume is less than 25 ml.
J13.3	Evaporate sample to less than 25 ml. Reject distillate and cool. Proceed to Section J14.	
J14	Distillation	
J14.1	Add by means of the separation funnel 1(± 0.1) ml silver perchlorate solution (J10.2) and 15 (± 0.5) ml 60% m/m perchloric acid solution (see note (C)).	(c) Additional silver perchlorate solution may be needed for samples containing high chloride concentration. As a guide, allow 1 ml silver perchlorate solution (J10.2) for each 0.1 g or part thereof of chloride.
J14.2	Place a 100 ml calibrated flask containing 2.0 ± 0.5 ml 0.1 M sodium hydroxide solution (J10.4) and 1 or 2 drops phenolphthalein solution (J10.6) under the condenser outlet as a receiver (see Note (d)).	(d) Ensure that the condenser outlet dips below the surface of the liquid in the receiver.
J14.3	Heat the solution in the distillation flask until the temperature reaches 125°C.	
J14.4	Reduce the rate of heating and pass steam through the solution.	
J14.5	Allow the temperature to rise to 135 ± 5°C and control within this range for the remainder of the distillation (see Note (e)).	(e) The temperature range is critical to ensure full recovery of fluoride and to prevent acid vapour distilling over. Should the temperature during distillation fall below 130°C reject the distillation and carry out a fresh separation.
J14.4	Distil at the rate of about 1.5ml/minute until about 90 ml have been collected (see Notes (f) and (g)).	(f) Keep distillate alkaline to phenolphthalein throughout the distillation.
		(g) To check the recovery it is advisable having collected the first 90 ml distillate to collect a further 90 ml in a separate flask using the same technique. Determine the fluoride separately in each portion. If the amount of fluoride in the second portion is significant report the total fluoride determined as the sum of the two portions. If the fluoride in the second portion is more than 5% of that in the first portion reject the sample and investigate the reasons for poor recovery.

Step	Procedure	Notes
J14.7	Neutralize the distillate with 0.1 M perchloric acid (J10.3), cool and make up to 100 ml. Determine the fluoride content by a suitable method (see Part 1, Methods A to D	
J15	**Blank** With each batch of determinations, carry out a blank distillation and a distillation of a control standard solution of fluoride at a concentration about midpoint of the expected range of fluoride in the sample.	

Fig. 6 STEAM DISTILLATION APPARATUS



K Pretreatment Procedure for the Separation of Fluorides by Diffusion

K1 Substance Determined

The method is designed to separate inorganic fluoride from samples in which it is in complex form or in which there are elements likely to cause interference in the direct determination.

K2 Type of Sample

(a) Aqueous non-saline samples containing excessive quantities of interfering substances. See under performance characteristics of appropriate methods.

(b) Sludge samples and samples containing organic matter. The latter samples should only be treated after the removal of organic matter by ashing. (See Pretreatment procedure G).

K3 Basis of the Method

Diffusion of fluoride as HF from perchloric acid.

K4 Range of Application

Given suitable measurement techniques, this method is capable of separating 0.05 μg to 200 μg of fluoride. The 200 μg upper limit must not be exceeded for the apparatus as specified.

K5 Standard Deviation

Details of standard deviation are not directly applicable to the separation alone, but the separation, coupled with determination of fluoride by alizarin fluorine blue complexone method has a relative standard deviation of 1.0% at the 200 μg level and 1.5% at the 1.0 μg level. (10 degrees of freedom). (Data from Ref. 5).

K6 Bias

Any bias is likely to be negative. Provided care is taken to ensure completely gas-tight apparatus this method can recover more than 95% of the fluoride from the sample (see Section K7).

K7 Recovery of Fluorine

The method is unsuitable for samples containing organic matter unless this is removed by ashing prior to separation (see Section K10 — Hazards).

Certain fluorine-containing minerals (e.g. apatites and fluorites) may require prolonged diffusion. This method is not recommended for this type of sample.

K8 Time required for Separation

Given suitable prepared apparatus a batch of samples can be separated by micro-diffusion in 20 hours. The majority of this time is associated with the micro-diffusion stage which does not require attention. The time spent on the processing of a batch of 20 samples is approximately 2 hours.

K9 Principle of the Method

The fluoride present in the sample is diffused overnight at 60°C from perchloric acid onto an alkali layer inside the lid of a gas-tight container. The alkali-layer is dissolved in water and the fluoride determined by a suitable method (Ref. 24).

