Lithium, Magnesium, Calcium, Strontium and Barium in Waters and Sewage Effluents by Atomic Absorption Spectrophotometry 1987

Methods for the Examination of Waters and Associated Materials

Her Majesty's Stationery Office

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The Calcium and Magnesium methods were first published in 1977.

This combined and expanded edition first published in 1987.

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This booklet contains the following methods:

A. Lithium in Waters by Atomic Absorption Spectrophotometry (Tentative method).

B. Magnesium and Calcium in Waters and Sewage Effluents by Atomic Absorption Spectrophotometry (Revised, Second edition).

C. Strontium and Barium in Potable Waters by Atomic Absorption Spectrophotometry (Tentative methods).

Except for additional information on interferences the methods for Magnesium and Calcium remain virtually unchanged from the first editions approved in 1977 which are therefore not withdrawn.

Because intereference effects are dependent on instrument settings and design, mention is made of the actual instruments used in obtaining the test data. This in no way endorses these models nor does it mean that subsequent models will give identical performance. Purchasers are advised to evaluate instruments for themselves.

Contents

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 These volumes inevitably took some years to prepare, so that they were often partially out of date before they appeared in print.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 seven 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
3.0 Empirical and physical methods
4.0 Metals and metalloids
5.0 General nonmetallic substances
6.0 Organic impurities
7.0 Biological 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 1986

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 require specialist treatment not normally encountered by most doctors. Similar warning should be given if a biological or radio-chemical injury is suspected. Some very unusual parasites, viruses and other micro-organisms are occasionally encountered in samples and when sampling in the field. In the latter case, all equipment including footwear should be disinfected by appropriate methods if contamination is suspected. 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.

General Note on Instrumentation

The instruments described in these methods are those used in the testing of the method. However equipment changes occur over the years. Hence care needs to be taken when using the more sophisticated equipment which allows use of non-linear analytical curves or gives direct concentration readout. Users of such equipment should always check using synthetic samples, spiked samples and added possible interferants to ascertain whether their suppositions are correct, and if necessary to discover what must be done in order to obtain corrrect analyses.

A Lithium in Waters by Atomic Absorption Spectrophotometry Tentative Method

A0 Introduction

A0.1 The commonest reason for determining lithium is for flow monitoring in pipes and open channels. A concentrated lithium solution (typically 30,000–50,000 mg/litre lithium) is dosed into the pipe of channel. Lithium is used for this procedure for the following reasons:

(a) The typical level of lithium in waste waters is usually less than 0.01 mg/litre.

(b) Lithium is not significantly absorbed by the suspended solids in the flow and cannot be degraded.

(c) Lithium is relatively non-toxic to aquatic flora and fauna at the typical concentrations employed.

The dosing rate of the lithium is normally set to give a lithium concentration in the pipe or channel or 0.5–2 mg/litre after complete mixing. It should be noted that for flow monitoring in potable water systems, the Joint Committee on the Medical Aspects of Water Quality has stated that the mean concentration of lithium just below the point of application should not exceed 0.1 mg/litre.

In order to calculate the flow in the channel, it is essential to take a representative sample of the flow to be measured *prior* to dosing lithium. This will allow the background level of lithium to be determined. For most waste waters this should be less than 0.02 mg/litre lithium.

A number of texts dealing with lithium dilution flow monitoring have been published (1–5).

A0.2 Lithium occurs naturally in some waters and analyses may occasionally be required, especially for spa waters which may, if bottled, be required to comply with the Natural Mineral Water Regulations 1985 etc. For such waters, this method could be used after appropriate quantitative dilution or concentration by evaporation. See Section A10.

A1 Performance characteristics of Method

(For further information on the determination and definition of performance characteristics see General Principles of Sampling and Accuracy of Results 1980, also published in this series (7))

A1.1	Substance Determined	All forms of lithium are likely to occur in potable, river and waste waters.
A1.2	Type of Sample	Potable, river and waste waters.
A1.3	Basis of Method	Direct aspiration of the acidified samples pretreated if necessary, into the flame of an atomic absorption spectrophotometer.
A1.4	Range of Application	Up to 2 mg Li/l. (See Section A10)
A1.5	Calibration Curve	Linear to 1 mg Li/l, slight non-linearity to 2 mg Li/l.

A1.6	Standard Deviation	See Table 1.
A1.7	Limit of Detection	See Table 1.
A1.8	Sensitivity	See Table 2.
A1.9	Bias	None known.
A1.10	Interferences	See Section A3.
A1.11	Time Required for Analysis	The total analytical time for a batch of 20 samples is approximately 4 hours of which the pretreatment stage occupies approximately 3 hours. The operator time is 1½ hours.

Table 1 Limits of Detection and Standard Deviations (Within-Batch) for Lithium in the Air-Acetylene Flame and Nitrous Oxide Acetylene Flames

			Standard deviations (μg/l) for a lithium concentration of:						
Instrument		Degrees of freedom	Limit of detection	0 (e)	100 (e)	1000 (e)	2000 (e)	(f)	(g)
IL 257	(a)	9	3.1		0.4	1.6	–	0.4	6.4
			(6.1)		(1.2)	(7.9)	(20.9)	(1.3)	(13.1)
IL 351	(b)	9	13.8		2.0	8.8	36	1.0	6.8
Varian 175	(c)	9	7.7	1.5	2.2	8.0	8.5	3.1	2.8
			(30)	(5.8)	(9.6)	(29.6)	(43.6)	(8.1)	(34.0)
Varian 275	(d)	9	21.7		4.3	15.4	28.9	1.9	17.9
			(65)		(12.9)	(59.6)	(113)	(5.5)	(30.8)

Notes for Tables 1–3
(Figures in brackets refer to nitrous oxide acetylene flame.)
Non-bracketed figures refer to air-acetylene flame.
(a) Determined by Yorkshire Water Authority
(b) Determined by Thames Water Authority
(c) Determined by South West Water Authority
(d) Determined by British Drug Houses Ltd
(e) Distilled or deionized water spiked with the stated concentration of lithium
(f) Tap water
(g) Tap water spiked with 1000 μg/litre lithium

Table 2 Sensitivity (1% Absorption) Figures

		Sensitivity (μg/l)	
Instrument		Air-Acetylene	Nitrous Oxide-Acetylene
IL 257	(a)	16	12
IL 351	(b)	15	–
Varian 175	(c)	13	13
Varian 275	(d)	65	150
Perkin Elmer 460	(h)	27	19
	(i)	15	–

Notes a–d as Table 1
(h) WRC Stevenage – flow spoiler
(i) WRC Stevenage – impact bead

A2 Principle

The sample is acidified and spiked with 1,000 mg/litre potassium to minimize ionization of lithium in the flame. It is then allowed to stand for 2 hours to ensure solubilization of all lithium. It is then filtered and the lithium determined in the filtrate by atomic absorption spectrophotometry.

A3 Interferences

(See also Table 3)

Although most standard atomic absorption texts state that lithium is not prone to chemical interference effects in the air-acetylene flame, the collaborative results obtained in the preparation of this method clearly demonstrated that chemical interference effects could be significant. The use of the hotter nitrous oxide-acetylene flame appears to minimize these effects but results in a decrease in precision. However, one laboratory observed significant interference effects in this flame. The effects appear to be instrument and burner dependent. Such effects have also been found for some other elements such as iron, chromium and manganese. It is recommended that each laboratory using this method assesses the typical interferences on their own instrument(s) and selects the most appropriate flame.

