Acid Soluble Aluminium in Marine, Raw and Potable Waters (Second Edition) 1987

Methods for the Examination of Waters and Associated Materials

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About this Series

This booklet is part of a series intended to provide both recommended methods for the determination of water quality, and in addition, short reviews of the more important analytical techniques of interest to the water and sewage industries.

In the past, the Department of the Environment and its predecessors, in collaboration with various learned societies, have issued volumes of methods for the analysis of water and sewage culminating in 'Analysis of Raw, Potable and Waste Waters'. These volumes inevitably took some years to prepare, so that they were often partially out of date before they appeared in print. The present series will be published as series of booklets on single or related topics; 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 and notes 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 technical staff to decide which of these methods to use for the determination in hand. Whilst the attention of the users 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 a committee of the Department of the Environment set up in 1972. Currently it has nine Working Groups, each responsible for one section or aspect of water cycle quality analysis. They are as follows:

1.0 General principles of sampling and accuracy of results
2.0 Microbiological methods
3.0 Empirical and physical methods
4.0 Metals and metalloids
5.0 General nonmetallic substances
6.0 Organic impurities
7.0 Biological monitoring
8.0 Sewage Works Control Methods
9.0 Radiochemical methods

The actual methods and reviews are produced by smaller panels of experts in the appropriate field, under the overall supervision of the appropriate working group and the main committee.

The names of those associated with this method are listed inside the back cover. Publication of new or revised methods will be notified to the technical press, whilst a list of Methods in Print is given in the current HMSO Sectional Publication List No 5.

Whilst an effort is made to prevent errors from occurring in the published text, a few errors have been found in booklets in this series. Correction notes and minor additions to published booklets not warranting a new booklet in this series will be issued periodically as the need arises. Should an error be found affecting the operation of a method, the true sense not being obvious, or an error in the printed text be discovered prior to sale, a separate correction note will be issued for inclusion in that booklet.

L R PITTWELL
Secretary

1 July 1987

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 for one's self, one's colleagues, those outside the laboratory or work place, or subsequently for maintenance or waste disposal workers. 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. Reagents of adequate purity must be used, along with properly maintained apparatus and equipment of correct specifications. Specifications for reagents, apparatus and equipment are given in manufacturers catalogues and various published standards. If contamination is suspected, reagent purity should be checked before use.

Lone working, whether in the laboratory or field, should be discouraged.

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 waste, 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. Hazardous reagents and solutions should always be stored in plain sight and below face level. Attention should also be given to potential vapour and fire risks. 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.

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

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 required 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. If an ambulance is called or a hospital notified of an incoming patient give information on the type of injury, especially if poisoning is suspected, as the patient may be taken directly to a specialized hospital.

About these methods

When the first edition of this booklet first appeared in 1979 it only contained the present Method A as a tentative method and was intended only for quality control in Water Works and similar potable water analyses. Since then, much information has been sent in from users, so that the method as now given, while virtually the same, contains additional information, which it is hoped, will make the method more reliable.

Method B is not so susceptible to pH dependent variation as Method A and is about as sensitive as method A but is very difficult to automate. However, when water is used for Haemodialysis units, where a low aluminium content is essential, or when low levels of aluminium need to be measured in natural waters, more sensitive methods are required [1]. Method C is a spectrofluorimetric method, subject to some interference effects but with a limit of detection about one fiftieth of that for method A. Method D, which is even more sensitive than method C, can be used for all types of water, but requires special equipment. Part E gives details of ICP and other emission spectrophotometric methods. Methods C and D can also be used in Marine waters.

Method	Approximate Limit of Detection	Constraints
A	0.01–0.02 mg/lAl	pH sensitivity, need to check reagent quality; may not include all the colloidal soluble aluminium if the acid digestion is omitted or too short, see Section A8
B	0.02/mg/lAl	Difficult to automate; as A, may not include all the colloidal soluble aluminium
C	0.2 μg/lAl	Needs a spectrofluorimeter (commerically available) also some interference effects
D	0.03 μg/lAl	Requires a polarograph capable of operating as a differential pulse cathodic stripping voltammeter with reproducible hanging mercury drop electrode (commercially available)
E	<0.01 mg/lAl	Includes colloidal soluble aluminium

Part F gives information on other methods that have been studied. The booklet concludes with information on method testing (Part G)

Reference 1, Cronan C S, Walker W J, Bloom P R, *Nature* **324**. 140. 1986.

Forms in which Aluminium may Occur

1. Aluminium occurs in a variety of types of compound in nature, in acid, neutral and alkaline solution. It can also form collidal polymeric solutions and gels, as well as insoluble flocculent precipitates, all based on aquated positive ions or hydroxylated aluminates.

2. In addition, it can form complexes with organic acids and ions such as fluorides, chloride and sulphate, most but not all of which are soluble. Some of the organic acid derivatives, for instance the tartrate, are soluble at alkaline pH values.

3. Aluminium can also form two or three dimensional lattice compounds with oxygen (and hydroxyl), silicon, and some metals. Although insoluble, some of these compounds, notably the clays, micas and zeolites, can be found as fine suspended insoluble particles in rivers. Although containing aluminium, these insoluble lattice compounds are not usually considered as aluminium compounds in regard to the water cycle.

4. This booklet restricts itself to the determination of the aquated positive cation and those other forms of aluminium readily converted to that cationic form by warming with dilute acids, chiefly those mentioned in the first two paragraphs above (but see 7 below).

5. Chiefly, these methods are intended for the controlled use of aluminium salts as fluoculating agents for collioids (such as those in paragraph 3), and for microorganism removal. They may also be used for quality assessment of astringent naturally occurring waters found in parts of Britain and elsewhere, and similar compounds in raw, river and marine waters.

6. Some methods, such as DC arc emission spectroscopy, or methods in this booklet if preceded by strong acid treatments with hydrofluoric or sulphuric acid or by fusion with pyrosulphates, will determine lattice bound aluminium. However, except for certain specific geonose diseases such as asbestosis in which fibres or micro crystals of a specific mineral penetrate the body, these latter compounds are unimportant from a water quality standpoint, other than the esthetic problem of turbidity. They are usually assessed as turbidity or suspended solids. In the rare event of a geonose problem arising, identification of the actual mineral by x-ray diffraction and spectrographic techniques is usually required, not an aluminium analysis per-se.

7. ICPS, with a 0.45 (or 0.15) μm filtered sample, determines both simple soluble and colloidal soluble aluminium. Hence this method will often give higher aluminium values than the colorimetric methods unless this colloidal material is dissolved in the pretreatment stage of these latter methods.

Contamination

Aluminium is a constituent of many glasses and ceramics. The metal is in common use. Many soil and rock minerals contain aluminium. Hence contamination can be a problem. Analysts are advised to check new glassware by running blank samples and comparing results with earlier blank determinations. Carefulness and cleanliness are essential.

A Soluble Aluminium in Raw and Potable Waters by Spectrophotometry (1987 version)

Note: Throughout this method aluminium is expressed as the element (A1).

A1 Performance Characteristics of the Method

(For further information on the determination and definition of performance characteristics see reference 5).

A1.1	**Substance determined**	Those forms of aluminium reacting with pyrocatechol violet, α, α-bis (3,4-dihydroxphenyl) toluene-2, α-sultone. (See sections A2 and A8).
A1.2	**Type of Sample**	Raw and potable waters.
A1.3	**Basis of method**	The reaction of aluminium with pyrocatechol violet to form a blue-coloured complex the concentration of which is measured by spectrophotometry at 585 nm.
A1.4	**Range of application**	Up to 0.3 mg/1.
A1.5	**Calibration curve (a)**	Linear to at least 0.3 mg/1.
A1.6	**Total Standard Deviation (a)**	

Aluminium Concentration (mg/1)	Standard Deviation (mg/1)	Degrees of Freedom
0.060(b)	0.005	18
0.180(b)	0.004	18
0.300(b)	0.005	17
0.017(c)	0.005	14
0.318(d)	0.008	12

A1.7	**Limit of detection (a)**	0.013 mg/1 with 10 degrees of freedom.
A1.8	**Sensitivity (a)**	0.1 mg/1 gives an absorbance of approximately 0.16.
A1.9	**Bias (a)**	No bias detected except when interferences occur (see Section A1.10).
A1.10	**Interferences (a)**	Certain substances are known to cause interference in this determination (see Section A3).
A1.11	**Time required for analysis (a)**	The total analytical and operator times are the same. Typical times for 1 and 10 samples are approximately 60 and 90 minutes excluding any pretreatment time.

A1.12 For test data on an adaption to IQAS analysers see Section A15.

(a) These data were obtained at the South-West Water Authority Countess Weir Laboratory[1] using a spectrophotometer with 10 mm cells at 585 nm. Similar performance data has since been obtained by numerous other Water Authority and Water Company laboratories provided attention is paid to details (See Section A3).
(b) Distilled water spiked with the stated concentration of aluminium.
(c) Tap water.
(d) Same tap water spiked with 0.3 mg/1 aluminium.

A2 Principle

A2.1 The method described is that used by the South West Water Authority[4]. It is based on experimental work carried out by the Water Research Centre (Medmenham Laboratory)[2][3] but with minor modifications to the procedure to enable a 30 ml sample aliquot to be used and a final volume of 50 ml to be obtained after the addition of all the reagents.

A2.2 It is based upon the spectrophotometric measurement at 585 nm of the blue coloured complex formed by the reaction between aluminium and pyrocatechol violet in a suitably buffered solution. The method incorporates a means of overcoming interference effects due to iron by the addition of 1,10-phenanthroline/ hydroxyammonium chloride reagent which converts this metal to a stable iron (II) chelate (see Section A3).

A2.3 Correction for the natural colour and turbidity is achieved by means of a control test omitting the 1,10-phenanthroline/hydroxylammonium chloride reagent and the pyrocatechol violet solution.

A2.4 Acidification of samples is normally sufficient treatment to convert many forms of aluminium to those which react with pyrocatechol violet. However, certain samples may need more rigorous pretreatment to convert non-reactive aluminium to the reactive form (see Section A8).

A3 Interferences

A3.1 Fluorides, phosphates, detergents, iron and chromium all cause significant interference. The effect of these and some other substances on the determination of aluminium by the method described by the Water Research Centre[2] is shown in Table A1. The effect of 1mg/1 fluoride on the determination of aluminium by this method has been investigated by several laboratories[4] and the results are given in Table A2.

A3.2 A number of potable water supplies have fluoride added to bring the fluoride concentration to 1.0 ±0.1 mg/1. To determine the aluminium content in these waters the procedure specified in Sections A 8.1 and A9 should be followed except that the aluminium concentration (Steps A9.10 to A9.12) should be determined by reference to an appropriate calibration curve prepared from standards to which 1.0 mg/1 of fluoride has been added (see Section A11.3). This procedure gives satisfactory results and has been checked by 3 laboratories using this method[4]. If the fluoride concentration in the water is outside the range 0.9 to 1.1 mg/1 the analyst must decide for himself whether to use a calibration curve prepared from standards containing the concentration of fluoride in the sample or to extrapolate from a calibration curve prepared from standards containing 1.0 mg/1 fluoride.

A3.3 Interference effects caused by up to 1 mg/1 iron are minimized by the addition of the 1,10-phenanthroline/hydroxyammonium chloride reagent as described in the method. For samples containing condensed inorganic phosphates, hydrolysis of the acidified sample for 2 hours at 100°C before analysis minimizes interference effects.

A3.4 The method has been found to be very sensitive to variations in pH which may pass unnoticed when automated versions are used unless prior checks are made after step A9.2. (Yorkshire WA.)

A3.5 Pyrocatechol Violet is produced for a variety of uses including dyeing, where the only criterion is its colour, not its composition, whereas for reliability in this method it is the reactivity with aluminium which is important. Always specify use when ordering and verify that the material supplied is suitable before routine use. (Newcastle and Gateshead W.Co, South West WA Truro Laboratory and others.)

Table A1

Other substance	Concentration of other substance, mg/l	Effect* in mg/l Al of other substances at aluminium concentration of:	
		0.000 mg/l	0.300 mg/l
Calcium (as CA^{++})	500	+0.006	+0.003
	100	+0.003	+0.004
Magnesium (as Mg^{++})	100	+0.004	+0.006
Sodium (as NA^{+})	100	+0.002	+0.004
Sulphate (as $SO_4^{=}$)	100	+0.001	0.000
Nitrate (as NO_3^{-})	80	+0.005	+0.003
Potassium (as K^{+})	50	+0.005	+0.003
Silicon (as SiO_2)	50	+0.009	+0.005
Nitrite (as NO_2^{-})	10	+0.002	+0.005
Zinc (as Zn^{++})	2	0.000	+0.010
Cobalt (as Co^{++})	2	−0.002	−0.009
Nickel (as Ni^{++})	2	−0.002	−0.006
Cadmium (as Cd^{++})	2	−0.003	−0.003
Copper (as Cu^{++})	2	+0.034	+0.006
	1	0.000	+0.003
Lead (as Pb^{++})	2	+0.052	+0.007
	1	+0.004	0.000
Iron III (as Fe^{+++})	1	+0.011	+0.014
	0.3	+0.006	+0.004
Manganese II (as Mn^{++})	2	+0.012	+0.006
Manganese II (as Mn^{++})	1	0.000	−0.006
Chromium III (as Cr^{+++})	0.5	+0.004	+0.028
	0.25	+0.002	−0.015
	0.025	+0.005	−0.002
Tin II (as Sn^{++})	2	+0.002	−0.015
	1	+0.002	−0.007
Fluoride (as F^{-})	1	−0.005	−0.023
	0.5	−0.002	−0.011
Orthophosphate (as P)	8.2	−0.005	−0.050
	4.1	−0.005	−0.038
	1.7	0.000	−0.002
Condensed inorganic phosphates following acid hydrolysis for 2 hours at 100°C:—			
Pyrophosphate (as P)	1.0	+0.003	−0.005
Hexametaphosphate (as P)	1.0	+0.001	−0.002
Tripolyphosphate (as P)	1.0	0.000	+0.004
Commercial polyphosphate	10.0	+0.001	−0.037
Detergents†	5	−0.003	−0.042

* If the other substances had no effect, results would be expected (95 per cent confidence) to lie within the following ranges;
0.000±0.003 for 0.00 mg/l Al
0.000+0.006 for 0.300 mg/l Al

† Six commercial detergent powders (equal proportions by weight were used); the exact composition of these detergents was not investigated.

Other substance	Concentration of other substance, mg/l	Effect* in mg/l Al of other substances at aluminium concentration of:	
		0.000 mg/l	0.300 mg/l
Alkalinity (as $CaCO_3$)	300	+0.006	+0.007
	200	0.000	−0.002
Humic acid }	10 }	+0.001	−0.004
Fulvic acid }	10 }		
Chlorine	5	+0.001	0.000
Chlorine and	5 }	+0.001	0.000
Ammonia (as N)	0.5 }		
Coagulant Aids:			
polyacrylamide A	0.5	+0.005	+0.003
polyacrylamide B	0.5	+0.002	+0.002
polyacrylamide C	0.5	+0.002	+0.001
Starch D	3	+0.002	+0.003
Starch E	3	+0.003	+0.003

Table A2

Aluminium concentration (mg/l)	Effect* of 1 mg/l fluoride in mg/l Al			
	Water Research Centre	Yorkshire Water Authority	Thames Water Authority	South West Water Authority
0.000	−0.005	−0.003	+0.003	−0.006
0.043	−0.009			
0.050		−0.027		
0.060			−0.007	−0.010
0.100		−0.018		
0.120			−0.012	−0.011
0.130	−0.011			
0.180			−0.014	−0.018
0.200		−0.025		
0.240			−0.017	−0.021
0.300	−0.023	−0.025	−0.015	−0.024

* If 1 mg/l fluoride had no effect the results would be expected (95 per cent confidence) to lie within the following ranges:
0.000±0.002 to 0.004 for 0.000 mg/l Al
0.000±0.004 to 0.006 for 0.300 mg/l Al

A4 Hazards

A4.1 The reagents described in Sections A5.4 and A5.6 should be regarded as special hazards. Care must be taken to avoid ingestion, inhalation of vapours and to protect the hands, eyes and face.