K10 Hazards

Samples containing organic materials or other volatiles require pre-treatment to remove the organics which would otherwise present a hazard. This pre-treatment is normally carried out by ashing (see Pretreatment Procedure G).

This separation involves the use of 72% m/m perchloric acid. Any spillage of this reagent must be treated immediately with copious quantities of water and wiped up at once. Great care must be taken to ensure that all organic material has been removed from the sample by means of a suitable ashing technique. The hazards associated with the handling of perchloric acid and the precautions to be taken in dealing with spillages, etc., should be borne in mind. A metal (preferably stainless steel) spillage containment tray of suitable volume must be used. (Perchloric acid may spontaneously ignite organic matter. A special hazard exists from the contamination of wooden structures with perchloric acid. Fume cupboards in which perchloric acid is stored must conform to British Standard 3202.

Sodium fluoride is toxic, care must be taken when handling the solid material. All pipetting operations on solutions containing sodium fluoride must be carried out using a safety pipette.

Silver salts are toxic if ingested in large amounts. They temporarily stain the skin brown.

It is recommended that a full length plastic reinforced apron with quick release fastening be worn. Safety spectacles or full face visor should be used.

K11 Reagents

Analytical reagent grade chemicals are suitable unless otherwise stated. Water should be distilled and deionised. Reagents should be stored in polyethylene bottles unless otherwise stated.

K11.1 **Perchloric acid 72% m/m.** high purity analytical reagent grade.

NOTE HAZARD

If the blanks on this reagent are too high, it may be purified as follows: Place the appropriate volume of 72% m/m perchloric acid into a clean covered borosilicate glass beaker. Place in an oven regulated at 60°C and allow to stand overnight. Cool and store in glass bottles.

K11.2 **Dilute Perchloric acid:** To 90 ± 5 ml water add 10 ± 1 ml 72% m/m perchloric acid, mix well.

K11.3 **Silver sulphate**

K11.4 **Perchloric acid – silver sulphate solution.** Disslive 5.0 ± 0.1 g silver sulphate (K11.3) in 100 ± 5 ml 72% m/m perchloric acid (K11.1). Store in glass bottles. NOTE HAZARD.

K11.5 **Sodium hydroxide approximately 0.1 M.** Dissolve 4.0 ± 0.1 g sodium hydroxide in 1000 ± 20 ml water.

K12 Apparatus

K12.1 **Diffusion Cell**

The diffusion cell consists of a heavy walled wide mouth screw-capped polyethylene sample bottle. The cap should be capable of providing a gas-tight seal. The seal on each bottle and cap should be tested prior to each use by immersing the bottle in water and applying hand pressure. It no gas bubbles are seen to be emitted from the seal on application of moderate pressure, it can be assumed to be gas-tight. Having ensured gas tightness, both the bottle and lid should be identified in a suitable manner to ensure that no interchange of bottles and lids can occur. The size of the diffusion cell should be such that it is approximately one third to one half full when in use. Cells of sizes 5 and 50 ml may be suitable. The size of the sample to be handled will therefore determine the size of the cell to be used. Prior to use, the diffusion cell and lid should be cleaned by warming to 70°C in dilute perchloric acid solution (K11.2). The cells should be held at this temperature for approximately 20 minutes and then allowed to cool naturally. When cool the cells and lids should be washed with water and dried at 60°C. In order to minimise the need for cleaning the cell it may be advantageous to place a disposable polyethylene or polypropylene lining cup within the diffusion cell.

K12.2 Micropipettes

A range of sizes should be available. The volume delivered by the pipette should have a tolerance equal or better than the following:

(a) Fixed volume — volume delivered 200 μl.

(b) Variable volume — volume range 25 to 200 μl.

The tolerance of volume delivered by the variable volume pipette should be equal to or better than the following:

Volume delivered μl	Tolerance μl
25	0.2
200	1.0

K13 Analytical Procedure

Read section K10 on Hazards before starting this procedure.

