The determination of Antimony, Beryllium, Chromium, Cobalt, Copper, Gallium, Germanium, Indium, Nickel, Silver, Thallium, and Vanadium, in Raw and Potable Waters by Electrothermal Atomization Atomic Absorption Spectrophotometry with Notes on the Determination of Arsenic, Selenium and Zinc by this method. 1988

Methods for the Examination of Waters and Associated Material

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CONTENTS

Other Related Methods

The methods for the determination of Lead and Cadmium by this technique are contained in Ref 1.

Methods for determining Cadmium, Chromium, Cobalt, Copper, Iron, Lead, Manganese, Nickel and Zinc by this technique after solvent extraction or carrier precipitation concentration steps are contained in Ref 3.

Methods for determining Organic and Inorganic Tin are given in Ref 12.

Antimony, Cadmium, Copper, Lead, Manganese and Thallium can also be determined as in Method N using the appropriate wavelengths given respectively in Method A, Ref 1, Method E, Ref 1, Ref 3 and Method K.

If the sample contains an appreciable amount of suspended solids, these should be filtered off after first determining that the filter material does not absorb the determinand. The solid may then be analysed by other methods such as Ref 13 or 16. After bringing into solution, quantification can also be by the methods herein.

About this Series

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

In the past, the Department of the Environment and its predecessors, in collaboration with various learned societies, have issued volumes of methods for the analysis of water and sewage culminating in 'Analysis of Raw, Potable and Waste Waters'. These volumes inevitably took some years to prepare, so that they were often partially out of date before they appeared in print. The present series will be published as series of booklets on single or related topics; thus allowing for the replacement or addition of methods as quickly as possible without need of waiting for the next edition. The rate of publication will also be related to the urgency of requirement for that particular method, tentative methods and notes being issued when necessary.

The aim is to provide as complete and up to date a collection of methods and reviews as is practicable, which will, as far as possible, take into account the analytical facilities available in different parts of the Kingdom, and the quality criteria of interest to those responsible for the various aspects of the water cycle. Because both needs and equipment vary widely, where necessary, a selection of methods may be recommended for a single determinand. It will be the responsibility of the users—the senior technical staff to decide which of these methods to use for the determination in hand. Whilst the attention of the users is drawn to any special known hazards which may occur with the use of any particular method, responsibility for proper supervision and the provision of safe working conditions must remain with the user.

The preparation of this series and its continuous revision is the responsibility of the Standing Committee of Analysts (to review Standard Methods for Quality Control of the Water Cycle). The Standing Committee of Analysts is a committee of the Department of the Environment set up in 1972. Currently it has nine Working Groups, each responsible for one section or aspect of water cycle quality analysis. They are as follows:

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

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

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

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

L R PITTWELL
Secretary

1 July 1987

Warning to Users

The analytical procedures given in this booklet should only be carried out by competent trained persons, with adequate supervision when necessary.

Local Safety Regulations must be observed.

Laboratory procedures should be carried out only in properly equipped laboratories.

Field Operations should be conducted with due regard to possible local hazards, and portable safety equipment should be carried.

Care should be taken against creating hazards for one's self, one's colleagues, those outside the laboratory or work place, or subsequently for maintenance or waste disposal workers. Where the Committee have considered that a special unusual hazard exists, attention has been drawn to this in the text so that additional care might be taken beyond that which should be exercised at all times when carrying out analytical procedures. Reagents of adequate purity must be used, along with properly maintained apparatus and equipment of correct specifications. Specifications for reagents, apparatus and equipment are given in manufacturers' catalogues and various published standards. If contamination is suspected, reagent purity should be checked before use. Lone working, whether in the laboratory or field, should be discouraged.

The best safeguard is a thorough consideration of hazards and the consequent safety precautions and remedies well in advance. Without intending to give a complete checklist, points that experience has shown are often forgotten include: laboratory tidiness, stray radiation leaks (including ultra violet), use of correct protective clothing and goggles, removal of toxic fumes and 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. 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 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. 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 specialised hospital.