A4.2 Hydroxyammonium salts and solutions are severe irritants and burn the eyes. Contact with the skin must be avoided. Continued contact may cause dermatitis. Systemically, methaemoglobinaemia may occur. Topically, hexamethylene tetramine (hexamine) is a skin sensitizer and irritant. If swallowed it can cause irritation of the alimentary tract, kidneys and bladder and is a strong diuretic.

A5 Reagents

Analytical reagent grade chemicals are suitable unless otherwise specified.

A5.1 Water

The water used for blank determinations and for preparing reagents and standard solutions should have an aluminium content which is negligible compared with the smallest concentration to be determined in the samples. Deionized water or water distilled from an all-glass apparatus is normally suitable.

A5.2 5M Hydrochloric acid

Add 445±5 ml of hydrochloric acid (d_{20} 1.18) to approximately 400 ml of water in a 1-litre calibrated flask, mix, allow to cool and dilute with water to the mark. Check the molarity of this solution by titration with standard alkali solution and adjust, if necessary, to 5.00±0.02M. Alternatively commercially available standardized 5M hydrochloric acid may be used. Store in a polyethylene bottle.

A5.2.1 0.1M Hydrochloric acid

Pipette 20.0±0.1 ml of 5M hydrochloric acid into a 1-litre calibrated flask and dilute with water to the mark. Store in a polyethylene bottle.

A5.3 50% V/V Ammonium hydroxide solution

Dilute 50±1 ml of ammonia (d_{20} 0.880) with water to 100 ml in a measuring cylinder. Store in a polyethylene bottle.

A5.4 1,10-Phenanthroline/hydroxyammonium chloride reagent

This reagent is hazardous (see Section A4). Dissolve 50.0±0.5 g of hydroxyammonium chloride in approximately 400 ml of water, add 0.500±0.005 g of 1,10-phenanthroline hydrate and dissolve. Transfer the solution to a 500-ml calibrated flask and dilute with water to the mark. Store in a polyethylene bottle. The solution is stable for at least 2 months.

A5.5 α, α-Bis (3,4-dihydroxy phenyl) toluene-2, α-sultone (pyrocatechol violet) solution

Not all batches of this reagent are satisfactory for this method (see Section A3.5). Test every new batch of reagent before routine use by analysing a series of standard samples including at least a duplicate at 0.02 mg/1A1.

Dissolve 0.187±0.001 g of pyrocatechol violet in approximately 40 ml of water. Transfer the solution to a 500-ml calibrated flask and dilute with water to the mark. Store the solution in a borosilicate glass bottle in a cool, dark place. The solution is stable for at least 2 months although there is a tendency for slight mould growth which, however, does not affect the performance if only clear solution is used.

A5.6 Hexamethylene tetramine (Hexamine) buffer solutions

A5.6.1 Hexamine/ammonia buffer

This reagent is hazardous (see Section A4). Dissolve 150.0±0.5 g of hexamine in approximately 350 ml of water and cool. If the solution is not clear, filter it through a glass fibre filter (pore size 1.2 μm). To the clear solution add slowly and carefully 17.0±0.2 ml of freshly prepared 50% v/v ammonium hydroxide solution. Transfer the solution to 500-ml calibrated flask and dilute with water to the mark. Store in polyethylene bottle, replacing the cap immediately after use. The solution is stable for at least 5 weeks. Before using this buffer solution for any determinations, check that the reaction pH value obtained is 6.1±0.1 (step A9.2, note k) by adding the reagents to a blank (step A9.4 onwards).

A5.6.2 Hexamine/ethanolamine buffer

An alternative buffer based on ethanolamine and hexamine has been used in some laboratories where it is desirable to avoid the use of ammonia. It can be prepared by dissolving 150.0±0.5 g of hexamine in approximately 350 ml of water and cooling; weighing out 7.50±0.01 g of ethanolamine, transfering it quantitatively to the hexamine solution using water. Transfer the mixture to a 500-ml calibrated flask and dilute to the mark with water. Performance characteristics using this buffer are not available. Any analyst using this buffer should check the reaction pH and check that the performance characteristics are adequate for the requirements.

A5.7 10% V/V Nitric acid

Dilute 100±1 ml of nitric acid (d_{20} 1.42) with water to 1 litre in a measuring cylinder. Store in a polyethylene bottle.

A5.8 Standard aluminium solutions

A5.8.1 Solution A:1 ml contains 0.36 mg Al

Dissolve 0.360±0.001 g of aluminium wire (at least 99.9% purity) in 20±1 ml of hydrochloric acid (d_{20} 1.18). Transfer the solution to a 1 litre calibrated flask and dilute with water to the mark. Store the solution in a polyethylene bottle. It is stable for at least 2 years.

A5.8.2 Solution B:1 ml is equivalent to 1.8 μg Al

Add 5.00±0.01 ml of solution A to a 1-litre calibrated flask, followed by 20.0±0.1 ml of 5 M hydrochloric acid, and dilute with water to the mark. Store the solution in a polyethylene bottle. It is stable for at least 6 months.

A5.9 Standard fluoride solution

A5.9.1 Solution contains 100 mg/l fluoride

Dissolve 0.221±0.001 g of sodium fluoride (previously dried in an oven at 105°C) in 20.0±0.1 ml of 5 M hydrochloric acid. Transfer quantitatively to a 1-litre calibrated flask and dilute to the mark with water. Store in a polyethylene bottle. This solution is stable for at least 2 months.

A6 Apparatus

A6.1 Cleanliness

Both British and American analysts have reported pick up of aluminium from glassware. Users are advised to pre-acid-leach all glassware and test it on blank samples before use.

If possible, apparatus should be reserved solely for aluminium determinations: all residual aluminium from previous determinations must be removed. Clean all glass and plastic ware by filling with or soaking in 10% v/v nitric acid over-night. Rinse thoroughly with water. Do not use detergents or chromic acid (see Section A3).

A6.2 100-ml translucent silica beakers
50 ml calibrated polypropylene flasks

A6.3 Spectrophotometer of prism or grating type or absorptiometer fitted with a filter having its maximum transmission at 585 nm and 10-mm cells.

A6.4 pH meter

A7 Sample Collection and Preservation

Clean a polyethylene bottle by the procedure given in Section A6.1, add to the empty bottle 20.0±0.5 ml of 5 M hydrochloric acid per litre of sample to be collected and collect the sample. The acidification minimizes the adsorption of aluminium on the walls of the bottle and assists in the dissolution of colloidal and particulate forms of aluminium. The dilution of the sample by the acid must be allowed for when calculating the final results (see Step A9.12). With raw water samples, insoluble matter may be removed by filtering through a 0.45 (or 0.15) μm filter, if so required; however the filter material should be checked that it does not absorb aluminium.

A8 Sample Pretreatment

A8.1 In many cases acidification of the sample by collection into hydrochloric acid will provide sufficient pretreatment to convert most forms of aluminium into those which will react with pyrocatechol violet. However, certain samples may contain suspended aluminates which do not readily react with cold dilute hydrochloric acid and in these cases a more rigourous pretreatment will be necessary. This involves boiling the acidified sample. A method for determining 'total' aluminium in waters cannot be recommended due to the many different forms in which aluminium can occur in minerals. The most common forms will be clays and feldspars which would normally be assessed as turbidity and removed during treatment. If aluminium must be determined in such material see Ref 8. Experience will indicate to analysts whether pretreatment is needed for their particular water samples. It is recommended that analysts check their particular water samples by comparing the results obtained by carrying out the procedure in Section A9 with those obtained following the procedures outlined in Section 8.2 and Section A9. If pretreatment is used the performance characteristics of the complete method, and in particular the precision, may differ from those given in Section A1.

A8.2 Pretreatment procedure

This procedure is used when insoluble aluminates are present and it involves boiling the acidified sample.

Step	Procedure	Notes
	Pretreatment procedure (notes a, b, c, d and e)	
A8.2.1	Add 30.0±0.5 ml of the well mixed sample to a 100-ml translucent silica beaker. Cover the beaker with a silica watch glass and heat to boiling. (PTFE beakers and watch glass may be used instead of silica). (The duration of simmering or gentle boiling required to dissolve colloidally soluble aluminium compounds will vary depending on the degree of polymerization and the other occluded ions. Analysts are advised to ascertain the required time for their samples by initially analysing a series of aliquots of samples to find the time giving the true maximum aluminium value. A blank and a standard must be included to guard against risks of pick-up and hydrolysis during the test).	(a) If pretreatment is carried out a calibration curve must be prepared with calibration standards which have been run through the whole pretreatment procedure (see Section A11). (b) Precautions must be taken to minimize contamination during this step. (c) An appropriate quality control solution (see Section A14) should be run through this procedure for each batch of determinations for which pretreatment is required using the same batch of reagents and apparatus as for samples. (d) If polyphosphates are present continue boiling for 2 hours with addition of water to avoid evaporation to dryness (see Section A3). (e) If fluoride is present a calibration curve should be prepared with calibration standards which contain fluoride (see Sections A3.2 and A11.3). As some fluoride can be volatilized during this procedure, if fluoride containing standards are used they must be treated exactly as samples.
A8.2.2	Cool the solution, adjust its temperature to 15–30°C and transfer it quantitatively to a 50-ml calibrated polypropylene flask and proceed as in Section A9 using this solution as the sample.	

Step	Procedure	Notes
	Blank determination	
A8.2.3	A blank must be run for each batch (eg up to 10 samples) of determinations for which pretreatment is required using the same batch of reagents as for samples. Add 30.0±0.5 ml of 0.1 M hydrochloric acid to a 100-ml translucent silica beaker. Cover the beaker with a watch glass and heat to boiling. Cool the solution, adjust its temperature and transfer it quantitatively to a 50-ml calibrated polypropylene flask, using not more than 5 ml of water for rinsing. Then proceed as in step A9.5.	
	Compensation for colour and turbidity in the sample	
A8.2.4	A sample compensation solution must be run for each sample for which pretreatment is required and for which a colour/turbidity correction is necessary using the same batch of reagents as for samples. Carry out steps A8.2.1 and A8.2.2 but omit the addition of 1,10-phenanthroline and pyrocatechol violet in step A9.2.	

A9 Analysis of samples (notes f, g, h and i)

Step	Procedure	Notes
A9.1	Add 30.0±0.5 ml of well mixed sample to a calibrated 50-ml polypropylene flask. Adjust the temperature of the sample, if necessary, to between 15 and 30°C.	(f) If polyphosphates are present see Section A8.2.1, note d. If colloidal forms of aluminium hydroxide are suspected, see A 8.2.1 second paragraph.
		(g) An appropriate quality control solution (see Section A14) should be run through this procedure for each batch of determinations for which pretreatment is not required, using the same batch of reagents as for samples.
		(h) If fluoride is present, a calibration curve should be prepared with standards which contain fluoride (see Sections A3.2 and A11.3)
		(i) If the sample contains more than 0.3 mg/l Al see Section A12.
A9.2	Add to the flask, swirling after each addition, 1.0±0.1 ml of 1,10-phenanthroline reagent, 2.00±0.05 ml of pyrocatechol violet solution and 10.0±0.1 ml of hexamine/ammonia buffer solution (or hexamine/ethanolamine buffer solution—see Section A5.6.1) and dilute with water to the mark. Stopper the flask and mix the contents well (notes j and k). Allow to stand for 15±5 minutes	(j) If a batch of samples is to be analysed each reagent can be added to all samples before adding the next reagent.
		(k) The pH value must be 6.1±0.1. Each time a new batch of hexamine buffer is used the pH value of a blank should be checked using a pH meter (see Section A5.6).
		It is also advisable occasionally to check the pH value of real samples and if necessary to adjust the buffer solution A 5.6.1.
A9.3	Meanwhile set up the instrument (see Section A6.3) according to the manufacturer's instructions. Adjust the zero of the instrument with water in the	

Step	Procedure	Notes
	reference cell. Measure the absorbance (see Section A10) of the well mixed solution at 585 nm using 10-mm cells. Recheck the instrument zero. Let the absorbance of the sample be S.	
	Blank determination **(if pretreatment not required) (note l)**	(l) Blanks for pretreated samples will already be being processed and should be treated as samples.
A9.4	A blank must be run for each batch (eg up to 10 samples) of determinations for which pretreatment was not required using the same batch of reagents as for samples. Add 30.0±0.5 ml of 0.1 M hydrochloric acid to a 50 ml calibrated polypropylene flask and adjust the temperature to between 15 and 30°C.	
A9.5	Carry out steps A9.2 and A9.3. Let the absorbance of the blank be B.	
	Compensation for colour and turbidity in the sample	
A9.6	A sample compensation solution must be run for each sample for which a colour/turbidity correction is necessary using the same batch of reagents as for samples. Carry out steps A9.1 to A9.3 inclusive, omitting the additions of 1,10-phenanthroline reagent and pyrocatechol violet solutions in step A9.2. Let the absorbance of the sample compensation solution be A.	
	Determination of aluminium in the water used for the blank (note m)	
A9.7	Add 50.0±0.5 ml of 0.1 M hydrochloric acid to a 100-ml translucent silica beaker. Cover the beaker with a watch glass and evaporate carefully (note n) on a hot plate until the volume in the beaker is about 20 ml. Add a further 4 times 50±1 ml portions of water, evaporating to 20 ml after each of the first 3 additions, and to 50±2 ml after the final addition. Cool the beaker.	(m) This determination is not needed if the aluminium content of the water used for the blank is known or is negligible (Section A13.2). (n) Precautions must be taken to minimize contamination during this step.
A9.8	Analyse a 30.0±0.5 ml portion of the solution as in steps A9.1 to A9.3 inclusive. Let the absorbance of this solution be E.	
A9.9	The absorbance W, due to the aluminium in the water used for the blank is given by: $W = \frac{E - B}{4}$ Calculate the aluminium content of the water, A_w, from W and the calibration curve (note o).	(o) See Section A11 for the preparation of the calibration curve.

Step	Procedure	Notes
	Calculation of Results	
A9.10	Calculate the apparent absorbance due to aluminium in the sample, R, from: $R = S - B$ or, when a correction for colour/turbidity is made: $R = S - B - A + C$ where C = absorbance when both the sample cuvette and the reference cell are filled with water.	
A9.11	Determine the apparent aluminium concentration A_a, in the sample from R and the calibration curve (see Section A11).	
A9.12	Calculate the aluminium concentration in the original sample, A_r $A_r = 1.02(A_a + A_w)$ (note p).	(p) The factor 1.02 allows for the dilution of the sample by the acid into which it was collected (see Section A7).

A10 Measurement of Absorbance

The exact instrument setting for the wavelength of the absorption peak must be checked for each instrument and then used in all future work. The procedure used for measuring absorbance should be rigorously controlled to ensure satisfactory precision. The same cells should always be used and should not be interchanged between the reference and sample. They should always be placed in the same position in the cell holder with the same face towards the light source.

It is difficult to ensure reproducible alignment of cells with chipped corners, and therefore they should be discarded. Similarly, the slide of the cell holder should be kept scrupulously clean. Before every set of measurements the absorbance of the sample cell should be measured against the reference cell when both are filled with water. This will also enable the true absorbance of the blank to be determined.

A11 Preparation of the Calibration Curve

A11.1 The calibration curve is linear to at least 0.3 mg/l Al when measurements are made at 585 nm using a spectrophotometer or an absorptiometer fitted with a suitable filter. The sensitivity with the latter is less than that obtained by measuring with a spectrophotometer at 585 nm. For measurements with a spectrophotometer at 585 nm, the slope of the calibration curve decreases by approximately 0.2% for an increase in temperature of 1°C.

A11.2 When pretreatment is carried out

To a series of 100 ml translucent silica beakers add from a burette 30.0, 29.0, 28.0, 27.0, 26.0 and 25.0 ml (all ±0.5 ml) of 0.1 M hydrochloric acid. Pipette into these beakers 0.0, 1.0, 2.0, 3.0, 4.0 and 5.0 ml, respectively of standard aluminium solution B. Mix by swirling and carry out steps A8.2.1, A8.2.2 and A9.2 onwards as appropriate. Subtract the absorbance of the blank from the absorbances of the other solution and plot the corrected results against the concentration of aluminium. The above solutions are equivalent to 0.00, 0.06, 0.12, 0.18, 0.24 and 0.30 mg/l Al respectively. The calibration curve should be checked at frequent intervals.