Step	Procedure	Notes
K13.1	Preparation of diffusion cell Before each batch of determinations check the gas-tightness of each cell/lid combination as outlined in Section K12.1	
K13.2	Using the fixed volume micropipette place 200 µl 0.1 M sodium hydroxide solution (K11.5) unto the centre of each cell lid. (See Note (a)).	(a) The use of a micro-pipette is recommended to minimise variation of error due to fluoride in the sodium hydroxide. 200 µl of 0.1 M sodium hydroxide will absorb a maximum of 380 µg F. This method is not recommended for fluoride contents in excess of 200 µg F.
K13.3	Evaporate the solution to dryness under vacuum over sodium hydroxide using a vacuum desiccator. (See Note (b)).	(b) Once dried the lids should be stored in the dessicator under vacuum until required.
K14	**Procedure for ashed samples** Moisten ashed sample containing not more 200 µg F^- with water and transfer quantitatively into the lined or unlined diffusion cell using the perchloric acid/silver sulphate solution. (See Notes (c), (d) and (g)).	(c) Volume of water should be kept to minimum to enable the smallest possible diffusion cell to be used. (d) Group samples so that the same volume of water can be used for all samples in the batch. This will affect the size of the cell used and the blank obtained.
K15	**Procedure for water samples** Transfer by pipette a known volume of water (v ml) containing an appropriate amount of fluoride not exceeding 200 µg F into the diffusion cell. (See Notes (d) and (e)).	(e) Keep the volume of sample to the minimum whilst providing sufficient fluoride to exceed the limited of detection of the analytical method to be used.
K16	**Diffusion stage**	(f) If the recovery on the control is below 95% investigate the cause and repeat the separation.
K16.1	Carry out a full reagent blank with each batch of samples analysed, using the same size diffusion cell and volume of water as for the samples. Also include a control sample containing a known volume of standardised sodium fluoride solution having a fluoride content equivalent to the mid range of the analytical method to be used but not exceeding 200 µg F. To each cell add 5 v ml of perchloric acid – silver sulphate solution (K11.4). (See Notes (f) and (g)).	(g) The final acid concentration is 60% m/m.
K16.2	Place cell lid in position immediately and close tightly (see note (h)).	(h) For safety the cell should be placed in a polyethylene beaker for support.
K16.3	Place sealed diffusion cell into an oven at 60°C for 16 to 20 hours.	
K16.4	Remove from the oven and allow to cool to room temperature.	
K16.5	The fluoride originally present in the sample should have been completely absorbed by the alkali layer on the cell lid. (See Note (f)). Dissolve the alkali layer in an appropriate volume of water or other suitable solvent (e.g. buffer for use with fluoride ion selective electrodes) for analysis by an appropriate method.	

L Pretreatment Process of the Separation of Fluoride by Pyrohydrolysis

L1 Substance Determined

Inorganic and organic fluoride which is converted to HF under the conditions of the technique.

L2 Types of Sample

Raw, potable and effluent waters (after prior evaporation to dryness) sediments and sludges.

L3 Basis of the Method

The ignition of the fluorine containing compound in the presence of a metal oxide catalyst followed by pyrolysis over platinium catalyst in an air/steam atmosphere.

L4 Range of Application

Given suitable care and attention to detail, the method is capable of removal of upwards of 10 μg fluorine from most substances.

L5 Efficiency of Separation

Providing due care is taken to ensure the apparatus is gas-tight, ignition at 1100°C for 15 minutes will remove more than 95% of fluorine from sample.

L6 Precision

Data from this technique on its own is not available.

L7 Time Required for

The operator time should not exceed 30 minutes, but total time is dependent on the evaporation stage and the volume or wet weight of the sample taken.

L8 Principle of the Method

The sample is mixed with a metal oxide catalyst (e.g. V_2O_5 or WO_3), ignited at a temperature of between 800 and 1100°C and the resultant gases pyrolysed in an air/steam atmosphere over platinised silica at 1100°C to convert fluorine to HF. The HF is adsorbed in water or a suitable buffer solution. (Reference 25)

L9 Recovery of Fluorine

L9.1 Fluorine can be recovered from all non-volatile fluorine compounds by this method, but certain fluorine containing minerals, e.g. apatites and fluorites may require prolonged treatment.

L9.2 Substances which contain volatile fluorides (i.e. fluorine-containing compounds which volatilize below 95°C) may require pre-treatment with a low temperature ashing technique prior to pyrohydrolysis.

L10 Hazards

Silica combustion tubes may become embrittled by heating in the presence of fluorine compounds.

Suitable protective clothing and eye protection must be worn.

