Acid Soluble Aluminium in Raw and Potable Waters by Spectrophotometry

using pyrocatechol violet

1979

Tentative Method

Methods for the Examination of Waters and Associated Materials

Contents

London Her Majesty's Stationery Office

Warning to users

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

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

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

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

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About this series

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

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

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

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

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

TA DICK
Chairman

LR PITTWELL
Secretary

20 July 1977

Acid Soluble Aluminium in Raw and Potable Waters by Spectrophotometry

Tentative Method

(1979 version)

1 Performance Characteristics of the Method

(For further information on the determination and definition of performance characteristics see another publication in this series)

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

1.1	Substance determined	Those forms of aluminium reacting with pyrocatechol violet, α, α-bis (3, 4-dihydroxyphenyl) toluene-2, α-sultone. (See Sections 2 and 8).		
1.2	Type of sample	Raw and potable waters.		
1.3	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.		
1.4	Range of application	Up to 0·3 mg/l.		
1.5	Calibration curve (a)	Linear to at least 0·3 mg/l.		
1.6	Total Standard Deviation (a)	Aluminium Concentration (mg/l)	Standard Deviation (mg/l)	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
1.7	Limit of detection (a)	0·013 mg/l with 10 degrees of freedom.		
1.8	Sensitivity (a)	0·1 mg/l gives an absorbance of approximately 0·16.		
1.9	Bias (a)	No bias detected except when interferences occur (see Section 1.10).		
1.10	Interferences (a)	Certain substances are known to cause interference in this determination (see Section 3).		
1.11	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.		

(a) These data were obtained at the South-West Water Authority[1] using a spectrophotometer with 10-mm cells at 585 nm.
(b) Distilled water spiked with the stated concentration of aluminium.
(c) Tap water.
(d) Same tap water spiked with 0·3 mg/l aluminium.

2 Principle

2.1 The method described is that used by the South West Water Authority[1]. 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.

2.2 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 3).

2.3 Correction for 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.

2.4 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 8).

3 Interferences

3.1 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 1. The effect of 1mg/l fluoride on the determination of aluminium by this method has been investigated by several laboratories[4] and the results are given in Table 2.

3.2 A number of potable water supplies have fluoride added to bring the fluoride concentration to 1·0 ± 0·1 mg/l. To determine the aluminium content in these waters the procedure specified in Sections 8.1 and 9 should be followed except that the aluminium concentration (Steps 9.10 to 9.12) should be determined by reference to an appropriate calibration curve prepared from standards to which 1·0 mg/l of fluoride has been added (see Section 11.3). 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/l 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/l fluoride.

3.3 Interference effects caused by up to 1 mg/l 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.

Table 1

Other substance	Concentration of other substance, mg/l	Effect * in mg/l Al of other substances at an aluminium concentration of:	
		0·000 mg/l	0·300 mg/l
Calcium (as Ca^{++})	500	+0·006	+0·003
Calcium (as Ca^{++})	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
Copper (as Cu^{++})	1	0·000	+0·003
Lead (as Pb^{++})	2	+0·052	+0·007
Lead (as Pb^{++})	1	+0·004	0·000
Iron III (as Fe^{+++})	1	+0·011	+0·014
Iron III (as Fe^{+++})	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
Chromium III (as Cr^{+++})	0·25	+0·002	–0·015
Chromium III (as Cr^{+++})	0·025	+0·005	–0·002
Tin II (as Sn^{++})	2	+0·002	–0·015
Tin II (as Sn^{++})	1	+0·002	–0·007
Fluoride (as F^{-})	1	–0·005	–0·023
Fluoride (as F^{-})	0·5	–0·002	–0·011
Orthophosphate (as P)	8·2	–0·005	–0·050
Orthophosphate (as P)	4·1	–0·005	–0·038
Orthophosphate (as P)	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
Alkalinity (as $CaCO_3$)	300	+0·006	+0·007
Alkalinity (as $CaCO_3$)	200	0·000	–0·002

Table 1

Other substance	Concentration of other substance, mg/l	Effect * in mg/l Al of other substances at an aluminium concentration of:	
		0·000 mg/l	0·300 mg/l
Humic acid } Fulvic acid }	10 } 10 }	+0·001	–0·004
Chlorine	5	+0·001	0·000
Chlorine } Ammonia (as N) }	5 } 0·5 }	+0·001	0·000
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

* 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 0·000 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.

Table 2

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

4 Hazards

4.1 The reagents described in Sections 5.4, 5.6 and 8.1.4 should be regarded as special hazards. Care must be taken to avoid ingestion, inhalation of vapours and to protect the hands, eyes and face.