A11.3 When pretreatment is not carried out

To a series of 50-ml calibrated polypropylene flask add from a burette 30.0, 29.0, 28.0, 27.0, 26.0 and 25.0 ml (all ±0.5 ml) of 0.1 M hydrochloric acid. Pipette into these flasks 0.0, 1.0, 2.0, 3.0, 4.0 and 5.0 ml, respectively, of standard aluminium solution B. Mix by swirling and carry out step A9.2 onwards as appropriate. Subtract the absorbance of the blank from the absorbances for the other solutions, and plot the corrected results against the concentration of aluminium. The above solutions are

equivalent to 0.00, 0.06, 0.12, 0.18, 0.24 and 0.30 mg/l Al respectively. The calibration curve should be checked at frequent intervals.

A11.4 When 1.0±0.1 ml/l fluoride is present

To a series of 100-ml translucent silica beakers (Section A11.1) or 50-ml calibrated polypropylene flask (Section A11.2) add from a burette 15.0, 14.0, 13.0, 12.0, 11.0 and 10.0 ml (all ±0.5 ml) of 0.1 M hydrochloric acid. Pipette into these flasks 0.0, 1.0, 2.0, 3.0, 4.0 and 5.0 ml of standard fluoride solution. Mix by swirling and carrying out the steps specified in Sections A11.1 or A11.2 as appropriate to prepare the appropriate calibration curve. The calibration curve(s) should be checked at frequent intervals. If correction needs to be made for the other fluoride concentrations, change the volume of standard fluoride solution used proportionately.

A11.5 Reagent Evaluation Standard

A 0.02 mg/l Al standard may be needed if the quality of the Pyrocatechol Violet reagent has to be checked. Prepare an extra 0.06 mg/l Al standard, pipette out 10.0 mls (for A11.1 or A11.2) or 5.0 mls (for A11.3) and add 20.0 or 10.0 mls of 0.1 M hydrochloric acid respectively. Treat as other standards.

A12 Change in the Concentration Range of the Method

For samples containing aluminium concentrations greater than 0.3 mg/l an appropriately smaller volume of sample should be taken. Dilute this volume v ml to 30 ml with 0.1 M hydrochloric acid in a 50-ml calibrated polypropylene flask. The aluminium concentration in the original sample is given by:

$$C = 1.02 \frac{30}{v} (C_a + C_w)$$

A13 Sources of Error

The analytical procedure can be applied to a wide range of raw and potable waters and the attention which it is necessary to pay to sources of error depends upon the accuracy required. The aluminium concentration should be verified, if in doubt, by the use of the pretreatment procedure (see Section A8). The following sub-sections describe the main sources of error and how they can be minimized, but analysts must decide what precautions are appropriate to their particular requirements.

A13.1 Correction for colour and turbidity in samples

In spectrophotometric methods of analysis, the presence of coloured and or suspended materials in samples will cause falsely high results to be obtained. Whether or not a correction is required for this effect depends on the error that can be tolerated and the nature of samples. The procedures in steps A8.2.4 and A9.6 allow a correction to be made if required.

A13.2 Effect of aluminium in the water used for blank determinations

If the water used for the blank determination contains aluminium, the blank correction will be falsely large and results for samples falsely low. Again, whether or not a correction is required for this effect depends on the error that can be tolerated and the concentration of aluminium in the blank water. The procedure in steps A9.7 to A9.9 allows a correction to be made when required.

When it is necessary to make a correction, to avoid the need for determining C_w in every case, it is convenient to estimate C_w for one large batch of water. This value of C_w may then be used for all subsequent batches of analyses when the same water is used for the blank.

A13.3 Interfering substances

See Section A3.

A13.4 Unusual sample pH values

Samples with unusual pH values or unexpected self buffering capacity may not give the correct pH value at step A9.2 and so give the wrong absorption. If this is suspected, check the pH value of a sample and either adjust the buffer addition accordingly or use a different method.

A13.5 Pyrocatechol Violet Quality

Occasionally rogue batches of reagent A5.5 have been encounted. See Sections A5.5 and A11.5.

A14 Checking the Accuracy of Results

(For further information see references 5, 6 and 7.

Once the method has been put into normal routine operation many factors may subsequently adversely affect the accuracy of analytical results. It is recommended that experimental tests to check certain sources of inaccuracy should be made regularly. Many types of tests are possible and they should be used as appropriate. However, as a minimum, it is suggested that a solution of known aluminium concentration should be analysed at exactly 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.

A15 Adaptation to Automatic Analysers

This method has been successfully adapted to a variety of air-segmented, flow injection and discrete sample analysers. The following example is from an IQAS instrument.

A15.1 Principle of Method

As A2 above

A15.2 Performance Characteristics

A15.2.1	Types of Sample:	Raw, potable and river waters.
A15.2.2	Calibration Range:	0.0 to 1.0 mg/l
A15.2.3	Criterion of Detection:	0.0016 mg/l Mean: 0.0133 mg/l
A15.2.4	Reporting Limits:	0.01 to 1.00 mg/l
A15.2.5	% Carry Over:	0.07%
A15.2.6	Precision:	Typical data obtained

	Concentration mg/l Al	Degrees of Freedom	Standard Deviation mg/l Al	Mean Bias mg/l Al
Within Batch	0.09	10	0.00249	+0.0095
	0.90		0.01798	+0.0037
Between Batch	0.09	9	0.007598	+0.0095
	0.90		–	+0.0037
Total	0.09	19	0.007996	+0.0095
	0.90		0.01798	+0.0037

A15.3 Apparatus

A15.3.1 An IQAS instrument/Note, similar modifications can be made for other types of analyer.

A15.3.2 The reaction tubes have plastic inserts to avoid interferences from aluminium in glass reaction tubes.

A15.3.3 Reagent Dispenser Details

	CONTENTS	Amount Dispensed (g)
	Sample	1.01
R1	Acid/Aluminium spike	0.12
R2	Phenanthroline	0.31
R3	Catechol violet	0.58
R4	Hexamine buffer	0.36
R5	Acid/Aluminium spike	0.97
R6	Milli-Q water	1.04

A15.3.4 Operating Temp °C: 37.0

A15.3.5 Wavelength: 590 nm

A15.3.6 Analytical Guide Times

Instrument time for 1 sample: 16 min 3 s
Index rate for each additional sample: 18 s

A15.4 Reagent Preparation (Based on Preceeding Section A5)

A15.4.1 Stock Standard Solution: 100 mg/l Al

Weigh out 17.575 ±0.001 g Aluminium Potassium Sulphate decahydrate, dissolve in about 500 ml of water, add 5.0±0.1 ml hydrochloric acid (d_{20} 1.18) and make up to one litre in a calibrated flask with water.

A15.4.2 Hydrochloric Acid/Aluminium spike solution

Pipette 10.00±0.01 mls of 100 mg/l Aluminium stock standard solution into a 2 l calibrated flask, add about 890 mls of hydrochloric acid (d_{20} 1.18), and make up to two litres with aluminium free water. Dilute tenfold before use.

A15.4.3 Calibration Standards

Prepare five calibration standard solutions containing 0.00, 0.25, 0.50, 0.75. 1.00 mg/l Al by quantitatively diluting 0.0, 2.5, 5.0, 7.5 and 10.0 ml (all ±0.05 ml) of stock standard solution (A15.6.1) to 1 litre with water in calibrated flasks.

A15.4.4 Phenanthroline Reagent

Weigh out 50.0±0.1 g of hydroxyammonium hydrochloride, dissolved in about 100 ml of distilled water, weigh out 0.50±0.01 g of phenanthroline hydrate, dissolve in the same solution and make up to 500 ml in a calibrated flask, with water.

A15.4.5 Pyrocatechol Violet Reagent*

Weigh out 0.1880±0.0005 g Pyrocatechol violet, dissolve in about 200 ml of distilled water and make up to 250 ml in a calibrated flask, with water. Dilute fivefold before use.

* The reagent bottle on the IQAS will become stained, see A3.5 and A5.5.

A15.4.6 Hexamine Buffer Reagent

Weigh out 150.0±0.5 g of Hexamine and dissolve in about 300 ml of distilled water; add 8.40±0.05 ml of ammonia solution (d_{20} 0.88) and dilute to 500 ml with water in a calibrated flask.

A15.5 Procedural Details

Analysts should ascertain by tests, whether any predigestion or filtration is needed in order to dissolve colloidal material or remove insoluble matter (see Sections A7 and A8 (especially A8.2.1)).

A15.5.1 The samples are collected in the field in bottles predosed with half the acid required by the method.

A15.5.2 The remaining acid and an aluminium spike equivalent to 0.10 mg/l Al, are added by the IQAS. This spike is added in order to overcome inconsistencies in the method at low levels.

A15.5.3 Final reaction pH value 6.1 to 6.2. (This should be checked periodically).

A15.5.4 Proceed according to manufacturers instructions. Calibrate with standard samples; but allow for the spike addition at A15.5.2. Include Quality Control samples.

A16 References

(1) Department of the Environment, file WS/646/53, paper SCA/4.3/20, April 1978.
(2) Water Research Association, Medmenham, *Technical Paper 103*, August 1973.
(3) Dougan W K and Wilson A L, *Analyst*, 1974, **99**, 413–430.
(4) Department of the Environment, file WS/646/53, papers SCA/4.3/21 a, b and c November 1978.
(5) *General Principle of Sampling and Accuracy of Results 1980*, HMSO, in this series.
(6) Wilson A L and Cheeseman R. Water Research Centre *Technical Report 66*, WRC. Medmenham.
(7) British Standards BS 5700–5703.
(8) *Methods for the Determination of Metals in Soils, Sediments and Sewage Sludge, with a note on the determination of insoluble Metal Contents 1986*, HMSO, in this series.

B Acid Soluble Aluminium in Raw and Potable Waters by Spectrophotometry using Bromopyrogallol Red (Tentative Method)

B1 Performance Characteristics of the Method

(For further information on the determination and definition of performance characteristics see reference 2).

B1.1	Substance determined	Those forms of aluminium reacting with bromopyrogallol red in the presence of n-tetradecyltrimethylammonium bromide (see Section B2).
B1.2	Type of Sample	Raw and Potable Waters.
B1.3	Basis of the method	Acid soluble aluminium reacts with bromopyrogallol red in the presence of n-tetradecyltrimethylammonium bromide to form a blue complex which is measured colorimetrically at 625 nm. Potential interference from iron is masked with the use of 1,10-phenanthroline prior to mixing of the sample with the reagents.
B1.4	Range of application	Up to at least 0.8 mg/l
B1.5	Calibration curve (a)	Linear to at least 0.8 mg/l.

B1.6 Total Standard Deviation (a)

	Relative Standard Deviation %	Degrees of Freedom
Synthetic Sample 0.10 mg/l Al	1.34	9
Synthetic Sample 0.70 mg/l Al	0.33	9
Raw Water mean 0.455 mg/l	0.73	9

B1.7	Limit of detection (a)	0.016 mg/l	9
	Criterion of detection (a)	0.008 mg/l	9

B1.8	Sensitivity (a)	0.1 mg/l gave an absorbance of 0.095 units.
B1.9	Bias (a)	Recovery tests on six spiked real samples ranging from 0.044 mg/l Al to 0.38 mg/l Al indicate the possibility of a slight negative relative bias of between 0 and 5%.
B1.10	Interferences (a) (see also section B3)	Copper causes a slight positive interference. Zinc may cause a slight positive interference if aluminium is absent. Iron III would interfere but is reduced to iron II and complexed. Fluoride and Phosphate inhibit if present in large amounts.

(a) Yorkshire WA Sheffield data.

B1.11	Time required for analysis (a)	30 samples per hour. Operator time: start up 20 mins plus 10 mins per hour loading and 10 mins per hour calculation.

(a) Yorkshire WA Sheffield data.

B2 Principle

The method is based on reference 1 and work at YWA Sheffield. Iron is reduced with hydroxylammonium chloride and complexed with 1,10-phenanthroline. The aluminium complex with bromopyrogallol red is formed in the presence of n-tetradecyltrimethylammonium bromide.

The reagent absorption maximum is at 576.1 nm, the aluminium complex maximum is at 591.0 nm; but at 625 nm the reagent absorption is almost negligibie (0.03 units) while the complex is at about 85% of maximum.

B3 Interferences

Table B1 summarizes the interferences tests carried out.

Table B1

Interferent	Added as	Concentration (ppm)	Mean Effect for Aluminium concentrations of 0 (ppm)	0.80
Ca^{2+}	$CaCO_3$	300	+0.004	+0.004
Mg^{2+}	$MgSO_4.7H_2O$	100	+0.004	+0.008
Na^{+}	NaCl	300	+0.002	+0.003
K^{+}	KNO_3	20	+0.004	+0.002
Alkalinity	$CaCO_3$	500	+0.004	+0.004
Cu^{2+}	$CuSO_4.5H_2O$	6.0	+0.013	+0.009
Mn^{2+}	$MnCl_2.4H_2O$	2.0	−0.005	+0.001
Fe^{2+}	$Fe(NH_4)_2(SO_4)_2.6H_2O$	6.0	+0.003	+0.002
Fe^{3+}	$FeCl_3.6H_2O$	6.0	+0.019	+0.002
Ni_{2+}	$Ni(NO_3)_2.6H_2O$	2.0	−0.004	−0.005
Zn^{2+}	$ZnSO_4.7H_2O$	6.0	+0.008	−0.006
PO_4^{3-}	$K_2HPO_4.3H_2O$	6.0	−0.005	−0.016
SO_4^{2-}	$MgSO_4.7H_2O$	395	+0.004	+0.008
Cl^{-}	NaCl	308	+0.002	+0.003
NO_3^{-}	KNO_3	32	+0.004	+0.002
F^{-}	KF	1.0	+0.001	+0.000
		10	+0.003	−0.038

At 95% confidence limits, if no effect were present the results might be expected to be between ± 0.0040 for 0.0 mg/l Al and ± 0.0084 for 0.8 mg/l Al.

B4 Hazards

Hydroxyammonium salts and solutions are severe irritants and burn the eyes. Contact with the skin must be avoided. Continued contact may cause dermatitis. Systemically, methaemoglobinaemia may occur.

B5 Reagents

B5.1 Water

The water used for blank determinations and for preparing reagents and standard solutions should have an aluminium content which is negligible compared with the smallest concentration to be determined in the samples. Deionized water or water distilled from an all-glass apparatus is normally suitable.

B5.2 Reagent solution

Weigh out 0.117 ± 0.001 g bromopyrogallol red (BPR), 2.823 ± 0.001 g n-tetradecyl-trimethyl ammonium bromide (TDTA) and 15.982 ± 0.001 g hexamine AR; dissolve

successively in 750 ± 10 ml of industrial methylated spirit GPR and make up to 1 litre with water in a calibrated flask. The reagent should be stable for a week.

B5.3 Buffer/Masking solution

Weigh out 68.0 ± 0.1 g of sodium acetate trihydrate and 5.00 ± 0.01 g of hydroxy-ammonium chloride and dissolve in about 800 ml of water. Weigh out 0.150 ± 0.001 g of 1,10-phenanthroline and dissolve in 3.0 ± 0.1 ml of glacial acetic acid, add with stirring to the sodium acetate-hydroxylammonium chloride solution, add water to about 950 ml total volume, adjust the pH value to 5.50 ± 0.05 with glacial acetic acid, using a pH metre; transfer quantitatively to a 1 litre calibrated flask and make up to the mark with water. This reagent should be stable for at least a week.

B5.4 Nitric acid 5M

Add 312±5 ml nitric acid AR (d_{20} 1.42) to about 500 ml of water and make up to 1000 ± 20 ml with water.

B5.5 Acid wash solution

Prepared as required by dilution of 20.0 ± 0.1 ml of the reagent B5.4 to 1000 ± 20 ml with water. This reagent should be stable for at least a year.