L11 Apparatus

Furnace Equipment

(a) Tube furnace rated at 1300°C or above with temperature control capable of regulating the temperature within a range of ± 25°C at 1100°C. (See Figure 7)

(b) Smaller, moveable furnace rated at 1200°C or above with temperature control, capable of regulating the temperature within a range of ± 25°C over the temperature range 800 – 1100°C.

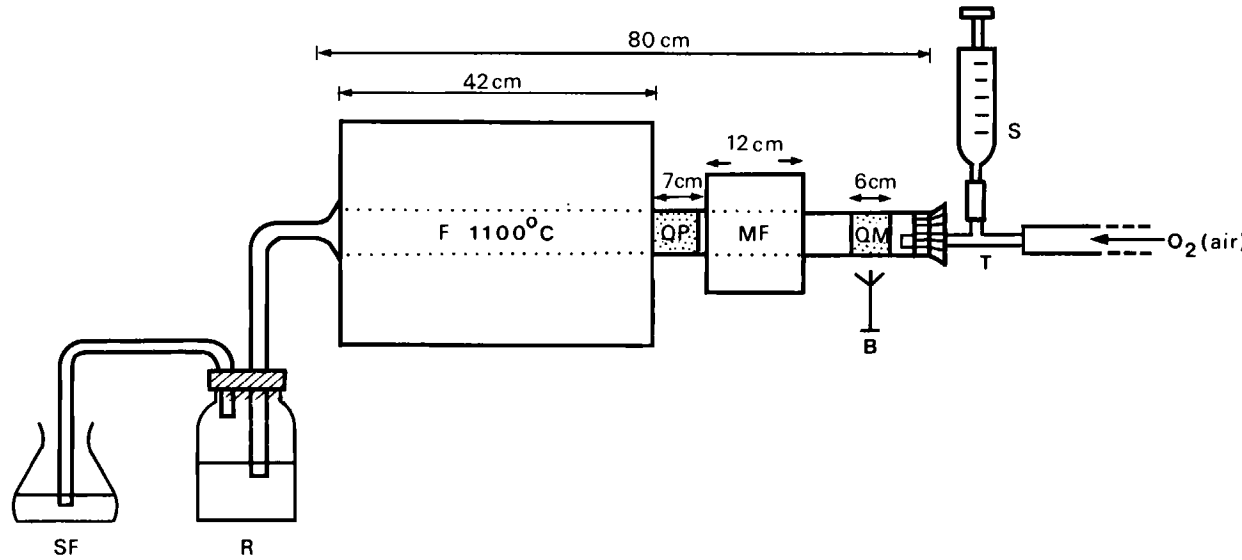
Platinum Ware

(a) For liquid samples, beakers or basins up to e.g. 200 ml capacity.

(b) For all samples, boats, as large as necessary consistent with the diameter of the combustion tube and length of combustion zones.

(c) Platinum tipped tongs. It is undesirable for platinum ware to come into contact with other metals.

Fig.7 COMBUSTION TRAIN



S - Syringe for injecting distilled water through T-piece into silica-wool plug, QM

B - Gas micro-burner

MF - Moveable furnace for heating sample (plus additive)

QP - Platinised silica wool

F - Furnace permanently maintained at 1100°C

R - Plastic receiver containing distilled water for the absorption of hydrofluoric acid

SF - Safety flask containing distilled water

QM Plain silica wool

67

(d) Platinum gauze.

For care of platinum ware see Method G, Section G11.2

Silica Ware

(a) Wide bore (15 – 35 mm) silica combustion tube of length 0.7 to 1.0m.

(b) Silica flask.

(c) Platinized silica wool

L12 Reagents

L12.1 **Water**

Water which complies with the requirements of the chosen end method should be used.

L12.2 **Catalysts**

Vanadium pentoxide or tungsten trioxide are suitable.