Table 3 Effect of Other Sustances on the Determination of Lithium

Other Substance	Concentration of other substance (mg/l)	Other substance added as	Effect in μg/l of other substances at a lithium concentraton of (μg/l) for both flames			
			Air– C_2H_2		N_2O– C_2H_2	
			0	1000	0	1000
Calcium (as Ca^{2+})	300	Chloride	3	−113	+3	−5(a)
			−2	−13	–	−(b)
Magnesium (as Mg^{2+})	100	Chloride	0	−89	+21	2(c)
			1	−57	−3	−1(d)
Calcium (as Ca^{2+})	300	Chloride	3	−74	−3	+1(a)
			−5	−5	–	−(b)
Sulphate (as SO_4^{2-})	300	Acid	0	−45	0	2(c)
			0	−37	−4	−33(d)
Silicon (as Si)	10	Ammonium Silicofluoride	3	−11	−3	−9(a)
			−5	+4	–	−(b)
			0	−45	0	10(c)
			−2	−11	−6	−47(d)
Iron (III)	50	Chloride	3	−20	+3	−11(a)
			−1	−39	–	−(b)
			0	−32	0	−2(c)
			−2	−15	−2	−27(d)
Aluminium (as Al^{3+})	20	Chloride	3	0	+3	−2(a)
Copper (as Cu^{2+})	20	Chloride	−1	−24	–	−(b)
Zinc (as Ca^{2+})	20	Chloride	0	−49	0	−11(c)
			−1	−13	−9	−34(d)
Phosphate (as P)	50	Acid	3	−72	+3	−2(a)
Calcium (as Ca^{2+})	300	Chloride	−5	+6	–	−(b)
			0	−62	+14	17(c)
			1	−48	−7	−23(d)
Potassium	1000	Chloride	–	–	+3	−1(a)
			−1	−50	–	−(b)
			0	−89	+21	−3(c)
			0	−53	−4	−26(d)

If other substances did not interfere the effect would be expected (95% confidence limits) to lie between:

	Air	– C_2H_2	N_2O	– C_2H_2	
Lithium Cone (mg/l)	0	1000	0	1000	
Expected Range	0 ± 2.9	1000 ± 7.0	0 ± 4.5	1000 ± 12.1	(a)
	0 ± 2.4	1000 ± 11.5	0 ± 3.8	1000 ± 18.7	(c) (d)

The range for (b) is similar.

Notes (a)–(d) are as Table 1.

A4 Hazards

The exhaust fumes from the atomic absorption spectrophotometer are toxic and must be ducted away. Normal laboratory safety precautions should be observed at all times. If a nitrous oxide–acetylene flame is used observe manufacturers instructions, ensure that ignition procedures, operating parameters and extinguishing procedures are strictly observed, and maintain equipment properly during use.

A5 Reagents

All reagents and standard solutions may be kept in glass or polyethylene bottles. 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 a lithium content that is negligible compared with the smallest concentrations to be determined in the samples. Deionized or distilled water is suitable.

A5.1.1 Evaluation of Blank and Reagent Water Quality

Take a sufficient sample from the batch of water to be used and, using a stainless steel beaker evaporate to one-tenth the initial volume. Carry out the analytical procedure (Section A9).

A5.2 Nitric acid (d_{20} 1.42)

A5.2.1 1% v/v nitric acid (see section A10.1)

Dilute 10 ml of nitric acid A5.2 to 1 litre in a measuring cylinder. Mix well, store in a prerinsed glass bottle with glass stopper.

A5.3 Potassium 100 g/l (as chloride)

Dissolve 191 ± 1 g of potassium chloride (dried for one hour at 105°C) in approximately 800 ml water and quantitatively transfer to a one litre calibrated flask and dilute to the mark. This solution is stable indefinitely.

A5.4 Standard Lithium Solutions

A5.4.1 Solution A 1 ml contains 1 mg Li

Dissolve 6.110 ± 0.005 g of anhydrous lithium chloride, dried for 4 hours at 105°C in approximately 400 ml of water, quantitatively transfer to a one litre calibrated flask and dilute to the mark. This solution is stable for at least several months.

A5.4.2 Solution B 1 ml contains 20 μg Li

Dilute 20 ml of solution A with water to one litre in a calibrated flask and mix well. This solution is stable for at least 2 weeks.

A5.4.3 Solution C, D, E and F. Equivalent to samples containing 0.5, 1.0, 1.5 and 2.0 mg/litre lithium.

Pipette 5, 10, 15 and 20 ml of solution B into four 200 ml calibrated flasks* and dilute to the mark with water. *After* dilution to the mark, add 2 ± 0.05 ml 10% m/V potassium solution followed by 2 ± 0.05 ml nitric acid (d_{20} 1.42). Mix the flask contents thoroughly. This over-dilution of the standards allows direct analysis of the samples with no final calculation being required. These solutions are stable for at least 2 weeks.

A6 Apparatus

A6.1 An atomic absorption spectrophotometer equipped for an air/acetylene or in some instances a nitrous oxide/acetylene flame (see Section A9.9 note b) is required. A lithium hollow-cathode lamp is required. Background correction is not required and should not be used.

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* Select 200 ml calibrated flasks with the calibration mark well down the neck of the flask so that an additional 4 ml of liquid can be added.

A6.2 Cleanliness

Cleanliness is essential for this determination, thorough rinsing of all glassware and plastic ware with hot tap water and then rinsing with distilled water has been found to be adequate.

A7 Sample Collection and Preservation

A sample should be collected in a clean glass or polyethylene bottle. No sample preservation is required.

A8 Sample Pretreatment

A8.1 Raw and Potable Water Samples

The method described specifies addition of nitric acid to the sample and allowing the acidified sample to stand for 2 hours. This procedure will ensure that any lithium present in suspended or collodial matter will be converted into a soluble form.

A8.2 Lithium Stock Dosing solution

The lithium stock solution dosed into the channel or pipe will typically have a lithium concentration between 30,000 and 50,000 mg/litre. This solution is often prepared on a gravimetric basis and consequently its concentration is accurately known. However in some instances only the approximate concentration is known and then a sample of this stock solution will require analysis. This involves a serial dilution to a concentration between one and 2 mg/litre lithium followed by analysis as described in Section A9. The dilution and analysis should be performed in duplicate to minimize the risk of dilution errors.

It is essential that the stock solution is kept separate from the samples during transport and handling. The stock sample container should be sealed in a polyethylene bag. The analyst should carefully wash his/her hands after handling the stock solution to prevent contamination of the samples. All glassware associated with the stock solution should be thoroughly rinsed with water and kept separate from that used for the samples.

A9 Analytical Procedure

READ SECTION A4 ON HAZARDS BEFORE STARTING THIS PROCEDURE.

Step	Procedure	Notes
	Analysis of Samples	
	Sample Preparation	
A9.1	Shake the sample thoroughly. Wash out a 100 ml stoppered measuring cylinder with the sample and fill the cylinder with 100 ± 1 ml of the shaken sample.	
A9.2	Add 1 ml of nitric acid (d_{20} 1.42).	
A9.3	Add 1 ml of 10% m/V potassium solution.	
A9.4	Stopper the cylinder and mix thoroughly. Allow to stand for 2 hours at room temperature.	