B5.6 Standard Aluminium Solutions

B5.6.1 Solution A:1 ml contains 1.0 mg Al

Dissolve 1.000 ± 0.001 g of aluminium wire (at least 99.9% purity) in 60 ± 1 ml of hydrochloric acid (d_{20} 1.18). Transfer the solution to a 1-litre calibrated flask, make up to the mark with water and mix well. Store this solution in a polyethylene bottle. It is stable for at least 2 years. Commercial standards of this strength may be substituted.

B5.6.2 Standard Solution B:1 ml contains 0.01 mg Al

Pipette 10.00 ± 0.01 ml of Solution A into a 1-litre calibrated flask, add 20 ± 1 ml of nitric acid (B5.4) and make up the mark with water. Mix well. Store in a polyethylene bottle. This solution should be stable for at least one month.

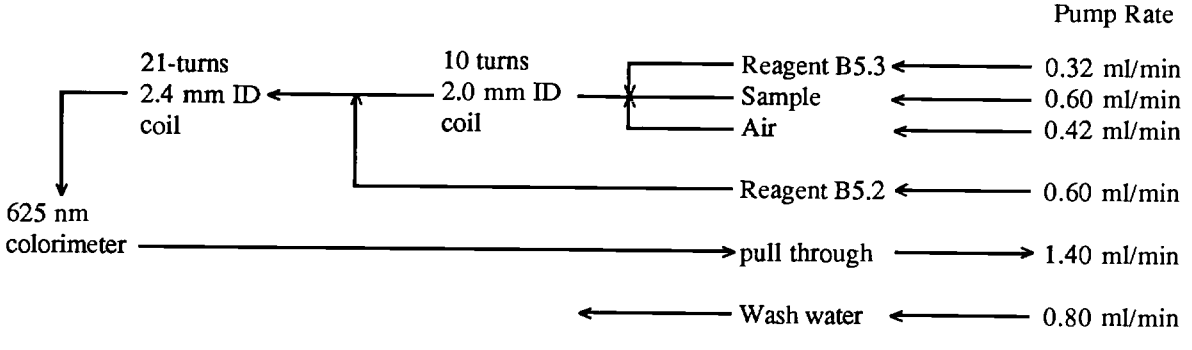
B5.6.3 Working Standard Solutions

As required, using a burette, transfer 10.0, 20.0, 40.0, 60.0 and 80.0 ml of Solution B (all ± 0.03 ml) to a series of 1-litre flasks, add 20 ± 1 ml of nitric acid (B5.4) and make up to the mark with water. Mix well. Prepare fresh weekly. Store in polyethylene bottles.

B6 Apparatus

B6.1 For Air Segmented Continuous Flow

Set up the following apparatus



B6.2 A Continuous Flow Injection apparatus can also be devised, see ref 1.

B6.3 Manual Operation is also possible, 8 ml of reagent (B5.3) being added to 15 ml of sample, mixed, stood for five minutes, 15 ml of reagent (B5.2) added and absorption read using a grating or prism spectrophotometer at 625 ± 1 nm. If necessary check the instrument calibration on a blank sample. The reagent absorption maximum should be at 576.1 nm.

B6.4 Glassware

Both British and American analysts have reported pick up of aluminium from glassware. Users are advised to pre-acid-leach all glassware and test it on blank samples before use.

If possible, apparatus should be reserved solely for aluminium determinations: all residual aluminium from previous determinations must be removed. Clean all glass and plastic ware by filling with or soaking in 10% V/V nitric acid over-night. Rinse thoroughly with water.

B7 Sample Collection and Preservation

To a precleaned polyethylene bottle add 1.00 ± 0.05 ml of nitric acid (B5.4) per 50 ml of sample to be collected. See also Section A7.

B8 Analytical Procedure

If soluble colloidal aluminium compounds are present, see Section A8 and use procedure A8.2 but substituting the 5M nitric acid of B7 for the 5M hydrochloric acid of A7.

Step	Procedure	Notes
B8.1	The apparatus is set up as detailed in Section B6.1 (note a).	(a) If flow injection or manual operation is used see Sections B6.2 and B6.3 for the modifications to this procedure.
B8.2	Following the manufacturer's instructions set the base line on the recorder. Then calibrate. A suggested sample order is	
B8.3	Analyse samples, interspersed with blanks and calibration standards (such as 0.1 mg/l and 0.8 mg/l Al) to every eighth sample	
B8.4	Provided there is no sudden significant drift, deduct the mean blank concentration on each side of a sample for the found sample concentration. If a slight steady drift occurs, correct proportionately. (note b).	(b) If results appear to be erratic, repeat the analysis.

cup	contents mg/l Al
1	0.0
2	0.0
3	0.8
4	0.0
5	0.8
6	0
7	0.1
8	0.2
9	0.4
10	0.6
11	0.8
12	0.0

B9 Sources of Error

B9.1 Correction for colour and turbidity in samples

In spectrophotometric methods of analysis, the presence of coloured and/or suspended materials in samples will cause falsely high results to be obtained. Whether or not a correction is required for this effect depends on the error that can be tolerated and the nature of samples. If necessary consider filtration after sampling (B7), but check that the filter used does not absorb soluble forms of aluminium.

B9.2 Effect of aluminium in the water used for blank determinations

If the water used for the blank determination contains aluminium, the blank correction will be falsely large and results for samples falsely low. Again, whether or not a correction is required for this effect depends on the error that can be tolerated and the concentration of aluminium in the blank water. The procedure in steps A9.7 to A9.9 allows a correction to be made when required, but replace steps A9.1 to A9.3 by B8 above.

When it is necessary to make a correction, to avoid the need for determining C_w in every case, it is convenient to estimate C_w for one large batch of water.

B9.3 Interfering substances

See Section B3.

B10 Checking the Accuracy of Results

See Section A 14 and Part F.

B11 References

1. Wyganowski C, Motomizu S, and Toei K. *Anal. Chim Acta* **140**, 313, 1982.
2. *General Principle of Sampling and Accuracy of Results 1980*, HMSO, in this series.

C Aluminium in Raw and Potable Waters by Spectrofluorimetry using Lumogallion

C1 Performance Characteristics of the Method

Note: Throughout this method aluminium is expressed as the element (A1).

C1.1	Substance determined	All forms of aluminium reacting with lumogallion, 2-hydroxy-3-(2,4-dihydroxphenylazo)-5-chlorobenzenesulphonic acid (see Section C2.3).
C1.2	Type of Sample	Raw, potable and marine waters.
C1.3	Basis of method	The reaction of aluminium with lumogallion to form a fluorescent complex.
C1.4	Range of application (a)(b)	Up to 55 μg/l (see Sections C10 and C11).
C1.5	Calibration curve (a)(b)	Linear to 55 μg/l (see Section C10).
C1.6	Standard deviation (a)	

Aluminium concentration (μg/l)	Within batch (μg/l)	Between batch (μg/l)	Total (μg/l)	Degrees of freedom
0.0(c)	0.03	—	—	10
10.0(c)	0.11	0.19	0.22	10,9,19
30.0(c)	0.13	0.52	0.54	10,9,19
50.0(c)	0.36	0.57	0.68	10,9,19
33.7(d)	0.08	0.38	0.38	10,9,19
35.3(e)	0.16	0.28	0.32	10,9,19

C1.7	Limit of detection (a)	0.17 μg/l with 10 degrees of freedom.
C1.8	Sensitivity (a)	Dependent upon the instrument used and the bandpass of the excitation and emission slits selected.
C1.9	Bias	Not known.
C1.10	Interferences (a)	See Section C3.
C1.11	Time required for analysis (a)	For 16 standards the total analytical time is about 210 min of which about 120 min is operator time. For 16 samples the total analytical time is about 270 min with the operator time remaining unchanged. These figures exclude any pre-treatment time.

(a) These data were obtained at the Department of Oceanography, University of Southampton, using a spectrofluorimeter at excitation and emission wavelengths of 480 nm and 590 nm respectively (see Section C9) and a 10 mm square cuvette.

(b) The linearity of the calibration curve is dependent upon the instrument used and the bandpass of the emission slit chosen, thus affecting the range of application.

Analysts should check the linearity for their particular instrument (see Sections C10 and C11).

(c) Sub-boiled distilled water spiked with the stated aluminium concentration.

(d) Manchester area tap water diluted with sub-boiled distilled water.

(e) River Ribble water filtered through a 0.45 μm pore size membrane filter and diluted with sub-boiled distilled water.

C2 Principle

C2.1 The method described is based on that of Nishikawa et al[1] as modified by Hydes and Liss[2].

C2.2 Dissolved aluminium is reacted with lumogallion in a suitably buffered solution at 80°C, or overnight at room temperature, to form a fluorescent complex.

C2.3 Pre-treatment of natural waters by boiling for up to 4 hours at pH values from 1.5 to 10.5 did not increase the amount of aluminium found[2]. The method detemines aluminium in solution as simple species, weakly adsorbed onto particulates or weakly bound to humic material. Aluminium contained within insoluble matter, eg fine clay particles, is not detected.

C3 Interferences

C3.1 Table C1 gives details of the effect of potential interfering substances which have been tested. These results were obtained at the Department of Oceanography, University of Southampton.

C3.2 The results show that interference in the procedure can be caused by the presence of cobalt, copper, iron, nickel, tin(II), vanadium, fluoride and humic material. Negative interferences have been reported[1] for chromium(VI), scandium, tin(IV), and titanium(IV) at the very high concentration of 4 mg/l, and a positive interference for gallium which forms a fluorescent complex with lumogallion. At a pH of 5, optimum for the aluminium determination, the ratio of fluorescence intensities of equal concentrations (μg/l) of aluminium and gallium was 14.6:1. A gallium interference equivalent to 1 μg/l aluminium would require a gallium concentration of about 15 μg/l, a level some 150 times greater than that reported for river waters[3]. A negative interference has been found[2] for phosphate at 0.3 mg/l in a solution containing 5 μg/l of aluminium, a result not confirmed by the data in Table C1. It is likely, however, that phosphate interferes at abnormally high ratios of phosphate to aluminium.

C3.3 At the concentrations usually encountered in potable and unpolluted fresh waters, the only substances that present potentially significant interference problems in the method are copper, iron, fluoride and humic acid.

C3.3.1 Copper

Preliminary work[7] has shown that the major interference of copper can be eliminated or substantially reduced at concentrations of up to at least 1 mg/l by the addition of hydroxylamine hydrochloride to reduce copper(II) and 1,10-phenanthroline to complex copper(I).

C3.3.2 Iron

Iron interferes with the method by forming a non-fluorescent complex with lumogallion thereby reducing the effective concentration of the reagent, and furthermore the absorption spectrum of the iron complex overlaps the excitation spectrum of the aluminium complex[2]. Addition of hydroxylamine hydrochloride to reduce iron(III) and 1,10-phenanthroline to complex iron(II) has been shown to be effective in reducing the interference[4,5,6]. However, as the absorption band of the iron(II)-1,10-phenanthroline complex overlaps the fluorescence spectrum of the aluminium complex, the slope of the calibration curve decreases at high iron levels. If this effect is significant for particular samples, a calibration curve obtained from standards with matched iron concentrations can be used to determine the amount of aluminium in these samples[4].

C3.3.3 Fluoride

A number of potable water supplies have fluoride added to increase the concentration to 1 mg/l. The addition of a large excess of calcium ions has been recommended[4] for the elimination of the fluoride interference by competitive complexation. Alternatively, the aluminium concentration of a water sample can be determined either from a calibration curve obtained with standards containing the same fluoride concentration as that in the sample, or by the method of standard additions.

C3.3.4 Humic acid

Photo-oxidation of dissolved organic carbon, including humic acid, both with and without hydrogen peroxide present, gave erratic results and incomplete recovery of added aluminium[2]. The addition of a large excess of calcium ions has been recommended[4] for the elimination of interferences from dissolved organic matter, fluoride (see Section C3.3.2) and phosphate by the competitive complexation of these substances.

Any interference caused by the natural fluorescence of humic substances overlapping that of the aluminium-lumogallion complex is allowed for by measuring the sample fluorescence in the absence of lumogallion (see Section C8.3).

C4 Hazards

C4.1 Glacial acetic acid is a strong irritant which can cause severe burns to skin and eyes. Continued contact with the skin can produce dermatitis and ulcers. The vapour irritates the respiratory system and the eyes causing lachrymation. The reagent must not be pipetted by mouth.

C4.2 As lumogallion is toxic, the solid and aqueous solutions should be handled with care to avoid skin contact, inhalation, ingestion or spillage.

C5 Reagents

Reagents and standard solutions should be kept as dust free as possible and stored in linear polyethylene, polypropylene or fluorinated ethylene-propylene (FEP) bottles which have been cleaned by the procedure described in Section C6.1. It is recommended that glass containers be avoided as substantial amounts of aluminium can be leached from the vessel walls into solution. Analytical reagent grade chemicals should be used wherever possible.

C5.1 Water

The water used for blank determinations and for preparing reagents and standard solutions should have an aluminium content which is negligible compared with the smallest concentration to be determined in the samples. Freshly prepared water from common laboratory all-glass stills may contain up to at least 0.7 μg/l Al, and the concentration may increase during storage in glass reservoirs. Water prepared by reverse osmosis, double distillation (second stage from silica) or sub-boiling distillation from an apparatus in which the cold finger and the drain tube for the condensate are of silica, is normally suitable.

C5.2 Sodium acetate-acetic acid buffer solution

Dissolve 55.4 ± 0.2 g of sodium acetate trihydrate in about 85 ml of water in a polyethylene or polypropylene bottle calibrated to contain 100 ± 2 ml. Dissolution will be assisted by heating the solution in a water bath. To the cooled solution carefully add 9.5 ± 0.1 ml glacial acetic acid and dilute with water to the calibration mark. The solution is stable for at least two months. A pH of 5.0 ± 0.1 should be obtained when 0.50 ± 0.02 ml of buffer is added to a blank (Section C8.5, note 1).

C5.3 0.02% m/v Lumogallion solution

Dissolve 20.0 ± 0.5 mg of lumogallion in water and dilute with water to 100 ml in a polypropylene calibrated flask. The solution should be discarded after one month to avoid gradual loss of measurement reproducibility.

C5.4 Standard aluminium solutions

C5.4.1 Solution A: 1 ml contains 100 μg Al

Dissolve 1.758 ± 0.001 g of aluminium potassium sulphate hydrate in water and dilute with water to one litre in a polypropylene calibrated flask. The solution is stable for at least four months.

C5.4.2 Solution B: 1 ml contains 1 μg Al

Dilute 10.00 ± 0.02 ml of Solution A with water to one litre in a polypropylene calibrated flask. This solution is stable for at least one month.

C5.5 50% v/v Hydrochloric acid

Dilute 500 ± 30 ml of hydrochloric acid (d_{20} 1.18) with water to one litre in a measuring cylinder. Store the solution in a polyethylene or polypropylene bottle.

C5.6 1M Hydrochloric acid

Dilute 9.0 ± 0.5 ml of hydrochloric acid (d_{20} 1.18) with water to 100 ml in a measuring cylinder. Store the solution in a polyethylene or polypropylene bottle.

C5.7 50% v/v Nitric acid

Dilute 500 ± 30 ml of nitric acid (d_{20} 1.42) with water to one litre in a measuring cylinder. Store the solution in a polyethylene or polypropylene bottle.

C6 Apparatus

C6.1 Cleanliness

Cleanliness is essential for this determination. Exposure of reagent solutions, standards or samples to dust can produce erratic fluorescence intensities. If possible, apparatus should be reserved solely for aluminium determinations. Clean all glass and plastic ware by degreasing in a phosphate-free detergent for 2–3 days, rinse thoroughly in running tap water and then with distilled water. Soak for several days in 50% v/v hydrochloric acid and again in 50% v/v nitric acid. Rinse thoroughly with water. Thereafter a thorough rinse in 50% v/v hydrochloric acid followed by a thorough rinse with water after each determination should suffice. If apparatus is dried, the process should be carried out in a laminar flow hood or other system which minimizes atmospheric particle concentrations.