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

5 Reagents

Analytical reagent grade chemicals are suitable unless otherwise specified.

5.1 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.

5.2 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.

5.2.1 *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.

5.3 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.

5.4 1,10-Phenanthroline/hydroxyammonium chloride reagent

This reagent is hazardous (see Section 4). 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.

5.5 α, α-Bis (3,4-dihydroxy phenyl) toluene -2, α-sultone (Pyrocatechol violet) solution

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.

5.6 Hexamethylene tetramine (Hexamine) buffer solutions

5.6.1 *Hexamine/ammonia buffer*

This reagent is hazardous (see Section 4). 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 μ). 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 a 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 obtained is 6·1±0·1 (step 9.2, note k) by adding the reagents to a blank (step 9·4 onwards).

5.6.2 *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. Weigh 7·50±0·01 g of ethanolamine and transfer quantitatively using water to the hexamine solution. 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.

5.7 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.

5.8 Standard aluminium solutions

5.8.1 *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.

5.8.2 *Solution B* 1 ml is equivalent to 1·8 ug Al

Add 5·00±0·01 ml of *solution A* to a 1-litre calibrated flask, followed by 20·0±0·1 ml of 5M hydrochloric acid, and dilute with water to the mark. Store the solution in a polyethylene bottle. It is stable for at least 6 months.

5.9 Standard fluoride solutions

5.9.1 *Solution A* 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 5M 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.

5.9.2 *Solution B* contains 2 mg/l fluoride

Add 20·0±0·1 ml of standard fluoride *Solution A* to a 1-litre calibrated flask followed by 20·0±0·1 ml of 5M hydrochloric acid and dilute to the mark with water. Store in a polyethylene bottle. This solution is stable for at least 2 months.

6 Apparatus

6.1 Cleanliness

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 3).

6.2 100-ml translucent silica beakers
50-ml calibrated polypropylene flasks

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

6.4 pH meter.

7 Sample Collection and Preservation

Clean a polyethylene bottle by the procedure given in Section 6.1, add to the empty bottle 20·0±0·5 ml of 5M 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 result (see step 9.12).

8 Sample Pretreatment

8.1 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 at this time. 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 9 with those obtained following the procedures outlined in Section 8.2 and Section 9. If pretreatment is used the performance characteristics of the complete method, and in particular the precision, may differ from those given in Section 1.

8.2 Pretreatment procedure

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

Step	Experimental Procedure	Notes
	Pretreatment procedure (notes a, b, c, d and e)	
8.2.1	Add 30·0±0·5 ml of the well mixed sample to a 100-ml translucent silica beaker. Cover the beaker with a watch glass and heat to boiling.	(a) If pretreatment is carried out a calibration curve must be prepared with calibration standards which have been run through this pretreatment procedure (see Section 11). (b) Precautions must be taken to minimize contamination during this step. (c) An appropriate quality control solution (see Section 14) should be run through this procedure for each batch of determinations for which pretreatment is required using the same batch of reagents as for samples. (d) If polyphosphates are present continue boiling for 2 hours with addition of water to avoid evaporation to dryness (see Section 3). (e) If fluoride is present a calibration curve should be prepared with calibration standards which contain fluoride (see Sections 3.2 and 11.3).
8.2.2	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 9 using this solution as the sample.	
	Blank determination	
8.2.3	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 and proceed as in step 9.5.	
	Compensation for colour and turbidity in the sample	
8.2.4	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 8.2.1 and 8.2.2 but omitting the addition of 1,10-phenanthroline and pyrocatechol violet in step 9·2.	

9 Analytical Procedure

READ SECTION 4 ON HAZARDS BEFORE STARTING THIS PROCEDURE

Step	Experimental Procedure	Notes
	Analysis of samples (notes f, g, h and i)	
9.1	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 8.2.1, note d. (g) An appropriate quality control solution (see Section 14) 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 3.2 and 11.3). (i) If the sample contains more than 0·3 mg/l Al see Section 12.
9.2	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 5.6.1) 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 5.6).
9.3	Meanwhile set up the instrument (see Section 6.3) according to the manufacturer's instructions. Adjust the zero of the instrument with water in the reference cell. Measure the absorbance (see Section 10) 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*)	
9.4	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.	
9.5	Carry out steps 9.2 and 9.3. Let the absorbance of the blank be B.	
	Compensation for colour and turbidity in the sample	
9.6	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 9.1 to 9.3 inclusive, omitting the additions of 1,10-phenanthroline reagent and pyrocatechol violet solutions in step 9.2. Let the absorbance of the sample compensation solution be A.	