Introduction

The reader is specifically referred to the short essay review on the principles of electrothermal atomization given in the lead and cadmium method booklet in this series (1). This review gives a brief introduction to the technique and highlights many of the problems that can be encountered when using it.

When adapting one of the methods in this booklet to a particular instrumental system, the following points should be carefully considered. (See also Section A12.3.1).

1. **Type of Graphite Tube**

   There are three basic types of graphite tubes: uncoated tubes, pyrolytically coated graphite tubes and wholly pyrolytic graphite tubes. (See Ref 1, Section A.2.2). Performance characteristics including interelement effects can vary markedly depending upon which type of graphite tube is employed. It is good practice to follow the graphite furnace manufacturer's instructions when selecting the type of graphite tube for a particular determination.

2. **Use of L'Vov Type Platforms**

   These devices delay the volatilization and atomization of the analyte and ensure that the argon atmosphere above the platform is at a significantly higher temperature than it would be if the analyte solution were volatilized and atomized directly from the inside surface of the graphite tube. (See Ref 1, Section A.3.7.7). This can result in a significant reduction of interelement effects especially for the more volatile elements. Platforms cannot be used in some systems and the manufacturers of these systems claim that platforms are of limited benefit when used in their graphite tubes.

3. **Matrix Modification**

   There are a very wide range of matrix modifiers available (See Ref 1, Section A.3.7.5). These include $La(NO_3)_3$, $Mg(NO_3)_2$, $(NH_4)_2HPO_4$, H_3PO_4, $Ca(NO_3)_2$, $Ni(NO_3)_2$, H_2SO_4, HNO_3, $Pd(NO_3)_2$ etc. If the matrix modifier given in the method does not effectively eliminate interference effects then an alternative matrix modifier can be tried. Ref 2 is a useful guide to the selection of matrix modifiers. (See also Ref 1 Refs 13–18 therein).

4. **Peak Height or Peak Area Measurement**

   Wherever the L'vov platform is used, the measurement mode should be peak area. Generally, peak height measurement is used if atomization from the wall is utilized.

5. **Background Correction Systems**

   At wavelengths below about 320 nm it is essential to use automatic background correction to ensure accurate results. At wavelengths above 320 nm (eg copper at 324.7 nm and chromium at 357.9 nm), ideally automatic background correction should be used. However, on some older instruments the intensity of the deuterium lamp is not adequate for acceptable automatic background correction. In these cases the measurements should be made without automatic background correction and if necessary a separate background correction measurement made using a deuterium hollow cathode lamp. For most typical raw and potable water samples background correction signals at wavelengths above 320 nm are negligible, but this cannot be assumed. It is essential to carry out a check on this. There are three main methods of automatic background correction, these are conventional deuterium background correction, Zeeman correction and Smith Hieftje correction. (See Ref 1 Section A.3.6). For potable waters all of these systems are thought to be suitable. For saline waters either Zeeman or Smith Hieftje is preferred, although satisfactory results have been obtained with conventional systems.

General Comments on Instrument Performance

The methods in this booklet are by Electrothermal Atomization Atomic Absorption Spectrophotometry.

The performance characteristics given throughout this booklet are illustrative of the performance achieved with the particular instruments listed in the corresponding methods; different results may be obtained from the same make and/or model of instrument in different laboratories with different operators. Other makes and models may give quite different performance and in some instances require change of matrix modifier. The results are not a guide to model or make superiority. The operating conditions are intended only as a guide and are examples of conditions used. Operating conditions must be optimized by each laboratory to give the best performance for each particular instrument. Matrix modifiers may either be automatically pre- or coinjected with the sample, standard or blank, or if necessary the appropriate amount can be premixed with the sample, dependent on the sampler used.

A. Antimony in Raw and Potable Waters

A1 Performance Characteristics of the Method

(For further information on the determination and definition of performance characteristics see General Principle of Sampling and Accuracy of Results 1980, (4) also published in this series.)