C6.2 Reaction bottles

Wide mouth bottles of 60-ml or 100-ml capacity made from liner polyethylene, polypropylene or FEP are suitable for the analytical procedure. Polypropylene and FEP bottles have the advantage of not deforming to any significant extent when heated to 80°C for extended periods. After initial cleaning (see Section C6.1) all reaction bottles must be checked for residual aluminium contamination by using them for reagent blank determinations (see Section C8.5). Bottles giving high blanks should be discarded or, alternatively, acid leached until normal blank values are consistently obtained.

C6.3 Volumetric apparatus

The use of polypropylene 50-ml calibrated flasks and calibrated pipettes minimizes the possible leaching of aluminium from vessel walls into reagent and sample solutions. If volumetric glassware is employed, contact time with solutions should be kept as short as possible. Glass pipettes should be rinsed before re-use if they have been allowed to stand for some time in a wetted state.

Automatic pipettes with acid-leached polyethylene tips are recommended for the dispensing of the lumogallion and buffer reagents.

C6.4 Plastic vacuum filtration unit with 0.45 μm membrane filters

Clean membrane filters by soaking in 1M hydrochloric acid. Rinse with water before use.

C6.5 Spectrofluorimeter

Clean the glass cuvette by degreasing in a phosphate-free detergent for 1 day, rinse thoroughly in running tap water and then with distilled water. Soak in 50% v/v hydrochloric acid for 2–3 days. Rinse thoroughly with water. Thereafter an overnight soak in 1M hydrochloric acid followed by a rinse with water after each set of determinations should suffice.

C6.6 Water bath fitted with plastic racks to hold the reaction bottles.

C6.7 pH meter.

C7 Sample Collection and Preservation

Collect the sample in a polyethylene, polypropylene or PEP bottle which has been cleaned by the procedure described in Section C6.1. Filter raw water samples through an acid-washed 0.45 μm membrane filter (see Section C6.4) before analyis or storage.

Ideally, samples should be analysed as soon as possible after collection. It appears, however, that aluminium concentrations of unacidified, filtered samples kept refrigerated in the dark for 5–10 days show at most minor changes[2,4,7,8]. Storage of acidified samples may lead to erratic results[2,7,8].

C8 Analytical Procedure

Step	Procedure	Notes
C8.1	Analysis of samples	
C8.1.1	Pipette a suitable volume V (not exceeding 45 ml) of the sample into a 50-ml calibrated flask (notes a and b).	(a) See Section C6.3. (b) See Section C11 for suitable sample volumes.
C8.1.2	Add to the flask 0.50 ± 0.02 ml of sodium acetate-acetic acid buffer and 0.50 ± 0.01 ml of lumogallion solution (note a). Dilute with water to the mark, stopper and mix thoroughly (note c).	(c) The solution pH must be 5.0 ± 0.1. If necessary add more buffer until this pH is reached. While sufficient buffer capacity is required to maintain sample pH within the optimum range, the volume of buffer should be minimized in order to reduce reagent blanks. For water samples which have a high buffer capacity, it is preferable to adjust the composition of sodium acetate-acetic acid buffer such that the addition of 0.50 ml of the reagent gives the required pH.
C8.1.3	Transfer the solution to a reaction bottle, cap tightly and heat for 60 to 90 min in a water bath at 80°C (notes d and e).	(d) See Section C6.2. (e) Since there can be considerable differences in aluminium reactivity in natural and treated waters, completeness of reaction must be checked if it is proposed to use heating times of less than 90 min.
C8.1.4	Remove the reaction bottle from the water bath and cool to room temperature. Measure the fluorescence intensity at the excitation and emission wavelengths optimized for the instrument employed (note f). Let the fluorescence intensity of the sample be S.	(f) See Section C9.

Step	Procedure	Notes
C8.2	Sample reagent blank A reagent blank must be run for each sample which required more than the standard volume (0.50 ml) of buffer or a change in the buffer composition (note g). Carry out steps C8.1.2 to C8.1.4 using the same reagent volumes and reagent batch as for the sample. Let the fluorescence intensity of the sample blank be T.	(g) If no change to the procedure in C8.1.1 was necessary, the sample reagent blank will be identical to the calibration reagent blank (see Section C8.5).
C8.3	Compensation for natural fluorescence in the sample. A sample compensation solution must be run for each sample containing substances whose fluorescence emission overlaps that of the aluminium-lumogallion complex. Carry out steps C8.1.1 to C8.1.4 using the same sample and reagent volumes and reagent batch as for the sample, but omit the lumogallion solution at step C8.1.2. Let the fluorescence intensity of the sample compensation be N.	
C8.4	Calibration standard	
C8.4.1	A duplicate calibration standard must be run with each batch of determinations. Add 1.50 ± 0.01 ml of aluminium solution B, 0.50 ± 0.02 ml of sodium acetate-acetic acid buffer and 0.50 ± 0.01 ml of lumogallion solution to each of two 50-ml calibrated flasks. Dilute with water to the mark, stopper and mix thoroughly. These solutions contain 30 μg/l Al.	
C8.4.2	Transfer the solutions to reaction bottles, cap tightly and heat for 90 min in a water bath at 80°C (note h).	(h) Heating for 60 min is adequate for calibration standards and the shorter period may be used if it is more convenient.
C8.4.3	Remove the bottles from the water bath and cool to room temperature. Measure the fluorescence intensities at the excitation and emission wavelengths optimized for the instrument employed. Let the fluorescence intensities of the calibration standards be C_1 and C_2, and the mean of these intensities be C.	
C8.5	Calibration reagent blank A duplicate calibration reagent blank must be run with each duplicate calibration standard. Carry out steps C8.4.1 to C8.4.3 using the same reagent batch and volumes as for the calibration standards, but do not add any aluminium standard solution (note i). Let the fluorescence intensities of the calibration reagent blanks be B_1 and B_2, and the mean of these intensities be B.	(i) The solution pH must be 5.0 ± 0.1. Each time a new batch of buffer is used, the pH of a reagent blank should be checked with a pH meter.
C8.6	Determination of aluminium in the water used for the blank (note j).	(j) This determination is not needed if the aluminium content of the water used for the blank is known or is negligible (see Section C12.2).

Step	Procedure	Notes
C8.6.1	Instrument blank (note k)	
	Measure the fluorescence intensity of blank water at the standard instrument settings. Let the fluorescence intensity of the instrument blank be D.	(k) The instrument blank includes instrument background noise, Rayleigh scattering, fluorescence from impurities in the water and the Raman band of water[7].
C8.6.2	Fluorescence intensity due to aluminium in the combined buffer and lumogallion reagents.	
C8.6.2.1	Add 0.75 ± 0.02 ml of sodium acetate-acetic acid buffer and 0.75 ± 0.02 ml of lumogallion solution to a 50-ml calibrated flask, dilute with water to the mark, stopper and mix thoroughly. Then carry out steps C8.4.2 and C8.4.3. Let the fluorescence intensity be E.	
C8.6.2.2	Add 0.25 ± 0.01 ml of sodium acetate-acetic acid buffer and 0.25 ± 0.01 ml of lumogallion solution to a 50-ml calibrated flask, dilute with water to the mark, stopper and mix thoroughly. Then carry out steps C8.4.2 and C8.4.3. Let the fluorescence intensity be F.	
C8.6.2.3	The Fluorescence intensity, G, due to aluminium contamination of the combined buffer and lumogallion reagents is given by: $G = E - F$ (note l).	(l) This value includes contributions from any fluorescent impurities in the lumogallion reagents (besides complexed aluminium) and buffer solution.
C8.6.3	The fluorescence intensity, H, due to aluminium in the water used for the blank is given by: $H = B - D - G$.	
C8.6.4	Calculate the concentration of aluminium in the blank water, A_w, from: $A_w = \frac{H}{C - B} \times 30\ \mu g/l$ This calculation assumes a linear calibration curve and linearity must be checked (see Section C10).	
C8.7	Alternative procedure at room temperature (note m)	
	Instead of being heated to 80°C in a water bath (steps C8.1.3 and C8.4.2), the reaction bottles are allowed to stand at room temperature for a minimum of 20 hours.	(m) This procedure may be followed when rapidity of analysis is unimportant. Operator time is reduced and the precision of analytical results is improved.
C8.8	Calculation of results	
C8.8.1	If the water used for the blank contains detectable aluminium, the sample blank will be falsely large and the results for samples falsely low. The sample blank fluorescence intensity corrected for aluminium in blank water, U, is given by: $U = \frac{(59 - V)H}{50}$ where V = the volume of sample.	

Step	Procedure	Notes

C8.8.2 Calculate the fluorescence intensity, I, due to aluminium in the sample from:

$$I = S - U$$

or, when a correction for natural fluorescence in the sample is made:

$$I = S - U - N.$$

C8.8.3 The concentration of aluminium in the sample, A_s, is given by

$$A_s = \frac{I}{C - B} \times 30\ \mu g/l$$

This calculation assumes a linear calibration curve and linearity must be checked (see Section C10).

Table C1 Effect of other substances

Other substance		Other substance added as	Concentration of other substance, mg/l	Effect (a) in μg Al/l of other substance at an aluminium concentration of: 0.0 μg/l	50.0 μg/l
Calcium	(as Ca^{2+})	Chloride	200	+0.1	+0.6
Chromium (III)	(as Cr^{3+})	Sulphate	0.25	+0.1	+0.8
Chromium (VI)	(as Cr)	Potassium chromate	0.25	0.0	0.5
Cobalt	(as Co^{2+})	Nitrate	0.1	0.0	+0.1
			0.25	0.0	−1.9
Copper	(as Cu^{2+})	Chloride	0.25	−0.4	−0.9
			0.15	−1.3	−4.5
			0.25	−0.9	−28.0
Iron	(as Fe^{3+})	Chloride	0.1	0.0	−1.3
			0.25	+0.1	−3.3
			0.5	0.0	−6.4
Potassium	(as K^{+})	Chloride	100	+0.1	−0.4
Magnesium	(as Mg^{2+})	Chloride	100	+0.1	+0.4
Manganese	(as Mn^{2+})	Chloride	1	+0.1	+0.2
Nickel	(as Ni^{2+})	Chloride	0.1	0.0	+0.5
			0.25	0.0	−1.6
			1	−0.2	−3.3
Lead	(as Pb^{2+})	Acetate	2	−0.3	+0.5
Tin	(as Sn^{2+})	Chloride	0.25	−0.2	+1.3
Titanium	(as Ti^{3+})	Sulphate	0.1	+0.5	+0.9
Vanadium	(as V)	Ammonium metavanadate	0.05	0.0	−0.7
			0.1	−0.3	−1.6
Zinc	(as Zn^{2+})	Sulphate	2	0.0	−0.1
Chloride	(as Cl^{-})	Sodium	500	+0.1	+0.3
Fluoride	(as F^{-})	Sodium	0.5	+0.1	−2.4
			1	0.0	−5.6
			1.5	0.0	−8.9
Bicarbonate	(as HCO_3^{-})	Sodium	200	+0.1	−0.2
Nitrate	(as NO_3^{-})	Sodium	100	0.0	+0.3
Orthophosphate	(as PO_4^{3-})	Soduim dihydrogen	20	+0.4	−0.7
Sulphate	(as SO_4^{2-})	Sodium	100	+0.1	+0.1
Silicate	(as SiO_2)	Sodium	10	+5.3	+5.1(b)
Humic acid			0.5	+4.5	+3.0(b)
			1	+9.6	+6.9(b)

(a) If the other substances had no effect, results would be expected (95% confidence) to lie within the following ranges:
0.0±0.35 μg/l for 0.0 μg Al/l
0.0±1.2 μg/l for 50.0 μg Al/l

(b) These substances contained aluminium as an impurity. The interference at 50.0 μg Al/l can be seen by subtracting the effect found at 0.0 μg Al/l from that found at 50.0 μg Al/l.

C9 Measurement of Fluorescence Intensity

The wavelengths observed for the excitation and emission band maxima can vary considerably among instruments (465–485) nm and 555–605 nm, respectively). The optimum values must be determined for each instrument and used thereafter. The procedure for measuring fluorescence intensity should be rigorously controlled to ensure satisfactory precision. The same cell should always be used and placed in the same cell holder position with the same face towards the light source. It is difficult to ensure reproducible alignment of cells with chipped corners, and they should therefore be replaced. The cell holder compartment should be kept scrupulously clean and as dust free as possible.

C10 Checking the Linearity of the Calibration Curve

This procedure for checking the linearity of the calibration curve must be carried out on at least two independent occasions before the method is applied to any samples and regularly thereafter.

C10.1 To a series of 50-ml calibrated flasks pipett 0.00, 0.50, 1.00, 1.50, 2.00, 2.50 and 3.00 ml (all ±0.02 ml) of standard aluminium solution B. respectively. Duplicate standards should be prepared for each concentration. Add to each flask 0.50 ±0.02 ml of sodium acetate-acetic acid buffer and 0.50 ±0.01 ml of lumogallion solution, dilute with water to the mark, stopper and mix thoroughly. These flasks contain 0.0, 10.0, 20.0, 30.0, 40.0, 50.0 and 60.0 μg/l Al respectively. Carry out steps C8.4.2 and C8.4.3. Subtract the mean fluorescence intensity of the blanks from the mean fluorescence intensities of each pair of calibration standards, and plot the corrected results against aluminium concentration.

C10.2 The linearity of the calibration curve is dependent upon the instrument used and the bandpass of the emission slits chosen. Should the calibration curve still be linear at 60 μg/l Al, an appropriately altered range of standards should be made up. If the linear region differs significantly from 0–55 μg/l Al, the calibration standard in step C8.4 is not appropriate, nor is the range of application given in Section C1.4. In such case, the range of application should be amended accordingly, and the calibration standard chosen for step C8.4 should have an aluminium concentration around the mid-point value of the linear section.

C11 Concentration Ranges of the Method

Suitable volumes of sample to be used may be estimated from the following table:

Expected concentration (μ g/l Al)	Sample volume to be used (ml)
<65	40.0
65– 130	20.0
130– 250	10.00
250– 500	5.00
500–1,300	2.00
1,300–2,700	1.00

If the linear range of the calibration curve differs significantly from 0.55 μg/l Al, the expected concentrations given in the table should be amended accordingly.

C12 Sources of Error

The attention which it is necessary to pay to sources of error depends on the accuracy required of the analytical results. The following sub-sections summarise the main sources of error.

C12.1 Contamination

It is desirable to carry out the analysis in a laboratory in which no appreciable amounts of aluminium or its compounds are handled. The technique and working conditions should be critically examined and any sources of contamination eliminated or minimised. In particular, it is desirable to reserve the apparatus used for the aluminium determination solely for this purpose, and to carry out a preliminary series of blank determinations to ensure low blank values before analysing any samples. See also sections C6.1 and C6.3

C12.2 Effect of aluminium in the water used for the blank determination

If the water used for the blank determination contains aluminium, the blank correction will be falsely large and results for samples falsely low. The importance of this error depends upon the aluminium content of the blank water and the concentrations of interest in the samples. The procedures given in steps C8.9 and C9.9.1 allows a correction to be made when required.

C12.3 Fluorescence intensity due to aluminium in the sodium acetate-acetic acid buffer solution

Some batches of sodium acetate trihydrate or glacial acetic acid can contain enough aluminium to cause unacceptably high reagent blanks. Recrystallisation of the sodium acetate from aluminium-free water in acid-leached plastic apparatus will usually reduce aluminium contamination of the buffer solution to a sufficiently low level. If necessary, aluminium in the acetic acid may be reduced by sun-boiling distillation from an apparatus with a silica cold finger and condensate drain tube. The following procedure can be used to determine the fluoresence intensity due to aluminium in the buffer solution:

(a) Prepare duplicate calibration reagent blanks as described in step C8.5. Let the fluorescence intensities of the calibration reagent blanks be B_1 and B_2, and the mean of these intensities be B.

(b) To each of two 50-ml calibrated flasks add 2.00±0.02 ml of sodium acetate-acetic acid buffer and 0.50±0.01 ml of lumogallion solution. Dilute with water to the mark, stopper and mix thoroughly. Carry out steps C8.4.2 and C8.4.3. Let the fluorescence intensities of these solutions be J_1 and J_2,

(c) The fluorescence intensity, K, due to aluminium in 0.50 ml of buffer solution is given by:

$$K = \frac{J - B}{3}$$

This procedure assumes fluorescent impurities in the buffer to be negligible.