Analytical Procedure

Step	Procedure	Notes
L13	**Setting up**	
L13.1	Set up apparatus (see Figure 7) and switch on fixed furnace and allow to reach desired temperature (1100°C).	
	Liquid Samples	
L13.2	Pipette a suitable volume of sample containing not more than 200 μg fluorine into a clean platinum basin add 0.50 ± 0.05 of catalyst (L12.2) and evaporate to dryness. (See Note (a)). Transfer to platinum boat (see Note (b)).	(a) The use of an infra-red lamp is suggested in order to inhibit 'spitting' during evaporation. (b) Break down encrusted residue with suitable implement.
	Solid Samples	
L13.3	Place a suitable amount of solid sample containing not more than 200 μg F into the platinum boat, add 0.50 ± 0.05g catalyst (L12.2) and thoroughly mix.	
	Pyrohydrolysis Procedure	
L13.4	Transfer platinum boat to combustion position in combustion tube, insert silica wool plug wrapped in platinum gauze (see Fig 2 and replace stopper).	
L13.5	Light bunsen burner, turn on compressed air stream and inject water into silica wool plug (see Note (c)).	(c) The air flow should be in the range 0.1 to 0.5 1 min^{-1}.
L13.6	Switch on moveable furnace and allow to reach desired temperature in range 800 – 1100°C (see Note (d)).	(d) It is essential to keep the silica wool (QM) moist in order to obviate low results.
L13.7	Absorb gaseous HF produced in 30 ml water or a suitable buffer (see Note (e)).	(e) After pyrolysing for 15 minutes check for completeness of removal by changing absorbate.
L13.8	Transfer the solution containing absorbed fluoride water to a calibrated 50 ml flask and make up to the mark. Determine the fluoride content of the sample by an appropriate method.	

M Effluent Disposal and Silver Recovery (from Methods J and K)

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

M1 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.

M2 Silver Recovery

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 (28). 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 ntiric acid to form crude silver nitrate, which can be crystallised out, converted to solid silver sulphate for use in COD determinations (29), or futher purified by electrolysis to silver metal which can be re-dissolved to nitric acid and a purer grade of silver nitrate obtained.

M2.1 **Reduction to Crude Silver**

M2.1.1 *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 M1. A few additional items are listed in the appropriate sections.

M2.1.2 *Reagents*

Silver chloride slurry produced in Step M1

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 decahydrate
Sulphuric acid solution 10% V/V.

M2.1.3 *Hazards* (see also Section M2.6)

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.

M2.1.4 *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 and wash with water. Discard the filtrate.

M2.2 **Formation of Silver Nitrate**

The same procedure is used either for the crude silver obtained in step M2.1.4 or for the purer silver obtained from step M2.4.

M2.2.1 *Reagent*

Nitric acid (d_{20} 1.42)

M2.2.2 *Solution Procedure*

Distribute the filtered residue from step M2.1.4 into three, 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 M2.2.3. If solid silver sulphate is required proceed with Section M2.3. If silver nitrate solution is required dilute as required.

M2.2.3 *Crystallisation 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 crystallise, 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 evaporation batches. Silver nitrate has an exceptionally high solubility in water which varies considerably with temperature (9.25 Kg/l at 100°C and 1.2 Kg/l at 0°C), hence filtrates still contain relatively large amounts of silver.

M2.3 **Formation of Silver Sulphate**

M2.3.1 *Reagents*

Sodium Sulphate decahydrate

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.

M2.3.2 *Procedure*

Divide the filtrate from steps M2.2.2 into three, 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 GF/C filter, collecting the filtrate in a litre Buchner flask and wash each full 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 re-precipitate as silver chloride the silver which has not been converted to silver sulphate.

Wash each full Hartely 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.

M2.4 **Preparation of Silver Crystals**

Compact the crude silver from Step M2.1.4 with a suitable central electrical connection of silver wire to form an anode. Set up, in a fumehood, a heated 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.

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 M1 above.

It can then be re-dissolved in nitric acid to form silver nitrate as in Section M2.2 above.

M2.5 **Efficiency data for steps M2.1, M2.2 (except step M2.2.3) and M2.3**

(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 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 sg 1.84 by the standard procedure (reference 29) was satisfactory.

Data supplied by North West Water Authority, Workington Laboratory.

M2.6 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.

N Checking the Accuracy of Analytical Results

Once the methods have been put into normal routine operation many factors may subsequently adversely affect the accuracy of the analytical results. It is recommended that experimental tests to check certain sources of inaccuracy should be made regularly. Many types of test are possible and they should be used as appropriate. As a minimum, however, it is suggested that a standard solution of a sodium fluoride of suitable concentration be analysed at the same time and in exactly the same way as normal samples. The results obtained should then be plotted on a quality control chart which will facilitate detection of inadequate accuracy, and will also allow the standard deviation of routine analytical results to be estimated. For more detailed information on the types of test available and the interpretation of their results, standards texts — such as those published by the Water Research Centre (30) and by the DOE/NWC Standing Committee Committee of Analysts (31) — should be consulted.