Step	Procedure	Notes
A9.5	Filter 10–15 ml of the sample through a suitable analytical quality fluted filter paper (medium flow rate) into a clean, dry 100 ml polyethylene bottle. Rinse out the bottle with this 10–15 ml of filtrate. Filter the remaining sample until 20–40 ml of filtrate are collected in the bottle and replace the bottle cap.	
	Blank determination	
A9.6	A blank must be run with each batch (eg up to 10 samples) of determinations using the same reagents as for the samples. Rinse a 100 ml stoppered measuring cylinder with water and fill the cylinder with 100 ± 1 ml of water.	
A9.7	Carry out steps A9.2–A9.5 inclusive.	
	Calibration standards.	
A9.8	It is recommended that the 4 calibration standards containing 0.5, 1.0, 1.5 and 2.0 mg/l of lithium are run with each batch of determinations (see Section A11.4). Standards preparation is described in Section A5.4.3. The instrument is adjusted so that direct concentration readout is obtained. Only one participating laboratory found a linear calibration graph up to 2 mg/litre lithium. The other laboratories found slight non-linearity above 1 mg/litre (see note a). If necessary prepare additional standards by the procedure given in Section A5.4.3.	
	Atomic Absorption Stage	
A9.9	Set up the instrument according to the manufacturer's instructions for the determination of lithium using an air-acetylene flame. (Notes a and b). Background correction is not necessary and should not be used. The wavelength required is 670.7 nm.	(a) The lithium hollow-cathode lamp should be run at a low current to minimize self-absorption and non-linearity of the calibration graph.
A9.10	Aspirate acidified wter (note c) until equilibrium conditions are established. Aspirate the 1 mg/litre calibration standard and adjust the instrument to give a suitable response.	(b) If chemical interference effects are suspected see Sections A3 and A12.3). Then a nitrous oxide-acetylene flame can be used. On certain instruments this may necessitate increasing the lithium hollow-cathode lamp current to the maximum value permitted in order to obtain a stable response.
A9.11	Aspirate acidified water and readjust the zero.	
A9.12	Aspirate the calibration standards with an aspiration of acidified water between each and obtain direct concentration readout (note d).	(c) To 200 ± 2 ml water add 2.00 ± 0.05 ml nitric acid d_{20} 1.42.
A9.13	Aspirate the blank followed by acidified water. Let the instrument response of the blank be B (note e).	(d) The instrument handbook will explain the procedure to be followed.

Step	Procedure	Notes
A9.14	Aspirate the samples with an aspiration of acidified water between each. Record the sample concentration S.	(e) The blank B should be negligible (0.01 mg/litre lithium). If it is greater than 0.02 mg/litre it suggests that significant contamination has occurred.
A9.15	Every 5 samples aspirate the 1 mg/litre lithium standard and re-calibrate the instrument (note d).	
	Calculation	
A9.16	Lithium concentration = S–B mg/litre.	

A10 Change of Concentration Range of the Method

For samples above 2 mg/l lithium.

If the lithium concentration of the sample is likely to exceed 2.0 mg/l an appropriate aliquot (V_1ml) of the sample must be taken for analysis, diluted with water to V_2ml and the procedure described in Section A9 carried out. The calculation of the result (Step A9.16) must then be multiplied by $\frac{V_2}{V_1}$.

If the calibration curve is linear beyond 2.0 mg/l for a particular spectrophotometer the range of the method may be extended up to the extent of the linearity of the calibration curve. Rotation of the burner can be used to extend the range of the method, but a new calibration is required.

A11 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 summarize the main source of error.

A11.1 Contamination

It is desirable to carry out the analysis in a laboratory in which no appreciable amounts of lithium or its compounds are handled. The technique and working conditions should be critically examined and any sources of contamination eliminated or minimized. In particular it is desirable to reserve the glass apparatus used for the lithium determinations solely for this purpose and to carry out a preliminary series of blank determinations to ensure low blank values before analysing any samples. Also the burner and the spray chamber of the atomic absorption spectrophotometer should be washed out before each set of determinations.

A11.2 Lithium content of the water used for preparing the blank

The lithium content of the water used should be negligible if prepared according to Section A5.1.1. If the blank levels are significant then fresh water, nitric acid and potassium chloride should be used.

A11.3 Interfering Substances

See Section A3 and Table 2. The effect of possible interfering substances may be determined by analysing water spiked with lithium and various concentrations of potential interfering substances. Reference 5 outlines some of the problems that may be encountered in this determination.

A11.4 Calibration Standards

The calibration curve for this method may be slightly non-linear above 1 mg/litre of lithium. All modern atomic absorption instruments have curve correction facilities that allow direct concentration readout. The user should refer to the instrument handbook and utilize the 4 calibration standards C, D, E and F (see Section A5.4.3) and the blank to achieve direct concentration readout. Re-calibration using the 1 mg/litre standard and the blank should be performed every 5 samples. All modern instruments have a facility for re-calibration using a single standard and a blank. If significant change in sensitivity is observed re-calibration using the 4 standards and the blank should be performed.

A12 Checking the Accuracy of 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 tests are possible (6) and they should be used as appropriate. As a minimum, however, it is suggested that a standard solution of lithium of suitable concentration be analysed at the same time and in exactly the same way as normal samples. The results obtained should then be plotted on a quality control chart, which will facilitate detection of inadequate accuracy and will also allow the standard deviation of routine analytical results to be estimated.

B Magnesium and Calcium in Waters and Sewage Effluents by Atomic Absorption Spectrophotometry 1977 (Combined Second Edition)

Note: Throughout this method magnesium and calcium are expressed as the elements (Mg and Ca).

B1 Performance Characteristics of the Methods

(For further information on the determination and definition of performance characteristics see another publication in this series(7).)

B1.1	Substance determined	All forms of magnesium and calcium (see Sections B2 and B8).
B1.2	Type of sample	Waters and sewage effluents.
B1.3	Basis of method	The acidified sample is treated with a lanthanum salt and aspirated into the flame of an atomic absorption spectrophotometer.
B1.4	Range of application (a)	
	Magnesium	Up to 5 mg/l (see Section B11).
	Calcium	Up to 40 mg/l (see Section B11).
B1.5	Calibration curve (a) (b)	
	Magnesium	Linear to 5 mg/l (see Section B10)
	Calcium	Linear to 40 mg/l (see Section B10).
B1.6	Standard deviation (a) (d) (within-batch)	

Magnesium

Magnesium concentration (mg/l)	Within-batch standard deviation (mg/l)
0.0	0.0158 (b)
0.0	0.0184 (c)
0.1	0.0215 (b)
5.0	0.0366 (b)

(Each estimate has 9 degrees of freedom.)

Calcium

Calcium concentration (mg/l)	Within-batch standard deviation (mg/l)
0.0	0.274 (b)
0.0	0.107 (c)
1.0	0.338 (b)
40.0	0.290 (b)

(Each estimate has 9 degrees of freedom.)

B1.7	Limit of detection (a) (d)	
	Magnesium	0.06 mg/l (with 9 degrees of freedom) (b) (c).
	Calcium	1.01 mg/l (9 degrees of freedom) (b). 0.38 mg/l (9 degrees of freedom) (c).
B1.8	Sensitivity (a) (c)	
	Magnesium	1.0 mg/1 gives an absorbance of approximately 0.067.
	Calcium	10.0 mg/l gives an absorbance of approximately 0.075.
B1.9	Bias	None known.
B1.10	Interferences	See Section B3.
B1.11	Time required for analysis (b) (c)	

The total analytical and operator times are the same. Typical times for one and 10 samples are 30 and 45 minutes respectively excluding any pretreatment time. Typical total analytical time for 10 samples including pretreatment time is 160 minutes.

(a) These performance characteristics are based on taking the equivalent of a 5 ml sample.

(b) These data were obtained at the Water Research Centre (Medmenham Laboratory)(8) using a single-beam atomic absorption spectrophotometer.

(c) These data were obtained at the Water Research Centre (Stevenage Laboratory)(9) using a double-beam atomic absorption spectrophotometer.

(d) These data were obtained using distilled water spiked with the stated concentration of magnesium or calcium. Pretreatment was not carried out.