A1.1	Substances determined	All forms of Antimony likely to occur dissolved in raw and potable waters.
A1.2	Type of sample	Raw and potable water.
A1.3	Basis of the method	Direct analysis by electrothermal atomization atomic absorption spectrophotometry of samples pre-treated with acid, calcium salt and a surfactant.
A1.4	Range of application	Up to at least 120 μgl^{-1}.
A1.5	Calibration curve	Typically Linear to 120 μgl^{-1}, but instrument dependent.
A1.6	Relative Standard Deviation	In the range 20–100 μgl^{-1} 3.3–4.3%. Note instrument type and model considerably affect these values.
A1.7	Limit of detection	0.5 μgl^{-1}.
A1.8	Sensitivity	Instrument dependent.
A1.9	Bias	Not Known.
A1.10	Interferences	Calcium, but See Section A3.
A1.11	Time required for analysis	The total analytical time for 20 pre-treated samples is approximately 1½ hours. The corresponding operator time is approximately 45 minutes, assuming automatic data calculation.

Note: See *General Comments on Instrument Performance*

Data by Yorkshire WA. York Laboratory.

A2 Principle

Antimony in potable waters is determined by direct electrothermal atomization atomic absorption spectrophotometry on acidified aqueous samples containing calcium and a surfactant as matrix modifier.

The conditions used are given in Table 1. It is essential that these conditions are used only as a guideline to determining optimum conditions for other instruments.

A3 Interferences

The effects of other substances vary considerably between makes and models of electrothermal atomization atomic absorption spectrophotometers. It is essential that all analysts using this technique must check the interference effects of other substances for their particular instruments and decide whether any effects are important enough to consider means of overcoming the interference. Tests show that if the matrix modifer A5.8 is omitted, calcium can give up to 100% positive bias. Sodium, potassium, magnesium, chloride and sulphate caused no interference with the instrument used. If pyrolitic graphite L'vov platforms are not used, serious interferences may occur. Surfactants improve sample spread and hence precision.

A4 Hazards

The exhaust fumes from the atomic absorption spectrophotometer are toxic and must be ducted away. Prolonged viewing of the atomization stage may cause cataracts and must be avoided.

Antimony compounds are toxic. Do not ingest or inhale. See Warning to users for further advice.

A5 Reagents

All reagents and standard solutions may be kept in glass or polyethylene bottles (see Section A6.3). Analytical reagent grade chemicals are suitable unless otherwise stated. Antimony contamination has been reported with reagents stored in brown glass bottles. Such bottles should not be used.

A5.1 Water

The water used for blank determinations and for preparing reagent and standard solutions should have an antimony content that is negligible, compared with the smallest concentrations to be determined in the sample. Deionized water or water distilled from an all glass apparatus is suitable.

A5.2 Nitric Acid (d_{20} 1.42), atomic spectroscopy grade

A5.3 10% V/V Nitric Acid (wash solution)

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

A5.4 50% V/V Nitric Acid

Dilute 50 ml ± 5 ml of nitric acid (d_{20} 1.42) with water to 1 litre in measuring cylinder. Store in a polyethylene bottle.

*Note: Nitric acid (d_{20} 1.42) is not the 100% acid. All dilution strengths given in this method are based on the d_{20} 1.42 acid and not on the true nitric acid content (which is about 0.6 times less than if the unstable 100% nitric acid had been used).

A5.5 Solution A: 1 ml is equivalent to 1 mg antimony

Dissolve 1.334 ± 0.003 g of potassium antimonyl tartrate (dried at 105 ± 5°C) in approximately 100 ml of water, transfer quantitatively to a 500 ml calibrated flask, add 2 ml of 50% V/V nitric acid (A5.4) for every 100 ml of water used, and make up to the mark with water. Mix thoroughly. This solution is stable for several months. Solution A5.5 may also be prepared by dilution of a commercially available standard antimony solution.

A5.6 Solution B: 1 ml is equivalent to 10 μg Sb

Dilute 5.00 ± 0.01 ml of Solution A with water to 500 ml in a calibrated flask containing 10.0 + 0.1 ml of 50% Nitric Acid (A5.4). Mix thoroughly. This solution is stable for several months.