Step	Experimental Procedure	Notes
	Determination of aluminium in the water used for the blank (note l)	
9.7	Add 50·0±0·5 ml of 0·1 M hydrocjhloric acid to a 100-ml translucent silica beaker. Cover the beaker with a watch glass and evaporate carefully (note m) 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.	(l) This determination is not needed if the aluminium content of the water used for the blank is known or is negligible (Section 13.2). (m)Precautions must be taken to minimize contamination during this step.
9.8	Analyse a 30·0±0·5 ml portion of the solution as in steps 9.1 to 9.3 inclusive. Let the absorbance of this solution be E.	
9.9	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 n).	(n) See Section 11 for the preparation of the calibration curve.
	Calculation of Results	
9.10	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 cuvette are filled with water.	
9.11	Determine the apparent aluminium concentration A_a, in the sample from R and the calibration curve (see Section 11).	
9.12	Calculate the aluminium concentration in the original sample, A_r from: $A_r = 1·02\,(A_a + A_w)$ (note o).	(o) The factor 1·02 allows for the dilution of the sample by the acid into which it was collected (see Section 7).

10 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.

11 Preparation of Calibration Curve

11.1 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 8.2.1, 8.2.2 and 9.2 onwards as appropriate. Subtract the absorbance of the blank from the absorbances of 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.

11.2 When pretreatment is not carried out

To a series of 50-ml calibrated polypropylene flasks 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 9.2 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.

11.3 When 1·0±0·1 mg/l fluoride is present

To a series of 100-ml translucent silica beakers (Section 11.1) or 50-ml calibrated polypropylene flasks (Section 11.2) 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 respectively of standard aluminium *solution B*. To each flask pipette 15·0 ml of standard fluoride *solution B*. Mix by swirling and carry out the steps specified in Sections 11·1 or 11·2 as appropriate to prepare the appropriate calibration curve. The calibration curve(s) should be checked at frequent intervals.

11.4 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 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.

12 Change in 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:

$$C = 1·02\left(\frac{30}{V}C_a + C_w\right)$$

13 Sources of Errors

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 8). The following sub-sections describe the main sources of error and how they can be minimized but each analyst must decide what precautions are appropriate to his/her particular requirements.

13.1 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 8.2.4, and 9.6 allows a correction to be made if required.

13.2 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 9.7 to 9.9 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.

13.3 Interfering substances

See Section 3.

14 Checking the Accuracy of Analytical Results

(For further information see another publication in this series)

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.

15 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 WK and Wilson AL, 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.

Appendix

Estimation of the Accuracy of Analytical Results Using the Aluminium Method

1 Introduction

Quantitative investigation of the accuracy achievable when the aluminium method is used appears to be limited to work at the South West Water Authority. Before firmly recommending the method for general use, it is desirable to know the accuracy achievable in other laboratories. It would, therefore, be of great value if any laboratory using or considering the use of this method, could estimate the accuracy of its own analytical results and report the findings to the Technical Secretary of the Metals and Metalloids Working Group of the Department of the Environment's Standing Committee of Analysts.*

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 of 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.

2 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, worse precision may be obtained with samples than with standard solutions. For these reasons the basic design recommended is the analysis of one portion of each of the following solutions 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/l Al
4	Standard solution 0·30 mg/l Al
5	Typical sample
6	Same sample spiked with 0·30 mg/l Al

It is essential that these solutions be treated exactly as if they were samples and the procedure specified in Section 9 (and Section 8.1 if necessary) of the method 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 hydrochloric 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. (The intermediate standard aluminium solution is prepared by diluting 8·5±0·1 ml of standard aluminium *solution A* with 0·1 M hydrochloric acid to 200 ml in a calibrated flask). When analysing solution 6 it will be necessary to take into account Section 12 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.

3 Evaluation of Results

The raw experimental results should 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.

3.1 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.

3.2 Calculate the mean concentration of the n results for each solution.

3.3 Calculate the standard deviation, s, of the n results for each solution from:

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

where x_i = the result from the ith batch

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

3.4 Calculate the within-batch standard deviation, s_w, of the blank from:

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

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

3.5 Calculate the mean percentage recovery, R, of the spiked aluminium solution 6 from:

$$R = (1{\cdot}02\bar{x}_6 - \bar{x}_5) \times \frac{100}{0{\cdot}3} \quad \text{mg/l}$$

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.

3.6 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 3.4 is entered for the blank solution 2 and the standard deviations from step 3.3 are entered for solutions 3 to 6. If the pretreatment procedure (Section 8.2) was carried out this should also be stated.

---

* *Results to be sent to:*

The Technical Secretary
Metals and Metalloids Working Group
Standing Committee of Analysts
Department of the Environment
2 Marsham Street
London SW1P 3EB

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