B2 Principle

B2.1 The method is based on experimental work carried out at the Water Research Centre (Medmenham(8) and Stevenage(9) Laboratories). The amount of magnesium or calcium in the treated sample is measured by atomic absorption spectrophotometry by aspirating directly into the flame. Lanthanum(10, 11) is present in the solution which is aspirated, in order to release magnesium and calcium from refractory compounds.

B2.2 Normally, collection of the sample into acid or acidification of the sample on receipt in the laboratory is sufficient to ensure that all forms of magnesium and calcium are dissolved. However, for certain types of sample, pretreatment with nitric acid may be necessary (see Section B8).

B3 Interferences

B3.1 The atomic absorption procedure given is specific for magnesium and calcium. Interferences(12, 13 and 14) caused by substances which produce refractory magnesium and calcium compounds such as aluminium compounds, phosphates, sulphates and silicates, can be minimized by the addition of a lanthanum salt.

B3.2 The acid concentration and acid used can affect the results, hence care is necessary to ensure that standards and samples have similar hydrochloric acid concentrations. The interference effects differ if nitric acid is used instead of hydrochloric acid.

B4 Hazards

The exhaust fumes from the atomic absorption spectrophotometer are toxic and must be ducted away.

B5 Reagents

All reagents and standard solutions should be kept in polyethylene bottles unless otherwise stated (see Section B6.2). Analytical reagent grade chemicals are suitable unless otherwise specified. Unless specifically stated all solutions in this section should be stable for at least a month if properly stored.

B5.1 Water

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

B5.2 5M Hydrochloric acid (approximately)

Dilute 445 ± 5 ml of hydrochloric acid (d_{20} 1.18) with water to one litre in a measuring cylinder.

B5.3 1% m/V Lanthanum/5M hydrochloric acid solution

Dissolve 11.70 ± 0.05 g of oven dried (120 ± 10°C) lanthanum oxide in one litre of 5M hydrochloric acid.

B5.4 Standard solutions

General

As both the acid used and concentration can affect the results. if commercial standards are used, only use standards made up in hydrochloric acid. Care is needed when diluting standards, to keep the acidity constant. Standards should be brought to approximately the same pH as samples before the final volume adjustment.

Magnesium

B5.4.1 Solution A 100 mg/l magnesium

Dissolve 0.166 ± 0.001 g of oven dried (120 ± 10°C) magnesium oxide in approximately 20 ml of 5M hydrochloric acid in a one litre calibrated flask and dilute with water to the mark.

Calcium

B5.4.2 Soltuion A 1 g/l calcium

Dissolve 2.50 ± 0.01 g of oven dried (120 ± 10°C) calcium carbonate in approximately 20 ml of 5M hydrochloric acid in a one litre calibrated flask and dilute with water to the mark.

B5.5 Nitric acid (d_{20} 1.42)

B5.5.1 10% V/V Nitric acid

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

B6 Apparatus

B6.1 An atomic absorption spectrophotometer equipped for an air/acetylene flame and with a magnesium and or calcium hollow cathode lamp.

B6.2 Cleanliness of glass and polyethylene ware

Clean all new glass and polyethylene ware by filling with or soaking in 10% V/V nitric acid for 2 days. Rinse thoroughly with water. Thereafter a rinse with 10% V/V nitric acid followed by thorough rinsing with water prior to analysis should be sufficient.

B7 Sample Collection and Preservation

Clean a polyethylene bottle by the procedure described in Section B6.2, add 2.0 ± 0.1 ml of 5M hydrochloric acid per litre of sample to be collected and then collect the sample. This acidification, which is preferable but not essential, is to prevent precipitation of calcium salts and to assist in the dissolution of collodial and particulate forms of magnesium and calcium.

B8 Sample Pretreatment

Potable waters should not require pretreatment as the collection of the samples into acid or the subsequent acidification on receipt in the laboratory should be sufficient to dissolve any suspended calcium or magnesium. Highly turbid samples (eg some raw waters and sewage effluents) may require pretreatment to solubilize all forms of calcium and magnesium. Experience will indicate to analysts whether pretreatment is necessary for their particular type of samples. It is recommended that this should be checked by analysts for their particular water samples by comparing the results obtained by carrying out the procedure including step B9.1 with those obtained from the procedure omitting this step.

B9 Analytical Procedure

READ SECTION 4 ON HAZARDS BEFORE STARTING THIS PROCEDURE

Step	Procedure	Notes
	If pretreatment necessary (note a)	(a) If pretreatment is not required start at step B9.2
	Samples	
B9.1	Add 50.00 ± 0.05 ml of well mixed sample (note b) to a 100 beaker. Add 5 ±1 ml nitric acid (d_{20} 1.42). Cover the beaker with a watch-glass and evaporate carefully to dryness on a regulated hot plate. Remove from the source of heat, cool and add 2.0 ± 0.1 ml of 5M hydrochloric acid. Replace the beaker on the hot plate and heat gently. Add approximately 5 ml of water and heat almost to boiling. Cool and transfer the contents quantitatively to a 50 ml calibrated flask. Dilute with water to the mark and mix. Allow any precipitate to settle before taking an aliquot from the supernatant liquid for step B9.2.	(b) If the sample was not collected into acid then 2.0 ± 0.1 ml of 5M hydrochloric per litre of sample must be added on receipt in the laboratory.
B9.2	Add 5.00 ± 0.02 ml of the well mixed sample (note b) or pretreated sample from step B9.1 to a 50 ml calibrated flask. Add 5.0 ± 0.1 ml of the 1% m/V lanthanum/5M hydrochloric acid solution. Dilute with water to the mark (note c) and proceed to step B9.7.	(c) All samples, blanks and standards must be processed to this stage before proceeding to the atomic absorption stage.

Step	Procedure	Notes
	Blank determination	
B9.3	A blank must be run with each batch of determinations of up to 10 samples using the same batch of reagents as for samples. Carry out the procedure commencing at either step B9.1 or step B9.2 using water instead of the sample, dependent on whether pretreatment is required or not. Blanks must be treated in the same way as samples.	
	Calibration standards	
B9.4	Duplicate calibration standards B9.5 or B9.6 must be run with each batch of determinations of up to 10 samples using the same batch of reagents as for samples, and following the identical procedure starting at step B9.1 or B9.2 as required.	
B9.5	***For Magnesium (5 mg/1)*** Dilute 2.50 ± 0.02 ml of standard magnesium solution A with water to 50 ml. (Notes d and e).	(d) Only 5 ml portions are needed if the pretreatment steps is omitted.
B9.6	***For Calcium (40 mg/l)*** Dilute 2.00 ± 0.02 ml of standard calcium solution A with water to 50 ml. (Notes d and e).	(e) Combined magnesium – calcium solutions may be prepared in the same 50 ml volume.
	Atomic absorption stage	
	All samples, blanks and standards (note f).	(f) See Section B12 for changing the concentration range of the method.
9.7	Set up an air/acetylene flame instrument according to the manufacturer's instructions.	
	For Magnesium Use the magnesium hollow cathode lamp. Set the spectrometer at 285.2 nm.	
	For Calcium Use the calcium hollow cathode lamp. Set the spectrometer at 422.7 nm.	
B9.8	Aspirate water until equilibrium conditions are established and adjust the zero. Aspirate one of the calibration standards and adjust the instrument to give a suitable response (eg approximately 80% of full scale deflection).	
B9.9	Aspirate water and re-adjust the zero. Aspirate both calibration standards with an aspiration of water after each and measure the maximum instrument responses C_1 and C_2 (eg peak height).	
B9.10	Aspirate the blank, followed by an aspiration of water. Measure the maximum instrument response B_1.	
B9.11	Aspirate the samples with an aspiration of water after each. Measure the maximum instrument response for the sample, S.	