C12.4 Temperature dependence of fluorescence

The fluorescence intensity of the aluminium-lumogallion complex decreases by 0.5–1% per °C (2,7). It is therefore essential that, after heating, all sample and standard solutions are cooled and equilibrated at room temperature before intensities are determined. It is recommended that the spectrofluorimeter be installed in a room that is subject to minimal fluctuations of temperature.

C12.5 Calibration standards

The calibration curve for this method has been found to be linear although its slope may vary from one set of determinations to another. Such variations are caused by changes in the ambient temperature of the laboratory and in the sensitivity of the spectrofluorimeter. Therefore a duplicate calibration standard must be run for each batch of analyses and steps C8.4 onwards give the necessary procedure.

C12.6 Correction for natural fluorescence in samples

The presence in samples of substance whose natural fluorescence emission overlaps that of the aluminium-lumogallion complex will cause falsely high results to be

obtained. The procedures in steps C8.3 and C8.8.2 allow a correction to be made if required.

C12.7 Interfering substances

See Section C3. The effect of possible interfering substances may be determined by analysing aluminium samples spiked with various concentrations of the potential interfering substances.

C13 Checking the Accuracy of Analytical Results

Once the method has been put into normal routine operation many factors may subsequently adversely affect the accuracy of the analytical results. It is recommended that experimental tests to check certain sources of inaccuracy should be made regularly. Many types of test are possible and they should be used as appropriate[9]. As a minimum, however, it is suggested that a standard solution of aluminium of suitable concentration be analysed at the same time and in exactly the same way as normal sample (see Section 8). The results obtained should then be plotted on a quality control chart which will facilitate detection of inadequate accuracy, and will also follow the standard deviation of routine analytical results to be estimated.

C14 References

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D Dissolved Aluminium in Sea Water and Other Natural Waters by Differential Pulse Cathodic Stripping Voltametry with the Hanging Mercury Drop Electrode

D1 Performance characteristics of the method

D1.1	Substance determined	Dissolved aluminium in oxidation state 3^+.
D1.2	Type of Sample	Sea Waters, other natural waters and drinking water
D1.3	Basis of the method	The electrodeposition of the complex formed between aluminium (III) and 1,2-dihydroxy anthraquinone-3-sulphonic acid, DASA, (or Alizarin Red S) at the surface of the hanging mercury drop electrode (HMDE), and its subsequent determination by differential pulse cathodic stripping voltammetry (DPCSV).[2]
D1.4	Range of application, (a)	Up to 13.5 μg/l Al (5×10^{-7}M), (b)
D1.5	Calibration curve, (a)	Linearity depends mainly on adsorption time and stirring rate. It is linear up to 13.5 μg/l Al (5×10^{-7}M). Under the stated conditions (b).

D1.6 Total standard deviation (a)

	Aluminium concentration		Within batch standard deviation		Degrees of freedom
(i)	416 ng/l	(15.4 nm)	9.5 ng/l	(0.35 nM)	8
(ii)	1.26 μg/l	(46.7 nM)	24.3 ng/l	(0.9 nM)	8
(iii)	1.26 μg/l	(46.8 nM)	38.9 ng/l	(1.4 nM)	8
(iv)	853 ng/l	(35.3 nM)	16.2 ng/l	(0.6 nM)	8
(v)	7.3 μg/l	(271 nM)	81 ng/l	(3.0 nm)	6

(i) Irradiated coastal sea waters.
(ii) Irradiated coastal sea water, spiked with Al standard.
(iii) Irradiated quartz distilled water.
(iv) Irradiated water from River Test.
(v) Irradiated tap waters.

D1.7	Detection limit, (a)	27 ng/l Al (1.0 nM) (c).

D1.8 Sensitivity, (a)

(i) 200 ng/l Al (7.4 nM) gives a peak current of 1.75 nA.
(ii) 7.3 μg/l Al (271 nM) gives a peak current of 7.3 nA.
(i) irradiated sea water, adsorption time 45s, stirred sample.
(ii) irradiated tap water, adsorption time 30s, unstirred sample.

D1.9	Bias	No bias was detected except when interference occurred.

D1.10 Interference	Certain substances cause interference in the determination of aluminium (see Section D3).
D1.11 Time required	The typical time required for the analysis of one 10 ml sample is approximately 20 minutes; this excludes two hours for UV irradiation of the sample which is sometimes necessary to destroy dissolved organic material; included are 8 minutes for purging of the sample and approximately 12 minutes for adsorption and scanning (when a 1 minute adsorption time is used) of the sample and two standard additions. The time required for analysis varies, however, according to the sample volume used because larger sample volumes require longer purging times.

(a) Work carried out at the Department of Oceanography, University of Liverpool.
(b) Several factors can affect the linear response of this determination. Saturation of the drop with dissolved organic interferents can severely limit the linear range.
(c) The detection limit can be further reduced by increasing the adsorption time.

D2 Principle

D2.1 The method is based upon the formation of complex ions between aluminium (III) and 1,2-dihydroxyanthraquinone-3-sulphonic acid (DASA) and their subsequent adsorption at the hanging mercury drop electrode (HMDE) at a controlled potential of -0.9 V (in sea water in absence of high Zn concentrations) vs a standard calomel reference electrode. The preconcentration is carried out over an accurately measured time period in a solution which is maintained at pH 7.1 by addition of a BES buffer and which is stirred at a constant rate throughout. Preconcentration, by adsorption, is followed by the analysis step in which the reduction current of the adsorbed ligand of aluminium is measured by differential pulse cathodic stripping voltammetry (DPCSV). The ligand is reduced from the electrode using a linear potential ramp with pulses superimposed.

D2.2 Prior to analysis the sample is passed through a 0.45 μm membrane filter (see Section D8) to remove particulate material, and is subsequently subjected to UV irradiation at a pH of 2.0 ± 0.2. UV irradiation is necessary to (i) release aluminium bound up with dissolved organic material, and (ii) destroy both surface active and complex forming organic material which can cause interference (see section D3). Acidification is necessary to prevent loss of metal by adsorption onto the vessel walls during UV irradiation.

D2.3 The sample is brought to neutral pH by addition of sodium hydroxide solution. The BES buffer and complexing agent, DASA are added to an aliquot for analysis, the mixture is then purged with inert gas (Ar or N_2) in order to remove oxygen which is an interferent (see section D3). The sample is initially purged for 8 minutes (10 ml sample volume) and is thereafter purged for 60s prior to subsequent measurements in the same sample solution.

D2.4 If all other conditions, (eg instrument settings, stirring rate, pH etc) are kept constant, the sensitivity of the technique is directly dependent on the rate of deposition, which is in turn proportional to the diffusion rate of the complex ion onto the HMDE surface. The diffusion rate is temperature dependent and it is therefore necessary to ensure that the temperature is constant to within ± 0.05°C during a set of measurements (a 0.5°C change in temperature results in a variation in the rate of adsorption, and hence in peak heights, of 1.5%). No special precautions need to be taken if the sample is at room temperature.

D2.5 Following the adsorption step, the stirrer is switched off and a period of 15s is allowed to elapse, during which the solution comes to rest, before stripping is initiated.

D2.6 Following the 15s waiting time, a potential ramp of 20 mVs^{-1} is applied, with pulses ($10s^{-1}$) superimposed on the ramp. Scanning, using a current range appropriate to the expected aluminium concentration, the current is recorded and the output is obtained in the form of peaks, with heights proportional to the amount of electroactive species formed in the preconcentration step. At pH 7.1 the aluminium peak is at a potential of -1.13 V vs a SCE (in sea water) and -1.06 V vs a SCE (in distilled water).

D2.7 The concentration of aluminium in the sample is determined by the method of standard additions.

D3 Interferences

Oxygen, surface active organic material, strong chelating compounds and some dissolved metals caused interference.

D3.1 The potential of the oxygen wave is very close to the aluminium—DASA potential. It is important therefore that the sample is completely purged with an inert gas (Ar or N_2) both prior to analysis and in between analytical steps.

D3.2 Surface active organic material reduces the peak current for aluminium considerably. The non-ionic surfactant Triton-X-100 has been previously used as a model for surface active organic material in sea water (1), and it was found that suppression of capacitance on a HMDE by surface active organic material in sea water was similar to that caused by 0.01–0.5 mgl^{-1} of Triton-X-100. The effect on the aluminium peak of additions of Triton-X-100 to U.V. irradiated sea water is shown in table D1. UV irradiation of a sample at pH value of 2.8±0.2 is sufficient to destroy surface active organic interferents.

D3.3 High concentrations of strong chelating compounds can mask metal peaks in electrochemical determinations. Additions of the chelating agent EDTA up to 10^{-4} M have no effect on the aluminium peak.

However, the addition of EDTA did have the beneficial effect of masking the Zn peak which precedes that of Al (see section D3.4).

D3.4 Other metal ions can interfere in the determination of aluminium if their complexes with DASA are adsorbed on the HMDE and their reduction potentials are close to that of Al. The following metals at stated concentrations do not interfere: 10^{-7} M Cu, Fe(III), Ni, As, In, Se(IV), V, Cr(III); 5×10^{-8} M Cr(VI); 10^{-8} M Cd, Pb, Ti, Sn, Sb, Mn; 10^{-9} M Se (VI), Tl, Ge, Ga. At concentrations several orders of magnitude higher than those occurring naturally Ga and Sb give peaks at or near the Al potential. High concentrations of Zn cause interference either as a discrete peak slightly positive of the Al peak or as a 'hump' on the Al peak. Interference from high concentrations of Zn in fresh waters is overcome by addition of 10^{-4} M EDTA to mask the zinc peak, and preconcentration at -1.0 V (as opposed to -0.9 V). In sea water, preconcentration at -1.0 V (followed by scanning from -0.9 V) is sufficient to overcome interference from zinc. (For necessary modification to the analytical procedure see section D9.12)

D4 Hazards

D4.1 Mercury

Mercury is toxic by inhalation and its effects as a poison are cumulative. Great care should therefore be taken in its handling and storage; mercury should be stored in a sealed container and waste mercury should be kept under water. Apparatus should be kept in a tray of sufficient volume to contain any spillage.

D5 Reagents

D5.1 Redistilled water

The redistilled water used in the preparation of reagents and for the rinsing of apparatus can best be obtained from a double silica still. The organic content of this water is generally less than that produced by deionisers.

D5.2 50% (v/v) Hydrochloric acid

To about 5 ml of water (D5.1) in a 200 ml calibrated flask add 100±0.1 ml of ultrapure hydrochloric acid (d_{20} 1.18) and make up to the mark by addition of more water. Prepare freshly each week, and store in a polyethylene container.

D5.3 O.1 M Hydrochloric acid

Add 4.40±0.05 ml of ultra pure, hydrochloric acid (d_{20} 1.18) to about 450 ml of water (D5.1), then make up to 500±1 ml by addition of water. Store in a polyethylene container and use in the preparation of working standard solutions.

D5.4 1 M Nitric or Hydrochloric acid

Add 63 ml of reagent grade nitric acid (d_{20} 1.42) or 89 ml of hydrochloric acid (d_{20} 1.18) to about 500 ml of water (D5.1) and make up to 1 litre (±10 ml) with water. Use this solution as an acid wash for soaking the cell, magnetic stirrer, glass pipettes and other glass and plastic ware.

D5.5 Standard aluminium solution

D5.5.1 1g/l Al standard, in 1 M HCl.

Dissolve 1.000±0.002 g of aluminium wire in 90 ml of high purity hydrochloric acid (d_{20} 1.18) with gentle heating. Cool and dilute the solution quantitatively to a volume of 1 litre with water. Store the solution in a clean polyethylene container. Alternatively, commercial standard solutions for atomic adsorption spectrophotmetry can be used.

D5.5.2 Suitable working standard solutions are prepared from the above solution (1 ml = 1 mg Al) by dilution with 0.1 MHCl. Stored in clean polyethylene containers these solutions are stable for up to 6 days.

D5.6 Mercury

Triple distilled mercury is used to fill the reservoir of the working electrode. This reagent is hazardous (see section D4).

D5.7 Saturated potassium chloride solution

Shake 25 g of high purity KCl with 50–60 ml of water (D5.1) until equilibrium is obtained. Use the solution to fill the salt bridge of the calomel reference electrode.

D5.8 1M (pH value 7.1) BES buffer solution

D5.8.1 0.5 m Sodium hydroxide solution

Dissolve 20.0±0.1 g of sodium hydroxide in 800 ml of water (D5.1) and make up to 1 litre with more water.

D5.8.2 Buffer Solution

Dissolve 4.265±0.001 g of high purity N,N-Bis-(2-hydroxyethyl)-2-amino-ethane sulphonic acid in 20 ml of 0.5 M sodium hydroxide solution. Adjust to a pH value of 7.10±0.05 by cautious addition of 50% (v/v) hydrochloric acid (D5.2). Store in a clean polyethylene container. This reagent may require treatment to remove zinc impurities, if so, carry out procedure D5.8.3.

D5.8.3 Zinc Removal

D5.8.3.1 Preparation of Manganese Dioxide Suspension

Weigh out and dissolve 0.80±0.05 g of sodium hydroxide in 50.0±0.1 ml of water (D5.1). Weigh out 1.58±0.01 g of potassium permanganate and dissolve this in the sodium hydroxide solution.

Weigh out and dissolve 2.97±0.01 g of manganese II chloride tetrahydrate ($MnCl_2$, $4H_2O$) in a small volume of water and make up to 75.0±0.1 ml with water (D5.1). Pour this solution into a 250 ml centrifuge container or tube. Add a magnetic stirrer bar and set up for stirring, with the electrodes from a pH meter dipping into the solution. Commence stirring slowly and carefully add the 50 ml of alkaline permanganate solution, adjusting the stirrer rate to prevent formation of lumps of manganese dioxide. Then adjust the pH value to 5.0±0.2 using 2 M sodium hydroxide solution (80 g of sodium hydroxide dissolved in water (D5.1) and made up to 1 litre (±10 ml) with water). Remove the electrodes but not the stirrer bar and centrifuge at 4,000 rpm for 30 mins. Decant off the supernatant liquid. Add 125 ml of water (D5.1) and resuspend using the magnetic stirrer. Replace the pH meter electrodes and readjust the pH value to 5.0±0.2 with 2 M sodium hydroxide solution as before. Remove the electrodes again and centrifuge as before.

Repeat this resuspension/centrifugation washing procedure three times. Finally quantitatively transfer the washed suspension to a 500 ml calibrated flask and make up to volume with water. Shake well to mix before use. The mixture is approximately 0.05 M MnO_2.

D5.8.3.2 Treatment of Buffer Solution

To the approximately 20 ml of buffer solution from D5.8.2 in a small stoppered bottle add 0.2 ml of the well shaken suspension D5.8.3.1 and shake overnight. Filter off the manganese dioxide using an 0.45 μm membrane filter. Use the filtered buffer for the analyses.

D5.9 0.001 M DASA solution

Dissolve 0.034±0.001 g of high purity 1,2-dihydroxyanthraquinone-3-sulphonic acid (DASA) in 100 ml of distilled water (D5.1). Store in a clean polyethylene container, replace after six days.

D5.10 2.5 M sodium hydroxide solution

Dissolve 10.0±0.1 g of high purity hydroxide in distilled water (D5.1). Transfer the solution to a 100 ml calibrated volumetric flask and dilute to the mark. Stored in a polyethylene container this solution is stable indefinitely.

D5.11 0.5 M sodium hydroxide solution

Dilute 20.0±0.1 ml of 2.5 M sodium hydroxide solution to 100±1 ml by addition of redistilled water. Store in a polyethylene container and use in the preparation of the BES buffer solution.

D5.12 0.1 M EDTA solution

Dissolve 3.722±0.001 g of EDTA disodium salt in 100 ml of distilled water (D5.1). Adjust to neutral (pH value 7.0) with 0.5 M sodium hydroxide.