O

Estimation of the Accuracy of Analytical Results Using the Tentative Methods in this Booklet

Before firmly recommending the tentative methods for general use, it is desirable to know the accuracy achievable in other laboratories. It would, therefore, be of great value if any laboratory using or considering the use of any of these methods could estimate the accuracy of its own analytical results and report the findings to the Technical Secretary of the General Non-Metallic Substances Working Group* of the DOE/NWC Standing Committee of Analysts, together with full details of the precise method used.

The precision achieved is of particular interest. The value of this information would be greatly enhanced if it were obtained at the same determinand concentrations as those for which some information has already been gained, as set out in the Performance Characteristics sections of these methods.

Similar information at other determinand concentrations, and in sample types other than those already studied, would also be of great assistance. Detailed specifications for the tests to be carried out are beyond the scope of this booklet, but standard texts – such as those published by the Water Research Centre (30) and by the DOE/NWC Standing Committee of Analysts (31) – provide guidelines from which precision tests may be designed. The same texts also provide guidelines for interference and recovery tests and any information on these matters would be gratefully received.

---

* Results should be sent to:

The Secretary
The General Non-Metallic Substances Working Group
The Standing Committee of Analysts
The Department of the Environment
Romney House
43 Marsham Street
London SW1P 3PY
England

Address for Correspondence

However throughly a method may be tested, there is always the possibility of a user discovering a hitherto unknown problem. Users with information on this method are requested to write to:

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

References

1. Frant MS, Ross JW, *Anal. Chem.* 1968, **40,** 1169.
2. Midgley D & Torrance K, *Potentiometric Water Analysis,* John Wiley & Sons, 1978.
3. *Boron in Waters, Effluents, Sewage and some Solids, 1980* Methods for the Examination of Water and Associated Materials, HMSO, London.
4. Cooke JR, Dixon EJ & Sawyer R, *Proc. Soc. Water Treatment and Examination,* 1965, **14,** 145.
5. Sawyer R, Grisley LM & Cox BG, *J. Sci. Fd. Agric.* 1967, **18,** 287.
6. Dixon EJ, *Analyst,* 1970, **95,** 272.
7. Dixon EJ, Grisley LM & Sawyer R, *Analyst,* 1970, **95,** 945.
8. Greenhalgh R & Riley JP, *Anal. Chem. Acta,* 1961, **26,** 179.
9. Belcher R, Leonard MA & West TS, *Talanta,* 1959, **2,** 92.
10. Small H, Stevens TS & Bauman WC, *Anal. Chem.* 1975, **47,** 1801.
11. Smith BW, Hall GEM & Koop DJJ, *Geochem. Explor.* 1978, **10,** 245.
12. Water Research Centre — *Notes on Water Research* No. 21 May, 1979.
13. Bureau of Analysed Standards. The BCS 382 has now been superseded by BCS 382/1 which is stated to contain 1017 mg/kg F.
14. Rea RE, M.Sc Thesis, Wolverhampton Polytechnic 1973.
15. Severn Trent Water Authority *Fluorides in Sewage Sludge, Technical Note 002,* October 1977.
16. Brand MJ, Rechnitz GA. Computer approach to Ion Selective Electrode Potentiometry by Standard addition procedure. *Anal. Chem.* 1970, **42,** 1172.
17. Atkinson SJ & Stockley M. Paper presented at the meeting of the Institution of Water Engineers and Scientists, 24th Arpil, 1979 at Sheffield.
18. *The sampling and initial preparation of sewage and waterworks sludges, soils, sediments and plant materials prior to analysis 1977.* Methods for the examination of waters and associated materials. London HMSO, 1978.
19. Water Research Centre, Stevenage Laboratory Report LR 1063, 1979.
20. *Emission Spectrophotometric Methods of Analysis for Waters, Sediments and other Materials of Interest to the Water Industry 1980* (also published in this series), Section 1.1.1(ii) HMSO, London.
21. Willard HH & Winter OB, *Ind. Eng. Chem. Anal. Ed.* 1933, **5,** 784.
22. British Standard 2690 *Method of Testing Water Used in Industry Pt 4, 1967. Aluminium, Calcium, Magnesium and Fluoride.* British Standards Institution, London.
23. *Official Standardized and Recommended Methods of Analysis.* The Society for Analytical Chemistry 1973 360–362.
24. Stuart JL, *Analyst,* 1970, **95,** 1032–1038.
25. Kakabadse GJ, *Proc. Analyt. Div. Chem. Soc.* 1977, **14**(1), 11.
26. British Standard 3202. *Fume cupboards for use with Perchloric Acid.* British Standards Institution London.
27. Macdonald AMG, *Analyst, 1961,* **86,** *3.*
28. *Kompass UK, Vol. 1, Products and Services.* Kompass Publishers Ltd, East Grinstead.
29. *Chemical Oxygen Demand (Dichromate Value) of Polluted and Waste Waters 1977.* Methods for the Examination of Water and Associated Materials, HMSO, London.
30. Wilson AL & Cheeseman RV, Water Research Centre, *Technical Report TR66,* 1978.
31. *General Principles of Sampling and Accuracy of Results 1980,* Methods for the Examination of Water and Associated Materials, HMSO, London.