Step	Procedure	Notes
B9.12	After each batch (eg 10 samples) re-aspirate the blank and the calibration standards with an aspiration of water between each. Measure the maximum instrument responses B_2, C_3 and C_4 respectively. If B_1 and B_2, and C_1, C_2, C_3 and C_4 are in satisfactory agreement calculate the means B and C respectively.	
	Calculation of results (see Section B11)	
B9.13	***For Magnesium*** Calculate the concentration, A, of magnesium in the sample from: $A = \frac{S - \bar{B}}{\bar{C} - \bar{B}} \times 5 \times 1.002$ mg/l Mg (note g) where $\bar{C} = \frac{C_1 \times C_2 \times C_3 \times C_4}{4}$ and $\bar{B} = \frac{B_1 + B_2}{2}$ ***For Calcium*** Calculate the concentration, A, of calcium in the sample from: $A = \frac{S - \bar{B}}{\bar{C} - \bar{B}} \times 40 \times 1.002$ mg/l Ca (note g) where $\bar{C} = \frac{C_1 \times C_2 \times C_3 \times C_4}{4}$ and $\bar{B} = \frac{B_1 + B_2}{2}$ These calculations assume a linear calibration curve. Linearity must be checked (see Section B10).	(g) The factor of 1.002 corrects for the dilution of the sample by the acid into which it was collected.

B10 Checking the Linearity of the Calibration Curve

The procedure given in this section must be carried out on at least 2 independent occasions before application of this method to any samples, and regularly thereafter as determined by control chart procedures (see Secton 14).

For Magnesium

To each of a series of six 500 ml calibrated flasks add 5.0 ± 0.1 ml of 1.0% m/V lanthanum/5M hydrochloric acid solution. Pipette into these flasks 0.0, 5.0, 10.0, 15.0, 20.0 and 25.0 ± 0.02 ml of standard magnesium solution A and dilute with water to the mark. Mix well. These flasks contain the equivalent of 0, 1, 2, 3, 4, 5 mg/l Mg respectively (based on a 5 ml effective sample). Carry out steps B9.7 on and plot the maximum instrument responses against mg/l Mg.

For Calcium

To each of a series of five 250 ml calibrated flasks add 5.0 ± 0.1 ml of 1.0% m/V lanthanum/5M hydrochloric acid solution. Pipette into these flasks 0.0, 2.5, 5.0, 7.5 and 10.0 ± 0.02 ml of standard calcium solution A and dilute with water to the mark. Mix well. These flasks contain the equivalent of 0, 10, 20, 30, and 40 mg/l Ca respectively (based on a 5 ml effective sample). Carry out step B9.7 on and plot the maximum instrument responses against mg/l Ca.

The calibration curves are normally linear to 5 mg/Mg and 40 mg/l Ca; but this will depend to some extent on the type of instrumentation used and therefore this must be checked. If the curve departs from linearity the calibration standards are not appropriate, nor is the range given in Section B1.4. In such a case the calibration standard chosen should be the highest concentration on the linear portion of the calibration curve and the concentration range of the method should be adjusted accordingly. (See also Section A11.4). Rotation of the burnerhead can also be used to extend the range of the method.

B11 Change of Concentration Range of the Method

For Magnesium

With appropriate instrumental settings the given procedure can be used to determine magnesium in the concentration range given in Section B1.4. When the magnesium concentration in the sample is likely to exceed 5.0 mg/l Mg, an appropriately smaller aliquot of the sample must be taken for analysis, eg an aliquot of 2.0 ml instead of 5.0 ml would increase the range to 12.5 mg/l Mg and the calculation (step B9.13) would be:

$$A = \frac{S - \bar{B}}{\bar{C} - \bar{B}} \times 12 \times 1.002 \text{ mg/l Mg}$$

and for samples in the range 0 to 0.5 mg/l Mg an aliquot of 40 ml should be taken and the calculation would be:

$$A = \frac{S - \bar{B}}{\bar{C} - \bar{B}} \times 0.625 \times 1.002 \text{ mg/l Mg}$$

For Calcium

With appropriate instrumental settings the given procedure can be used to determine calcium in the concentration range given in Section B1.4. When the calcium concentration in the sample is likely to exceed 50 mg/l Ca, an appropriately smaller aliquot of the sample must be taken for analysis, eg an aliquot of 2.0 ml instead of 5.0 ml would increase the range to 100 mg/l Ca and the calculation (step B9.13) would be:

$$A = \frac{S - \bar{B}}{\bar{C} - \bar{B}} \times 100 \times 1.002 \text{ mg/l Ca}$$

and for samples in the range 0 to 4 mg/l Ca an aliquot of 40 ml should be taken and the calculation would be:

$$A = \frac{S - \bar{B}}{\bar{C} - \bar{B}} \times 5 \times 1.002 \text{ mg/l Ca}$$

For some instruments the linear range may be extended well beyond 40 mg/l and up to 80 mg/l may be possible. In such a case 4.0 ml of standard calcium solution A (step B9.3) or 20.0 ml of standard calcium solution B (step B9.5) would be required. The calculation would then become:

$$A = \frac{S - \bar{B}}{\bar{C} - \bar{B}} \times 80 \times 1.002 \text{ mg/l Ca}$$

The range of application is then 0 to 80 mg/l Ca instead of 0 to 40 mg/l Ca as stated in Section B1.4. However, the other performance characteristics in Section B1 would no longer apply.

Rotation of the burner head can be used to extend the range to higher concentrations, but a new calibration curve is required.

B12 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 summarize the main sources of error.

B12.1 Contamination

The technique and working conditions should be critically examined and any contamination eliminated or minimized.

B12.2 Interfering substances

See Section B3. If in doubt, apply procedures similar to C13.3, but using calcium or magnesium.

B12.3 Calibration standards

The calibration curve for this method has been found to be linear though its slope may vary from one set of determinations to another. Such variations are caused by changes in the sensitivity of the atomic absorption spectrophotometer. Therefore a calibration standard must be run for each batch of analyses and steps B9.3 and B9.5 give the necessary procedure. This procedure assumes a linear calibration curve and the linearity must be checked (see Section B11).

B13 Checking the Accuracy of Analytical Results

(For further information see another publication in this series (7).)

Once the methods have been put into normal routine operation many factors may subsequently adversely affect the accuracy of the analytical results. It is recommended that experimental tests of the accuracy should be made regularly. Many types of tests are possible and they should be used as appropriate. As a minimum, however, it is suggested that standard solutions of magnesium and calcium of suitable concentration be analysed at the same time and in exactly the same way as normal samples. The results obtained should then be plotted on a quality control chart which will facilitate detection of inadequate accuracy, and will also allow the standard deviation of routine analytical results to be estimated.

B14 Estimation of the Accuracy of Analytical Results using this Method

B14.1 Introduction

Quantitative investigation of the accuracy achievable when the calcium method is used appears to be limited to work at the Water Research Centre (Medmenham and Stevenage Laboratories). 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 Secretary of the DOE/Standing Committee of Analysts, (for address see the end of this booklet).

The precision achieved and the 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.

B14.2 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 calcium or magnesium 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 up to 10.

Solution No	Description for Magnesium	for Calcium
1	Blank	Blank
2	Another blank	Another blank
3	Standard Solution 0.5 mg/l Mg	Standard Solution 4.0 mg/l Ca
4	Standard Solution 5.0 mg/l Mg	Standard Solutiion 40.0 mg/l Ca
5	Typical Sample†	Typical Sample†
6	Same sample spiked with 5.0 mg/l Mg‡	Same sample spiked with 40.0 mg/l Ca‡

† Diluted with water, if necessary, so that the determinand concentration is within the range of the method.
‡‡ If these spiking levels take the determinand concentration beyond the linearity of the method, see Section B12 and use smaller sample aliquots.