D6 Equipment

D6.1 Cleanliness

Where posssible, plastic and glassware should be reserved solely for low level Al determinations. Clean all glassware by standing it in 1 N nitric or hydrochloric acid when not in use, and before use wash it with redistilled water several times. Stand the platinum counter electrode, the magnetic stirrer bar and the PTFE bubbling tube in 1 N acid when not in use and before use rinse thoroughly with redistilled water. Stand the calomel reference electrode in 3 M KCl solution, which has been acidified to approximately 0.1 M with 50% (v/v) HCl, when not in use and rinse thoroughly with redistilled water prior to use. After the measurement of each sample rinse the outside of the working electrode glass capillary tube with redistilled water and after use store it either dry (covered) or in redistilled water.

D6.2 A hanging mercury drop electrode (HMDE)

D6.3 A suitable polarographic analyser.

D6.4 A good quality X—Y or Y-time chart recorder.

D6.5 A glass or PTFE electrochemical cell which is either readily incorporated as a part of the electrode assembly or has its own sealable polyethylene lid with apertures for working electrode, reference electrode, purge gas bubbling tube, platinum counter electrode and pH electrode (optional).

D6.6 Standard calomel (reference) electrode (SCE)

The reference electrode is filled with saturated KCl solution to a level such that when the SCE is immersed in the sample solution, the sample solution level is above the level of the KCl solution in the SCE (see figure D1); this is to prevent a net outflow of KCl solution, which may contain significant concentrations of Al to the sample solution. To avoid this form of contamination a double-junction reference electrode is recommended. The outer sleeve is then filled with 0.1 M KCl or with the sample.

D6.7 Platinum wire counter electrode.

D6.8 PTFE bubbling tube connected, via a drechsel bottle containing redistilled water, via a regulator to a cylinder of inert gas (Ar or N_2).

D6.9 An electronically controlled magnetic stirrer.

D6.10 A PTFE-coated magnetic stirrer bar.

D6.11 A polycarbonate pressure filtration apparatus for use with 47 mm diameter membrane filters (The Sartorius apparatus has been found satisfactory).

D6.12 UV irradiation chamber fitted with 1 KW-mercury lamp with concentrically arranged fused silica tubes of 150 ml capacity.

D6.13 An adjustable micropipette variable between 10 μl and 100 μl.

D6.14 A good quality pH meter and electrode.

D7 Sample collection

For the collection of surface water samples use clean, acid-washed plastic containers; for sub-surface collections use all-plastic sampling apparatus and suspend it on plastic-coated suspension cable. Care should be taken to avoid the collection of samples close to a ship or close to the exhaust of an outboard motor. In collecting a river or estuarine sample care should be taken to avoid collecting a non-representative sample.

D8 Pretreatment and storage of samples

Immediately after collection, pass the sample (500 ml) through a 0.45 μm membrane filter, which has been washed by soaking in 0.1 N hydrochloric acid and rinsing in redistilled water, using a pressure of 0.3 bar. Acidify 100.0 ± 0.2 ml by addition of 100 ± 5 μl of 50% (v/v) HCl. Irradiate the acidified sample for 2–3 hours in a clean silica tube. Store the irradiated sample in a clean PTFE or fused silica container until analysed.

D9 Analytical procedure

Read section D4 on hazards before starting this procedure.

Step	Procedure	Notes
D9.1	Bring 100 ml of the acidified, irradiated sample (see D8) to neutral pH (7.0 ± 0.4) by addition of 200 μl of 2.5 M sodium hydroxide solution.	

Step	Procedure	Notes
D9.2	Accurately pipette 10 ml of sample into the electrochemical cell. (see note a).	(a) If zinc is thought to be present see step D9.11
D9.3	Using a micropipette, add 100 μl of 1 M BES buffer to the sample solution.	
D9.4	Using a micropipette, add 100 μl of 0.001 M DASA solution to the sample.	
D9.5	Place a clean stirrer bar in the cell and put the cell into position on the stand ensuring an airtight seal around the rim.	
D9.6	Gently bubble an inert gas (N_2 or Ar) through the sample for 8 minutes (note a and b).	(b) Longer purging times are necessary for larger sample volumes.
D9.7	Meanwhile set up the polarograph as follows:	(c) Note that lower current range setting than 0.5 μA generally result in increased noise and hence difficulties in measuring peak heights; higher current range setting should be used for higher expected Aluminium concentrations.
	Initial potential -0.9 V (see note a and D9.12.3)	
	Modulation (pulse) amplitude 25 mV	
	Scan rate 20 mVs^{-1}(−ve direction)	
	Drop time 0.1 s	
	Operating mode Differential pulse	
	Low pass filter Off	
	Current range 0–0.5 μA. (c)	
D9.8	Once purging of the sample is complete and the polarograph is set up, adsorption may be commenced. First the magnetic stirrer and the potentiostat are switched on (d). Once the sample solution is in steady motion adsorption is commenced by extruding a fresh mercury drop (e) and the timer is started. After a fixed adsorption time the stirrer is switched off, and after a further 15 s waiting period, during which the chart recorder is activated, the scan is initiated over a current range corresponding to the expected Al concentration and the peak is recorded.	(d) The optimum stirring rate, which gives maximum sensitivity without too much turbulence in the sample solution, must be determined experimentally as it will vary with the shape of the electrochemical cell etc. (e) The mercury drop used when testing the method had a volume of 3.52×10^{-4} cm^3, a radius of 4.4×10^{-2} cm and a surface area of 2.4×10^{-2} cm^{-2}. Provided the same size drop is always used for analysis, standardization and control samples, a different similar drop size may be used.
D9.9	An appropriate standard addition of Al is then made to the sample with a micropipette and the solution purged with an inert gas for a one minute period. The previous mercury drop is discarded and a further drop is formed and discarded before the working drop is extruded. Repeat the measurement as described in section D9.8. (see note f).	(f) The volume of each standard addition should be small, ie 25 μl, so as not to significantly alter the volume of the sample.
D9.10	A further addition of Al standard is added and section D9.9 repeated. (note f).	
D9.11	**When Zn is present at high concentrations** in the sample it causes interference in this determination	

Step	Procedure	Notes
	(see section D3), however, this problem is overcome by adopting the following procedure.	
D9.11.1	If the sample is fresh water (ie drinking water, river water etc.) add 10 μl of 0.1 M EDTA solution to the sample along with the buffer and complexing reagent at steps D9.3 and D9.4.	
D9.11.2	For both fresh and sea waters proceed with steps D9.3 to D9.6 as usual.	
D9.11.3	Then with the cell disconnected from the polarograph (ie cell off), activate the recorder and scan from -0.9 V to -1.0 V then using the polarograph's HOLD function hold at -1.0 V. This operation is performed while the sample is being purged.	
D9.11.4	Once purging of the sample is complete, and the polarograph has been set up, adsorption may be commenced. First the magnetic stirrer and potentiostat are switched on. Once the sample solution is in steady motion, adsorption is commenced by extruding a fresh mercury drop and the timer is started. After a fixed adsorption time the stirrer is switched off, a period of 10 s is allowed to elapse and the potential is then returned to the initial potential (-0.9 V). A further period of 10 s is allowed to elapse, during which the recorder is activated, and the scan is initiated over a current range corresponding to the expected concentration and the peak is recorded.	
D9.11.5	Standard additions of Al are made as in steps D9.9 and D9.10. (also note f) and steps D9.11.2—D9.11.4 are repeated.	

D10 Measurement of peak heights

The peak heights for the sample and the sample plus standard additions of Al are plotted against the concentrations of added Al standard in the manner illustrated in figures D2 and D3. The concentration of Al in the sample is then read from the negative portion of the concentration axis.

D11 Sources of errors

The analytical procedure can be applied to samples ranging from ultrapure water to sea water, but as with most determinations of trace substances, the major source of error is the introduction of contaminants. The ways in which general contamination is avoided vary from laboratory to laboratory so analysts must decide on the precautions appropriate to their requirements. However, in the manipulation of samples, reagents and standards the use of a laminar flow clean bench is strongly recommended. A laminar flow clean bench can also be used to house the electrode assembly.

D11.1 Temperature variations

Temperature variations affect the diffusion rate of the complex on the HMDE surface (see section D2.5). Under conditions used in this method the temperature was constant to within $\pm$ 0.5°C during a set of measurements, resulting in variations in the diffusion rate, and hence in the peak heights, of <1.5%.

D11.2 Measurement of peak heights

Due to imprecisions in the drawing of base lines, thickness of lines etc these measurements are somewhat subjective and hence are liable to operator errors, especially for small peak heights. Errors will also tend to be higher when a very high sensitivity (low current range) is used because of increased instrumental noise.

D11.3 Introduction of contaminants via apparatus and reagents used. Contaminants can be introduced to the sample in two main ways:

D11.3.1 Leakage of contaminants into solution

Contaminants can leak into the sample solution from cell components, eg glass cell walls, the platinum electrode, or from the solution in the salt bridge of the reference electrode. This form of contamination manifests itself as successive increases in peak height when a series of replicate adsorptions and scans are carried out on the same solution; all other conditions, ie temperature, stirring rate, adsorption time etc, being constant. This type of contamination can be best avoided by leaving the cell components to soak in acid when they are not in use, and in the case of the reference cell by using it in the manner described in Section D6.6.

D11.3.2 Contaminants associated with reagents and standards

The second form of contamination may arise from the reagents used; taking into account the high quality of reagents that are available this is not likely to be a significant factor.

D11.4 Interfering substances

See section D3.

D11.5 Variation in peak current with pH value

The peak current is stable with respect to pH between 8.5 and 5.4–5.7. Between pH 5.4 and 5.7 the peak disappears—this coincides with the loss of solution colour—ie reagent change.

D12 Effect of preconcentration time

The Al peak current increases with adsorption time up to an adsorption time of 3 minutes (see fig D4). At longer adsorption times the Al peak begins to merge with the hydrogen wave.

D13 Checking the accuracy of analytical results

Once the method has been put into routine use the main factor which will affect the accuracy of results (apart from contamination) will be operator errors, eg pipetting, peak height measurement etc. The effect of this was assessed by the determination, on six successive days, of Al in a filtered and UV irradiated sea water sample. The mean concentration and standard deviation are represented here:

Mean concentration	11.6×10^{-9} M Al
Standard deviation	4.9×10^{-10} M Al
% standard deviation	4.2%

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

D14 References

(1) Cosovic B. and Vojvodic V. The application of AC polarography to the determination of surface-active substances in sea water. *Limnol. Oceanogr.* **27**, 361–369 (1982).

(2) van den Berg, C M G, Murphy, K and Riley, J P. The determination of aluminium in sea water and freshwater using cathodic stripping voltammetry. *Analyt. Chim. Acta.* **188,** 177–186 (1986).

Table D1

Effect of Triton-X-100 (non-ionic surfactant) on aluminium peak in irradiated sea water; conditions: 10^{-5} M DASA, 0.01 M BES (pH 7.1), 50 mVs^{-1} scan rate, 10 pulses s^{-1}, 50 mV pulse amplitude, 30 s adsorption time, Al concentration 35 nM.

Triton-X-100 concentration mg/l	Effect on Al peak current as a percentage of original peak
0	0
0.1	−12.5
0.2	−21.4
0.5	−15.4*
1.0	−100

* the peak current apparently increases with 0.5 mg/l. Triton-X-100. This is due to a broadening of the peak and a negative shift so that it begins to merge with the hydrogen wave.

Figure D1 Electrochemical cell and electrode arrangement

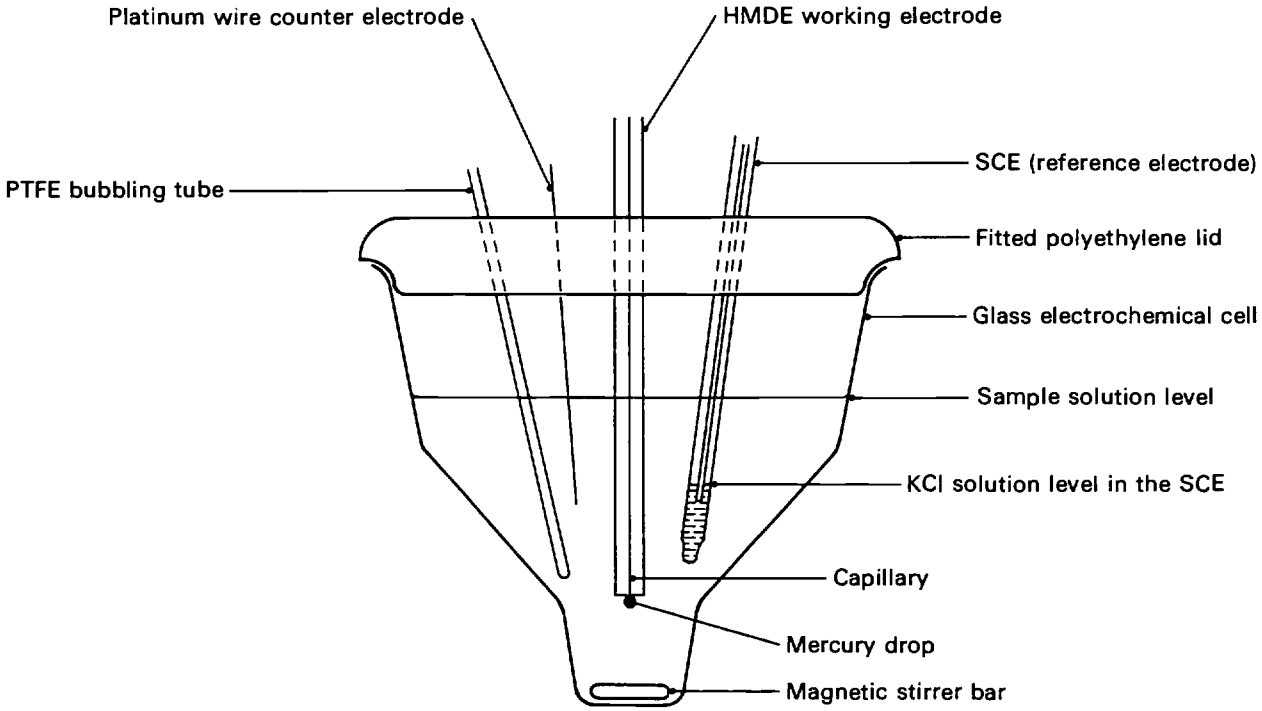
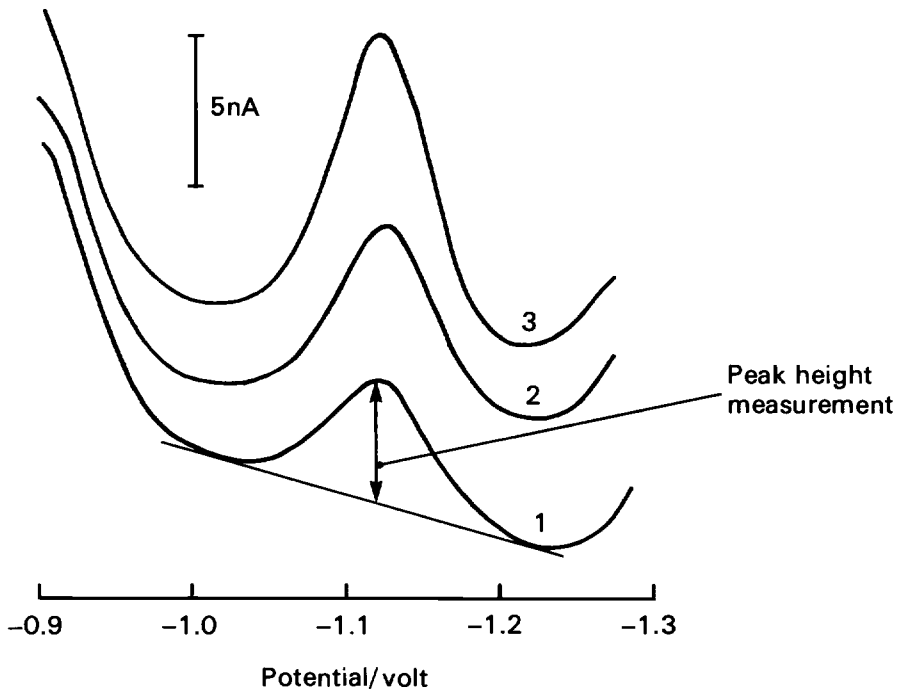