Department of the Environment/National Water Council

Standing Committee of Analysts

Members of the Committee Responsible for this Method:

Mr P Adams [2]		Mr D McIntyre [2]	
Dr G I Barrow [1]		Mr P Morries [1,2,3]	
Dr G A Best [1]	since December 1980	Mr C C Musselwhite [2,3]	occasional
Dr J M Carter [1]		Mr D Myles [1,2]	
Dr G W Clayfield [1]		Mr A H Nield [1]	
Mr B E P Clement [1]		Dr D I Packham [1]	since December 1980
Dr R L Cooper [1]		Dr H A Painter [1]	
Dr B T Croll [1]		Dr S J Patterson [1,2]	until June 1980
Mr B Dale [3]		Mr L R Pittwell [1,2,3]	
Dr J A W Dalziel [2]		Dr J E Portmann [1]	
Mr K G Darrall [2]	until August 1979	Mr L D Purdie [1]	
Mr J A Davis [2]		Mr R E Rae [3]	
Mr T A Dick [1]		Mr B D Ravenscroft [1]	
Mr E J Dixon [3]	until December 1979	Mr J J Reid [3]	occasional
Dr E J Duff [3]		Mr B Rhodes [1]	since July 1978
Dr J W R Dutton [1]		Prof J P Riley [1,3]	since December 1976
Mr A R Folkhard [1]		Mr D T Scofield [3]	since December 1979
Mr D Fogg [2]	died December 1978	Mr C C Scott [2]	
Dr J Gardiner [1]	since June 1980	Mr R Sinar [1]	died April 1979
Mr D Gelsthorpe [2]		Mr W A Smith [3]	until November 1976
Mr G I Goodfellow [1,2]	since June 1980	Mr D Stickley [3]	since September 1979
Mr K Goodhead [1]	until December 1980	Mr M Stockley [2,3]	
Mr T R Graham [1]		Mr A Tetlow [1]	since June 1980
Mr I Harper [1]	since July 1978	Dr A Ure [1]	since August 1979
Mr E Hodges [1]		Mr R J Vincent [2]	
Mr G J Holland [1,2]		Mr A Westwell [3]	corresponding
Dr D T E Hunt [1]	since June 1980	Mr C R Whitfield [3]	occasional
Mr R H Jenkins [3]	since January 1980	Mr B T Whitam [1]	
Mr P Jones [3]	until January 1980	Mrs R Williams [3]	occasional
Mr W M Lewis [1]	until January 1980	Dr R Wood [1]	until July 1978
Mr P J Long [1]		Mr T B Wood [3]	since December 1976
Mr J C McCullins [1]			

[1] Main Committee
[2] Working Group
[3] Panel

Printed in England for Her Majesty's Stationery Office by Linneys of Mansfield. Dd 718267 C12 5/83

HER MAJESTY'S STATIONERY OFFICE

Government Bookshops

49 High Holborn, London WC1V 6HB
13a Castle Street, Edinburgh EH2 3AR
41 The Hayes, Cardiff CF1 1JW
Brazennose Street, Manchester M60 8AS
Southey House, Wine Street, Bristol BS1 2BQ
258 Broad Street, Birmingham B1 2HE
80 Chichester Street, Belfast BT1 4JY

Government publications are also available through booksellers

ISBN 0 11 751662 7