It is essential that these solutions be treated exactly as if they were samples and the procedure specified in Secton B9 of the method be rigidly followed. These solutions should be analysed in random order in with 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. On any one day the same batch of water should be used to prepare these 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:

For Magnesium

Add with a pipette 4.0 ml of standard calcium solution A to 100 ml of solution 5.

For Calcium

Add with a pipette 4.0 ml of standard calcium solution A to 100 ml of solutions 5.

When analysing solution 6 it may be necessary to take into account Section B12 and to take an appropriately smaller aliquot. The total period of the tests may be any convenient time so long as the determinand 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 determinand from 100% may give an indication of the presence of interfering substances.

B14.3 Evaluation of Results

The raw experimental results may be sent direct to the Department of the Environment (at the address below) 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.

B14.3.1 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.

B14.3.2 Calculate the mean concentration of the n results for each solution.

B14.3.3 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

B14.3.4 Calculate the within-batch standard deviation, s_w, of the blank from:

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

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

B14.3.5 Calculate the mean percentage recovery, R, of the spiked magnesium or calcium in solution 6 from:

For Magnesium

$$R = \frac{(1.05\ \bar{x}_6 - \bar{x}_5)}{5} \times 100$$

For Calcium

$$R = \frac{(1.04\ \bar{x}_6 - \bar{x}_5)}{40} \times 100$$

where $\bar{x}_5$ = the mean value of the results for solution 5.
$\bar{x}_6$ = the mean value of the results for solution 6.

B15.3.6 Summarize the results as in the following tables:

For Magnesium

Solution	No of results n	Mean magnesium Concentration mg/l	Standard Deviation mg/1	Mean Recovery %
2 Blank				–
3 Standard, 0.5 mg/l Mg				–
4 Standard, 5.0 mg/l Mg				–
5 Sample				–
6 Solution 5 + 5.0 mg/l Mg				

For Calcium

Solution	No of results n	Mean calcium Concentration mg/l	Standard Deviation mg/l	Mean Recovery %
2 Blank				–
3 Standard, 4.0 mg/l Ca				–
4 Standard, 40.0 mg/l Ca				–
5 Sample				–
6 Solution 5 + 40.0 mg/l Ca				

The appropriate sample description should be entered in the space for solution 5. The standard deviation from step B14.3.4 is entered for the blank solution 2 and the standard deviations from step B14.3.3 are entered for solutions 3 to 6. If the pretreatment procedure (step B9.1) was carried out this should also be stated.

C Strontium and Barium in Potable Waters by Atomic Absorption Spectrophotometry (Tentative Method)

C1 Performance Characteristics of the Method

(For further information on the determination and definition of performance characteristics see General Principles of Sampling and accuracy of Results 1980,(7) also published in this series.)

C1.1	Substances determined	All forms of Strontium and Barium likely to occur in potable waters (see Sections C2 and C8).
C1.2	Type of sample	Potable water.
C1.3	Basis of the method	Direct aspiration of the acidified sample containing the lanthanum–potassium reagent into the nitrous oxide–acetylene flame of an atomic absorption spectrophotometer.
C1.4	Range of application	Up to 2.0 mg/l Strontium or 5.0 mg/l Barium for direct aspiration of samples.
C1.5	Calibration curve	Linear to 2.0 mg/l Strontium, or 5.0 mg/l Barium for direct aspiration of samples (see sections C10 and C11).

C1.6 Within-batch Standard Deviation (mg/l)

Strontium

	Standard Deviation (a)	(b)
Distilled Water	0.013	0.0012
Distilled Water + 0.1 mg/l Sr	0.0010	0.0012
Distilled Water + 1 mg/l Sr	0.0055	0.0018
Distilled Water + 2 mg/l Sr	0.0085	0.0041
Tap Water	0.0013	0.0017
Tap Water + 1 mg/l Sr	0.0041	0.0015

Barium

Barium concentration	Standard deviation (c) (mg/l)
distilled water	0.0083
+ 0.5 (mg/l)	0.0346
+ 1.0	0.0508
+ 2.0	0.0771
+ 3.0	0.1288
+ 4.0	0.1462
+ 5.0	0.1154
soft water	0.0534
soft water + 2.0	0.1082
hard water	0.0710
hard water + 2.0	0.0892

(each estimate has 10 degrees of freedom)

(a) Yorkshire WA (9 degrees of freedom), (b) Thames WA (9 degrees of freedom).
(c) Yorkshire WA (10 degrees of freedom).

C1.7	Limit of detection	0.0062–0.0067 mg/l Strontium. (9 degrees of freedom) 0.038–0.052 mg/l Barium. (10 degrees of freedom)
C1.8	Sensitivity	2 mg/l Strontium gives an absorbance of approximately 0.28 Absorbance Units. 5 mg/l Barium gives an absorbance of approximately 0.18 Absorbance units.
C1.9	Bias	None known for Strontium. Not thought to be significant for barium except for calcium concentrations above 100 mg/l. This can be instrument dependent(15).
C1.10	Interferences	Strontium is partially ionized and Barium is highly ionized in the nitrous oxide–acetylene flame. An ionization suppressant is added to overcome this. Lanthanum is added to minimize chemical interference effects (see Section C3 and Tables 4 and 5).
C1.11	Time required for analysis	For direct aspiration the total operator analytical time for 20 samples is approximately 30 minutes.

C2 Principle

Strontium and Barium in potable waters are determined by atomic absorption spectrophotometry by direct aspiration of the sample containing lanthanum–potassium reagent into the nitrous oxide–acetylene flame. If the air–acetylene flame is employed for strontium the sensitivity and precision are degraded and significant interference effects observed. The air–acetylene flame must not be used for barium determinations.

C3 Interferences

Strontium determination

In the nitrous oxide–acetylene flame no significant interference effects were observed (see Table 4). In the air–acetylene flame interference was observed from calcium, magnesium and sodium. Therefore, this flame cannot be recommended for this determination.

Barium determination

Substances usually present in potable waters at their normal concentrations do not cause interferences. Refer to Table 5 for details of interferants tested.

However, positive bias has been reported for barium when a high concentration of an easily ionized element (eg 1000 mg/l Na) is present. This interference is overcome by using a 3% m/V lanthanum — 12% m/V potassium reagent in place of the 3% m/V lanthanum — 6% m/V potassium reagent.

Table 4 Effect of Other Ions on the Determination of Strontium with a Nitrous Oxide-Acetylene Flame

Other Substance	Concentration added mg/l of element stated	Other Substance added as	Effect in mg/l Sr: Strontium Concentration 0 mg/l	1 mg/l	1 mg/l blank corrected*	
Calcium Magnesium	300 Ca 300 Mg	Chloride	0.073 0.555	0.065 0.553	−0.008 −0.002	(a) (b)
Calcium Phosphate	300 Ca 50 P	Chloride H_3PO_4	0.075 0.562	0.080 0.566	0.005 0.004	(a) (b)
Calcium Sulphate	300 Ca 300 SO_4	Chloride H_2SO_4	0.075 0.477	0.074 0.470	−0.001 −0.007	(a) (b)
Calcium	300 Ca	Chloride	0.073	0.069	−0.004	(a)
Magnesium	300 Mg	Chloride	0.005	0.001		(a)
Sodium	1000 Na	Chloride	0.005	−0.003		(a)
Silicon	10 Si	$(NH_4)_2$ Si F_6	0.007 0.013	−0.007 −0.007		(a) (b)
Aluminium Copper Zinc	20 Al 20 Cu 20 Zn	Nitrate	0.003 0.009	0.006 0.003		(a) (b)
Iron (III)	50 Fe	Nitrate	0.003 0.008	0.016 0.012		(a) (b)
Potassium	1000 K	Chloride	0.004 0.007	−0.006 −0.007		(a) (b)

If other substances did not interfere the effect without blank correction would be expected (95% confidence limits) to be between:

At mg/l Sr		
0	1	
± 0.002	± 0.012	(a)
± 0.004	± 0.004	(b)

* Calcium salts are known to be contaminated with strontium.