Figure D2 Differential pulse polarography of A1

Conditions: irradiated sea water, pH 7.1, 10^{-5}M DASA, 20mV s^{-1} scan rate, 10 pulses s^{-1}, 25mV pulse amplitude, −1.0V adsorption potential, scan initiated from −0.9V, 45s adsorption time

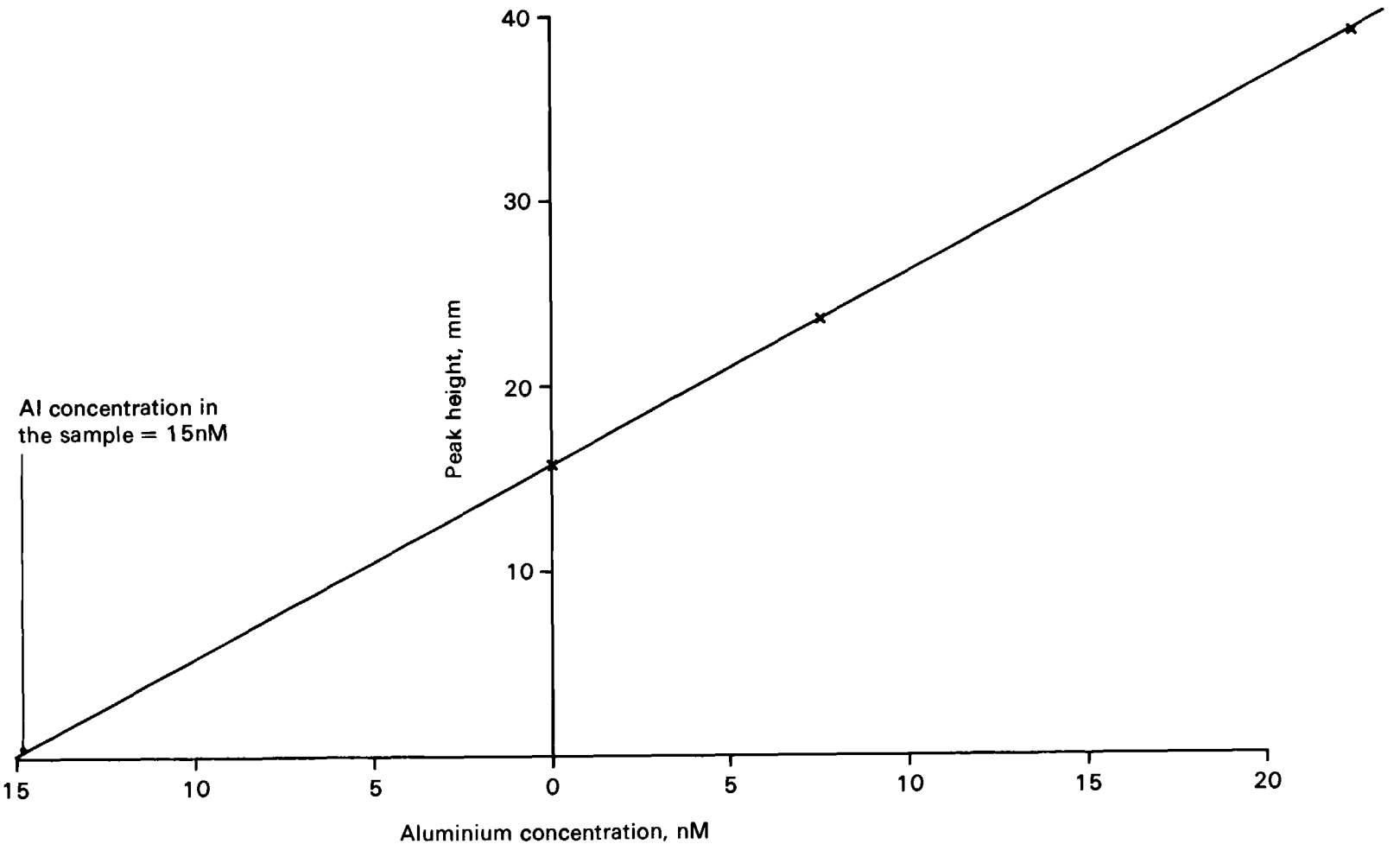


Scan 1 : irradiated sea water

Scan 2 : irradiated sea water + 7.4nM Al

Scan 3 : irradiated sea water + 22.2nM Al

Figure D3 Calibration curve for the determination of A1



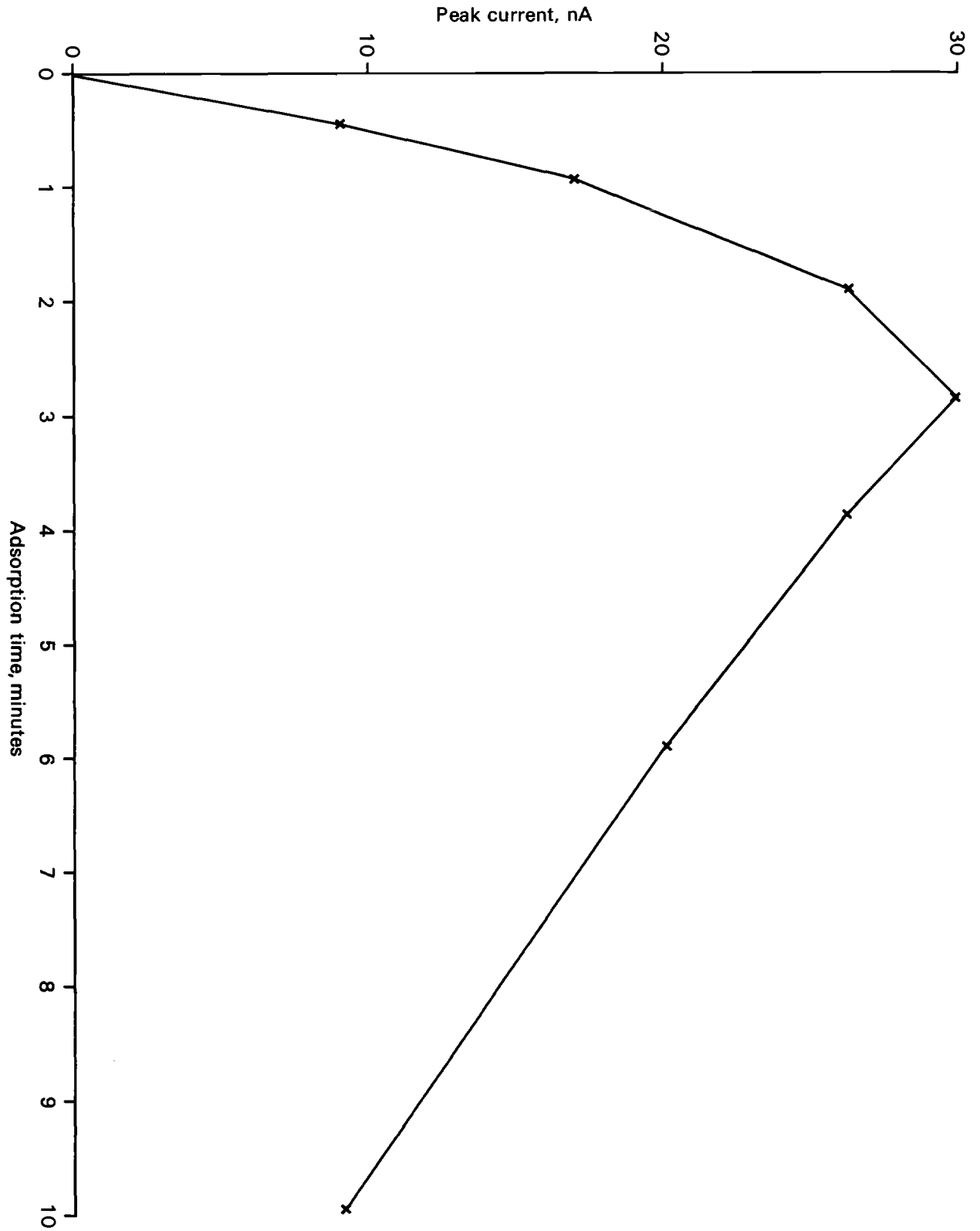


Figure D4 Effect of preconcentration time on peak current. Conditions: irradiated sea water 40 nM Al, pH 7.1, 10^{-5} M DASA

E Emission Spectrophotometry

Analyses are usually made directly on the sample, without any pretreatment except acidification, using Inductively Coupled Plasma Spectrophotometry (E1); but carrier concentration-internal standard DC arc emission (E2) has also been used.

E1 ICPS

If necessary the sample may be acidified for sample preservation and filtered prior to analysis. Samples are analysed according to instrument manufacturers instructions. Two analytical lines are used:

396.15 nm with a limit of detection of 0.002 mg/l without concentration. This line suffers from calcium interference at high concentrations of calcium. User should ascertain the degree of interference with their own instrument using a series of aluminium standards to which varying amounts of calcium have been added. Computer calculated correction will be possible (see Ref 1 under Interference).

167.08 nm with a limit of detection of <0.01 mg/l. This line requires a vacuum path instrument. It also suffers from slight iron interference due to a faint iron line at 167.07 nm and may also be subject to interference from very high concentrations of copper.

Users should ascertain the degree of interference using a series of aluminium standards to which varying amounts of iron or copper have been added. Care should be taken to ensure that the iron, copper and aluminium salts used to prepare these standards are sufficiently pure. Computer calculated correction will be possible (see Ref 1 under Interference).

The method determines total aluminium in the sample and may therefore give higher values than the colorimetric methods unless the acid pretreatments in these latter methods render colloidal material reactive. See Section A8.

Information: Yorkshire WA Sheffield Laboratory; South West WA, Truro and Countess Wear Laboratories; also wavelengths tables.

E1.1 Preconcentration

Resolution of the carrier precipitate from E.2 in acid, followed by inductivity coupled plasma spectrophotometry would considerably extend the range of the direct ICPS method. Some other elements such as beryllium, the lanthanides, gallium and indium could be determined simultaneously using lanthanum as an internal standard if desired.

E2 DC Arc Carrier Concentration Emission Spectrophotometry

A lanthanum carrier concentration-internal standard DC arc emission technique is described in another booklet in this series Ref 1.

E3 Reference

1. *Emission Spectrophotometric Multielement Methods of Analysis for Waters, Sediments and Other Materials of Interest to the Water Industry 1980.* HMSO in this series.

F Notes on Other Methods

F1 Atomic Absorption Spectrophotometric Methods

Aluminium can be determined either directly or by solvent extraction atomic absorption spectrophotometry. The air-acetylene flame is not sensitive enough and either nitrous oxide-acetylene (1) or electrothermal sources are used. However British experience reported to the SCA shows that the methods are highly instrument and operator dependent and very susceptible to interferences and minor variations. Hence very rigorous analytical quality control procedures with multiplicate analyses of samples, blanks and control standards are essential if reliable results are to be obtained. Tube life tends to be short and the sensitivity poor. Alternative methods are preferred.

Aluminium 8-Quinolinolate is soluble in methyl isobutyl ketone, as are the beryllium and several other derivatives. This can be used as a preconcentration stage prior to either nitrous oxide-acetylene (2) or electrothermal AAS methods;

F2 8-Quinolinol Fluorimetric Method

As mentioned above, aluminium 8 Quinolinolate is soluble in methyl isobutyl ketone and also in chloroform. These salts but not the free 8-Quinolinol can be made to fluoresce by UV irradiation. This has not been thoroughly investigated, but subject to the usual preliminary precision and interference testing this might be a suitable concentration method for some samples.

F3 References

1. APHA, AWWA, WPCF *Standard Methods 15th Edition* 1980 pp 157–9.
2. APHA, AWWA, WPCF *Standard Methods 15th Edition* 1980 pp 159–160.

G Estimation of the Accuracy of Analytical Results Using These Methods

G1 Introduction

Quantitative investigation of the accuracy achievable with some of these methods appears to be limited. 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 Secretary of the Department of the Environment's Standing Committee of Analysts (see Address for Correspondence).

The precision achieved and effects of any interfering substances that may be present in samples are of particular interest. Any information on these aspects would be useful, but the value of such information would be greatly enhanced if it were obtained to a common plan so that the information can be compared and valid conclusions drawn. Accordingly, suggestions for a suitable experimental design and analysis for results are given in the following sections and it is strongly urged that laboratories follow this design whenever possible. The design has been chosen to be as simple as possible, more complex designs are possible and would give more information.

G2 Basis of suggested Tests

The limit of detection is governed by the within-batch variability of blank determinations. The precision of analytical results may depend on the concentration of aluminium in the sample analysed and on the type of sample, eg poorer precision may be obtained with samples than with standard solutions. For these reasons the basic design recommended is the analysis of one portion each of solutions such as the following, on each of n days, where n is at least 5 and preferably greater up to 10.

Solution No	Description
1	Blank
2	Another blank
3	*Standard solution 0.06 mg/1 Al
4	*Standard solution 0.30 mg/1 Al
5	Typical sample
6	*Same sample spiked with 0.30 mg/1 Al

*Dependent on the range of the method

It is essential that these solutions be treated exactly as if they were samples and the procedure specified in the Analytical Procedure Sections of the methods must be rigidly followed. These solutions should be analysed in random order in each batch of analyses. Solutions 1 to 4 should be prepared each day exactly as described in the method and should contain the same amount of acid as is present in the samples. The same batch of water should be used on each day to prepare all 4 solutions. For solutions 5 and 6 a total of 2 litres of typical sample are required. Prepare solution 6 each day when required by spiking solution 5 as follows; add with a pipette 2.00 ml of an intermediate standard aluminium solution to 100 ml of solution 5. When analysing solution 6 it may be necessary to take the upper concentration limit into account and to take an appropriately smaller aliquot. The total period of the tests may be any convenient time so long as the aluminium concentration in solution 5 does not change appreciably (up to 2 weeks). The results of the analyses of solutions 5 and 6 will provide a check on the effect of sample type on precision. Any deviation of the recovery of spiked aluminium from 100% may give an indication of the presence of interfering substances.

G3 Evaluation of Results

The raw experimental results may be sent direct to the Department of the Environment for evaluation together with the results obtained from the standards used to establish the calibration curve in each batch of analysis. However, for those laboratories wishing to make the calculations themselves the details are given below.

G3.1 Convert all results to concentrations as described in the method. Deduct the first of the 2 blank values (solution 1) from each of the other solution values.

G3.2 Calculate the mean concentration of the n results for each solution.

G3.3 Calculate the standard deviation, s, of the n results for each solution from:

$$S = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n-1}}$$

where x_i = the result from the ith batch

$\bar{x}$ = the mean value of x_i

G3.4 Calculate the within-batch standard deviation, s_w, of the blank from:

$$S_w = \sqrt{\frac{\sum (x_{1i} - x_{2i})^2}{2n}}$$

where x_{1i} = the 1st blank result (solution 1) from the ith batch

x_{2i} = the 2nd blank result (solution 2) from the ith batch

G3.5 Calculate the mean percentage recovery, R, of the spiked aluminium solution 6 from:

$$R = (1.02\bar{x}_6 - \bar{x}_5) \times \frac{100}{0.3} \text{ mg/l}$$

where $\bar{x}_5$ = the mean value of the results for solution 5.

where $\bar{x}_6$ = the mean value of the results for solution 6.

G3.6 Summarize the results as in the following table

Solution	No of results (n)	Mean aluminium Concentration mg/l	Standard Deviation mg/l	Mean Recovery %
2 Blank				—
3 Standard, 0.06 mg/l				—
4 Standard, 0.30 mg/l				—
5 Sample				—
6 Solution 5 + 0.30 mg/l				

The appropriate sample description should be entered in the space for solution 5. The standard deviation from step G3.4 entered for the blank solution 2 and the standard deviations from step G3.3 are entered for solutions 3 to 6.

If any sample pretreatment procedure was carried out this should also be stated.

Address for Correspondence

However thoroughly a method may be tested there is always the possibility of a user discovering some hitherto undiscovered problem. Correspondence should be addressed to:

The Secretary
Standing Committee of Analysts
Department of the Environment
43 Marsham Street
Romney House
London SW1P 3PY
United Kingdom

Standing Committee of Analysts

Members of the Committee Responsible for this Method:

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1 Main committee member
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