A5.7 Solution C: 1 ml is equivalent to 1 μg Sb

Dilute 10.00 + 0.01 ml of Solution B with water to 100 ml in a calibrated flask containing 2.0 + 0.2 ml of 50% V/V nitric acid. Prepare immediately before use.

A5.8 Matrix Modifier: 1 ml contains 10 mg calcium plus surfactants

Dissolve 59 ± 1 g of Analytical Reagent Grade calcium nitrate, $Ca(NO_3)_2 . 4H_2O$, in approximately 200 ml of water. Quantitatively transfer the solution to a 1 litre calibrated flask, add 10 drops of 10% Triton X–100 or equivalent surfactant, dilute to the mark with water and mix thoroughly.

Alternatively, solution A5.8 may be prepared using 25.00 ± 0.02 g of high purity calcium carbonate dissolved in the minimum volume of nitric acid (A5.4)—about 60 ml, and make up to 1 litre with water and triton X–100 as before.

See also Note N.

A6 Apparatus

A6.1 An atomic absorption spectrophotometer equipped with an electrothermal atomizer and appropriate hollow cathode lamp. Background correction must be used; if the instrument is not equipped with facilities to make this correction automatically, a separate measurement for background must be made using a suitable continuum source.

A6.2 Appropriate graphite tubes and pyrolytic platforms should be pre-conditioned before use by making ten replicate injections of standard solutions and heating through the complete operating cycle until stable sensitivity is achieved.

A6.3 Cleanliness—Cleanliness is absolutely essential for this procedure. If possible a separate room with a clean environment should be reserved solely for electrothermal atomization work. All apparatus should be reserved for trace metal determinations. All residual trace metals from previous determinations must be removed. Clean all new glass and polyethylene ware by filling with or soaking in 10% V/V nitric acid for at least two days. Rinse thoroughly with water before use. It is advisable to soak all glass and polyethylene ware in 10% V/V nitric acid when not in use, merely rinsing in nitric acid before use may not be sufficient (See also A12.1).

A7 Sample Collection and Preservation

Clean a polyethylene bottle by the procedure described in Section A6.3, add 2.00 ± 0.05 ml of 50% V/V nitric acid per 100 ml of sample to be collected and then collect the sample. This acidification minimizes the adsorption of trace metals onto the walls of the bottle. The acidified sample should be allowed to stand for at least twenty-four hours to ensure that any trace metals in suspended or collodial forms are converted to soluble forms.

A8 Analytical Procedure

Read Section A4 on hazards before starting this procedure:

Step	Procedure	Notes
A8.1	Analyse the samples by Electrothermal Atomization Atomic Absorption Spectrophotometry. Each sample must be analysed in duplicate with blanks and calibration standards at the beginning and after at least every sixth sample. Wavelength 217.6 mm Follow the manufacturers operating instructions. A typical programme for each sample (developed for a Varian AA975/GTA95 with graphite tubes and a solid pyrolitic graphite L'vov platform is as follows:	

Programme Step	Tube Temp °C	Duration secs	Argon gas flow 1/min^{-1}
1	200	5	3
2	200	60	3
3	600	30	3
4	600	2	NIL
5	2300	0.9	NIL
6	2300	2	NIL
7	2600	0.2	3
8	2600	3	3
9	40	12	3 (a)

(a) To allow the L'vov platform to cool below 100°C before the injection of the next sample.

Step	Procedure	Notes
	15 ml of sample, standard or blank plus 2 ml of matrix modifier (A5.8) are injected simultaneously at the start of each programme. (note a).	
A8.2	Prior to analysing samples and wherever the calibration standards indicate that significant drifting of the analytical curve has occurred, analyse a series of standard antimony samples (eg 0, 20, 40, 60, 100 μgl^{-1} (Sb) in duplicate. (See also Section A9) plot the calibration graph from these results, plotting each replicate individually.	
A8.3	Determine the antimony content of each replicate sample from the calibration curve, correct for blank value using the mean of the two nearest sets of blank samples (one set on each side) Report the mean of the duplicate analyses for the sample.	(b) In the event of poor agreement between the duplicate results, repeat that sample analysis at least in duplicate.