Note (a) and (b) as in Section C1.6.

C4 Hazards

The exhaust fumes from the atomic absorption spectrophotometer are toxic and must be ducted away.

C5 Reagents

All reagents and standard solutions may be kept in glass or polyethylene bottles (see Section C6.2). Analytical reagent grade chemicals are suitable unless otherwise stated.

C5.1 Water

The water used for blank determinations and for preparing reagent and standard solutions should have both strontium and barium contents that are negligible, compared with the smallest concentrations to be determined in the sample (see Section C13.2). Deionized water or water distilled from an all glass apparatus is suitable.

C5.2 Hydrochloric acid (d_{20} 1.18)

C5.2.1 50% V/V Hydrochloric aid

Dilute 500 ± 5 ml hydrochloric acid (d_{20} 1.18) with water to one litre in a stoppered measuring cylinder and mix well.

Table 5 Effect of Other Substances on the Determination of Barium

Other Substance	Concentration of other substance (mg/l)	Other Substance added as	Effect in mg/l Ba			
			Barium Concentration			
			0 mg/l	2 mg/l	2 mg/l blank corrected	
Calcium	300	Chloride	0.045	0.055	0.01	
Magnesium	100	Chloride				
Calcium	300	Chloride	0.109	0.035	W0.074	
Phosphate	50	H_3PO_4				
Calcium	300	Chloride	0.113	0.035	−0.078	
Sulphate	300	H_2SO_4				
Calcium	300	Chloride	0.055	−0.05	−0.105	
Magnesium	300	Chloride	−0.018	0.02	0.038	
Sodium	1000	Chloride	−0.015	0.21	0.225	
			0.045	0.07	0.025	(a)
Silicon	10	$(NH_4)_2SiF_6$	−0.014	−0.015	−0.001	
Aluminium	20	Nitrate	−0.015	0.07	0.085	
Copper	20	Nitrate				
Zinc	20	Nitrate				
Iron (III)	50	Nitrate	−0.003	0.07	0.073	
Potassium	1000	Chloride	0.000	0.055	0.055	

(a) Re-analysed with 3% m/V lanthanum – 12% m/V potassium reagent.

If other substances did not interfere the effect (95% confidence) would be expected to be within the range:

0.0 ± 0.169 at 2.0 mg/l Ba
0.0 ± 0.235 at 0.0 mg/l Ba

C5.2.2 1% V/V Hydrochloric acid

Dilute 20 ± 0.2 ml of 50% V/V hydrochloric acid with water to one litre in a calibrated flask and mix.

C5.3 Standard solutions

Standard Strontium Solutions

C5.3.1 Solution A 1 ml contains 1 mg Sr

Dissolve 2.415 ± 0.001 g of anhydrous strontium nitrate in 20 ± 0.2 ml of 1:1 nitric acid, dilute quantitatively with water to a volume of one litre in a calibrated flask and mix well. (If not available cover 1.685 ± 0.001 g of dry strontium carbonate with a little water, add dropwise 30.0 ± 0.2 ml of 50% V/V hydrochloric acid until dissolved, then more rapidly, and dilute quantitatively with water to a volume of one litre in a calibrated flask and mix well.) This solution is stable for several months. Alternatively a commercial 1000 mg/litre strontium standard can be used.

C5.3.2 Solution B 1 ml contains 10 μg strontium

Dilute 10 ml of solution A with 1% V/V hydrochloric acid to one litre in a calibrated flask and mix well. This solution is stable for at least one month.

Standard Barium Solutions

C5.3.3 Solution C 1 ml is equivalent to 1 mg Ba

Dissolve 1.903 ± 0.001 g anhydrous barium nitrate in 20 ± 0.2 ml of 50% V/V hydrochloric acid and dilute quantitatively with water to a volume of one litre in a calibrated flask and mix well. Store in a polyethylene bottle. This solution is stable for several months. Alternatively, a commercial 1000 mg/1 barium standard can be used.

C5.3.4 Solution D 1 ml is equivalent to 100 μg Ba.

Dilute 10 ± 0.05 ml of solution C with water to 100 ml in a calibrated flask. This solution is stable for several months.

C5.4 10% m/V Lanthanum solution (as chloride)

Dissolve 117.4 ± 0.1 gms of lanthanum oxide (analytical reagent grade) in 500 ± 10 ml of hydrochloric acid (d_{20} 1.18) cautiously and with stirring. Dilute with water to one litre in a measuring cylinder. This solution is commercially available.

C5.4.1 3% m/V Lanthanum — 6% m/V Potassium Reagent

Dissolve 60.0 ± 0.1 g of potassium chloride in 300 ± 3 ml of water. Add 300 ± 3 ml 10% m/V Lanthanum Solution and dilute with water to one litre in a measuring cylinder.

C5.4.2 3% m/V Lanthanum — 12% m/V Potassium Reagent

If the sodium concentration is over 1000 mg/1, increase the potassium chloride for solution C5.4.1 to 120.0 ± 0.1 g.

C6 Apparatus

C6.1 An atomic absorption spectrophotometer equipped for nitrous oxide/acetylene flame and fitted with a strontium or barium hollow cathode lamp as appropriate. ***For barium determinations***, it is essential that a spectral bandpass of not more than 0.2 nm is used (see Section C10.2).

C6.2 Cleanliness

Cleanliness is essential for these determinations. If possible apparatus should be reserved solely for strontium or barium determinations and all residual strontium or barium from previous determinations must be removed. Clean all new glass and polyethylene by filling with, or soaking in 50% V/V hydrochloric acid for several hours. Rinse thoroughly with water. Thereafter a thorough rinse with 50% V/V hydrochloric acid followed by a thorough rinse with water after each determination should suffice.

C7 Sample Collection and Preservation

Clean a polyethylene bottle by the procedure described in Section C6.2 add 20.0 ± 0.2 ml of 50% V/V hydrochloric acid per litre of sample to be collected and then collect the sample. This acidification minimizes the adsorption of strontium or barium onto the walls of the bottle.

C8 Sample Pretreatment

Collect the sample into a bottle containing suficient 50% V/V hydrochloric acid to make the sample 1% V/V in hydrochloric acid (20 ml/litre). The acidified sample should be allowed to stand for at least 24 hours to ensure that any strontium or barium in suspended or colloidal forms are converted to soluble forms.

C9 Analytical Procedure

READ SECTION C4 ON HAZARDS BEFORE STARTING THIS PROCEDURE.