A9 Checking the Linearity of the Calibration Curve

The procedure given in this section must be carried out on at least two independent occasions before application of this method to any samples and regularly thereafter.

A9.1 Into a series of 100 ml calibrated flasks, pipette 2.0, 4.0, 6.0, 8.0 and 10.0 ± 0.05 ml of standard antimony Solution C. Dilute to 100 ml with water. Add 2.0 ± 0.05 ml of 50% V/V nitric acid. Mix well. These solutions correspond to antimony concentrations of 20, 40, 60, 80 and 100 μgl^{-1} respectively in the stabilized sample.

A9.2 The calibration curve is normally linear to at least 120 μgl^{-1}, but the linearity may depend on the type of instrumentation used and should therefore be checked. If the calibration curve significantly departs from linearity, the top calibration standard chosen for step A8.4 should be the highest concentration on the acceptable portion of the calibration curve and the concentration range of the method should be adjusted accordingly.

A10 Change of Concentration Range of the Method

If the analyte concentration in the sample is likely to exceed the highest calibration standard an appropriately smaller aliquot of the sample must be taken for analysis. To this volume of sample, V ml add sufficient 50% V/V nitric acid so that there is the same total volume of 50% V/V nitric acid present as there would be in 50 ml of sample. Dilute with water to 50 ml and proceed as in section A8. It is necessary to alter the calculation of the result, as follows:—

$$\text{Analyte concentration} = \text{Concentration obtained} \times \frac{50}{V}\ \mu gl^{-1}$$

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 sources of error.

A11.1 Contamination

It is desirable to carry out the analysis in a laboratory in which no appreciable amounts of the analyte or its compounds are handled. The technique and working conditions should be initially examined and any source of contamination eliminated or minimized. In particular it is desirable to reserve the apparatus used solely for this determinand and to carry out a preliminary series of blank determinations to ensure low blank values before analysing any samples. Avoid the use of glassware as much as possible and keep contact times with glass to a minimum.

A11.2 Analyte content of the water used for blank determinations

The antimony content of the water used should be negligible if prepared according to Section A5.1. If the blank levels are unacceptably high, then fresh water and nitric acid should be used.

A11.3 Interfering Substances

See Section A3. The effect of possible interfering substances may be determined by analysing samples spiked with analyte and various concentrations of the potential interfering substance.

A11.4 Calibration Standards

The calibration curve for this method has been found to be virtually linear though its slope may vary from one set of determinations to another. Therefore, calibration standards must be run for each batch of analyses. A suitable AQC standard should be analysed regularly within each sample run (see Section A8).

A11.5 Problems with Background Correction

Most modern instruments should be capable of operating with background correction at the required wavelength. Difficulty may be encountered with some instruments in matching the energy levels of the two hollow cathode and deuterium lamps. In this case, the analyst may prefer not to use background correction. See also Introduction Section 5.

A12 Checking the accuracy of Analytical Results

A12.1 Electrothermal atomization atomic absorption spectrophotometry, using commercially available furnaces, is often subject to large interference effects unless special procedures are employed. Moreover, such interferences may vary from atomizer to atomizer because of differences in basic design (for example, physical dimensions and heating rates).

A12.2 In the methods described in this booklet, any significant interference effects may be reduced using matrix modification techniques. The mechanisms of such techniques are not completely understood and their effectiveness may vary with the type of furnace used. It is recommended that analysts wishing to use the methods given in this booklet exercise particular caution, both in establishing them with their own instrumentation and, subsequently, in applying them routinely. The following approach is recommended.