Step	Procedure	Notes
	Pretreatment Stage	
C9.1	Allow the acidified sample (1% V/V in hydrochloric acid) to stand for at least 24 hours. To 100 ± 1 ml of sample add 3.0 ± 0.1 ml of the lanthanum/potassium chloride solution C5.4.1 (note a).	(a) If barium is to be determined, and the sodium content exceeds 1.0 g/l use solution C5.4.2 instead of C5.4.1. The blank and standard solutions must be prepared similarly to the samples. Strontium can also be determined using this modification.
	Blank Determination	
C9.2	A blank must be run with each batch (eg up to 10 samples) of determinations. Add 3.0 ± 0.3 ml of the lanthanum/potassium chloride solution to 100 ml of 1% V/V hydrochloric acid. (note a).	
	Calibration Standards	
C9.3	Duplicate calibration standards must be run with each batch (eg up to 10 samples) of determinations. Pipette 20.0 ml of Strontium solution B and or 5.0 ml of barium solution D into a 100 ml calibrated flask and dilute with 1% V/V hydrochloric acid to the mark. Add 3.0 ± 0.3 ml lanthanum–potassium chloride solution (note a).	(b) Volumetric flasks with a volume of at least 5 ml above the calibration mark should be used.
	Atomic Absorption Stage	
C9.4	Set up the instrument according to the manufacturers instructions for determining strontium in a nitrous oxide-acetylene flame. The wavelength required for strontium is 460.7 nm (note c) and 553.5 nm for barium (notes d, e and f).	(c) A red feather height of 5 mm is recommended. Background correction should *not* be used.
C9.5	Aspirate acidified water (1% V/V hydrochloric acid) until equilibrium conditions are established. Aspirate one of the calibration standards and adjust the instrument to give a suitable response. Aspirate acidified water and readjust the zero.	(d) A red feather height of 15 mm is recommended. (e) A spectral bandpass of 0.2 nm or less should be used.
C9.6	Aspirate the calibration standards with an aspiration of acidified water between each. Let the responses be C_1 and C_2. Aspirate the blank followed by acidified water. Let the instrument response of the blank be B_1.	(f) The hollow cathode lamp should be run at the maximum specified current. Background correction should not be used.
C9.7	Aspirate the samples with an aspiration of acidified water between each. Record the instrument response of the sample. Let the response be S.	
C9.8	After each batch of 10 samples re-aspirate the blank and both calibration standards with an aspiration of acidified water between each. Note the instrument response of the blank (B_2 and the calibration standards C_3 and C_4).	

Step	Procedure	Notes

C9.9 **Calculation of Result**

Strontium Concentration

$$= 1.02 \times \frac{S - \bar{B}}{\bar{C} - \bar{B}} \times 2 \text{ mg/l (note g)}$$

(g) The factor 1.02 allows for the dilution of the sample by the acid in which it was collected.

Barium Concentration

$$= 1.02 \times \frac{S - \bar{B}}{\bar{C} - \bar{B}} \times 5 \text{ mg/l (note g)}$$

where for either analysis $\bar{B} = \frac{B_1 + B_2}{2}$

and $\bar{C} = \frac{C_1 + C_2 + C_3 + C_4}{4}$

for the appropriate metal.

Those calculations assume a linear calibration curve. This must be checked (see Section C11).

C10 Problems Due to Emission

C10.1 Barium calibration curve is normally linear to 10 mg/l for direct aspiration of samples. Some instruments, however, may suffer from breakthrough due to barium emission. This is due to the inability of the measuring system to differentiate between the barium emission and absorption signals. Although this can be partially overcome by using the hollow cathode lamp at maximum current, with some instruments, the maximum barium concentration for linearity may be limited to 5 mg/l. The user should carry out tests to determine whether emission breakthrough is significant by analysing a series of standards of progressively increasing barium content until calibration is definitely non linear or the precision becomes unacceptable.

C10.2 The presence of large amounts of calcium can degrade the detection limit on some instruments. This is due to the inability of the measuring system to differentiate between the intense Ca OH band emission and the barium absorption signals(15). The effect is minimized by running the hollow-cathode lamp at maximum current and using a spectral bandpass of not more than 0.2 nm. In extreme cases a very significant bias can be observed with high calcium levels(15). Users should determine the maximum tolerable calcium concentration for their instrument. A calcium solution prepared from spectrographic grade calcium carbonate should be used for this test (see also Section C3).

eg IL 357 instrument	**Solution**	**Limit of detection (mg/1)**
	water	0.052
	water + 100 mg/1 Ca	0.252
	water + 200 mg/1 Ca	0.449
	water + 300 mg/1 Ca	0.769

C11 Checking the linearity of the Calibration Curve

This procedure must be carried out on at least 2 independent occasions before application of this method and regularly thereafter.

C11.1 ***Strontium determination***

Pipette respectively into a series of 100 ml calibrated flasks 0.0, 4.0, 8.0, 12.0, 16.0 and 20.0 ml of standard strontium solution B, dilute with 1% V/V hydrochloric acid to the mark and mix thoroughly. These flasks contain respectively 0, 0.4, 0.8, 1.2, 1.6 and 2.0 mg/1 Strontium.

C11.2 ***Barium determination***

Pipette respectively into a series of 200 ml calibrated flasks 0.0, 2.0, 4.0, 6.0, 8.0 and 10.0 ml of standard barium solution B, dilute with 1% V/V hydrochloric acid to the mark and mix thoroughly. These flasks contain respectively 0, 1, 2, 3, 4 and 5 mg/l barium.

Carry out the procedure given in Section C9 treating these solutions as if they were samples. Plot the instrument response of each solution against mg/l of strontium or barium. The calibration curve is normally linear; however, the linearity should be checked. If the calibration curve departs from linearity, the calibration standard in step C9.3 may not be appropriate, nor the range given in Section C1.4. In such a case, the calibration standard chosen for step C9.3 should be the highest concentration on the linear portion of the calibration curve, and the concentration range of the method and the calculation (C9.9) should be amended accordingly.

C12 Change of Concentration Range of the Method

If the strontium concentration of the sample is likely to exceed 2.0 mg/l or the barium concentration is likely to exceed 5.0 mg/l an appropriate aliquot (V_1 ml) of the sample must be taken for analysis, diluted with 1% V/V hydrochloric acid to V_2 ml and the procedure described in Section C9.1 carried out. The calculation of the result (Step C9.9) must then be multiplied by $\frac{V_2}{V_1}$.

It will be necessary to analyse separately for each metal.

C12.2 If the calibration curve is linear beyond 2.0 mg/l Sr or 5 mg/l Ba for a particular spectrophotometer, the range of the method may be extended up to the extent of the linearity of the calibration curve (see Section C10.1 and A11.4). Rotation of the burner can be used to extend the range of the method but new calibration curves are required.

C13 Sources of Error

The attention which it is necessary to pay sources of error depends on the accuracy required of the analytical results. The following subsections summarize the main sources of error.

C13.1 Contamination

It is desirable to carry out the analysis in a laboratory in which no appreciable amounts of strontium or barium and their compounds are handled. The technique and working conditions should be critically examined and any sources of contamination eliminated or minimized. In particular it is desirable to reserve the glass apparatus used for the strontium and barium determinations solely for this purpose and to carry out a preliminary series of blank determinations to ensure low blank values before analysing any samples. Also the burner and the spray chamber of the atomic absorption spectrophotometer should be washed out before each set of determinations.

C13.2 Strontium and Barium content of the water used for preparing the blank

The strontium and barium content of the water used should be negligible if prepared according to Section C5.1. If the blank levels are significant then freshly prepared by prepared water and hydrochloric acid should be used.

C13.3 Interfering Substances

See Section C3. The effect of possible interfering substances may be determined by analysing water spiked with strontium and barium and various concentrations of the potential interfering substance. If sodium, calcium and/or magnesium are high see Section C3.

C13.4 Calibration Standards

The calibration curve for this method has been found to be linear, though its slope may vary from one set of analyses to another. Therefore, a calibration standard must be run for each batch of analyses and steps C9.3 onwards give the necessary procedure. This procedure assumes a linear calibration curve and linearity must be checked (see Seciton C11).

C14 Checking the Accuracy of 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 tests are possible (6 and 7) and they should be used as appropriate. As a minimum, it is suggested that a standard solution of strontium and barium of suitable concentration be analysed at the same time and in exactly the same way as normal samples (see Step C9.3). 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.

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Address for Correspondence

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