A12.3 Establishment of the Method

A12.3.1 The extent to which the exact conditions of graphite furnace operation described can be reproduced with the users instrumentation will depend upon the characteristics of the particular furnace system. It should be noted that the same choice of heating rates, for example, may not be available even on closely-related furnaces of the same manufacturer, and furnaces from different manufacturers may often show greater differences. Although the trend towards greater flexibility of heating programmes, evident with the more recent furnaces, may reduce the difficulty of duplicating particular conditions, the user should exercise great care in matching (as closely as possible) the heating conditions and temperatures described. In doing so, analysts should follow the conditions which most closely suit their own furnace. Only if the particular characteristics of the available equipment dictate otherwise, or if unsatisfactory performance is shown by the preliminary tests, should analysts depart markedly from the conditions described in the method. Special care should then be taken.

A12.3.2 After suitable furnace conditions have been established, the calibration procedure described in the method should be carried through on at least two separate occasions. If curve linearization facilities are to be employed their operation should be carefully checked. If the results of these checks are satisfactory, assessment of random errors can proceed, together with recovery testing.

A12.3.3 The recommended approach to such assessment has been described elsewhere (references 4 and 5), and these references should be consulted for details. As a minimum, it is recommended that the following should be analysed as samples, in each of a number of batches:

i) A blank.

ii) Two standard solutions at concentrations near the upper and lower limits of the range of interest.

iii) A real sample, both unspiked and spiked.

The number of batches, and of replicates in each batch, should be selected appropriately, (references 4 and 5). The blank should always be determined in at least duplicate to allow an estimate of the limit of detection to be obtained. The real sample selected should be one from a type to be analysed routinely which is expected to be particularly susceptible to interferences (for instance, a sample with a high matrix concentration). If possible, the unspiked sample should contain only a negligible concentration of the determinand; spiking to about the mid-point of the range of interest will then be appropriate.

A12.3.4 If these precision and recovery tests give satisfactory results, further checks on bias should be undertaken. As a minimum, it is recommended that further recovery tests be undertaken using samples typical of those to be examined. These samples must, of course, be decided by the analyst in the light of all the information available. The following factors will obviously be important:—

a. The diversity of sample types to be analysed routinely.

b. The degree of similarity between the instrumentation employed and that used to obtain the performance data given here.

The test samples should, if possible, include unspiked samples with a low determinand concentration.

A12.3.5 If these further tests do not disclose the existence of important bias, the method can be put into routine operation. However, recovery tests cannot show the existence of bias which is independent of determinand concentration. Interference tests are also recommended. Guidance on the conduct of both recovery and interference tests has been given elsewhere (reference 5). It is recommended that a series of tests be made in which the effect on the calibration curve of major ions likely to occur in samples is determined, using at least zero, a low and high determinand concentration with at least a high concentration of each ion both individually and in combination.

A12.4 Routine Analytical Quality Control

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. As a minimum, however, it is suggested that both a standard solution and a spiked and unspiked sample should be analysed in the same batch and in the same way as normal samples (See Section A8). The result should then be plotted on quality control charts in order to facilitate detection of deterioration of accuracy. Guidance on the use of such control systems has been given elsewhere (references 4, 5, 9 and 10), and these references should be consulted for details. The sample used for the routine recovery test should again be one likely to be susceptible to interferences.

B Beryllium in Raw and Potable Waters

B1 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, (4) also published in this series.)

B1.1	Substances determined	All forms of Beryllium likely to occur in raw and potable waters.
B1.2	Type of sample	Raw and potable waters.
B1.3	Basis of the method	Direct analysis by electrothermal atomization atomic absorption spectrophotometry of sample pre-treated with acid. Magnesium nitrate is used as a matrix modifier.
B1.4	Range of applications	Up to 4 μgl^{-1} Be.
B1.5	Calibration curve	Typically linear to 4 μgl^{-1}
B1.6	Standard deviation	Beryllium Concentration μgl^{-1}: 0.4 — Standard Deviation μgl^{-1}: 0.03 (n=9)* Beryllium Concentration μgl^{-1}: 3.6 — Standard Deviation μgl^{-1}: 0.07 (n=9)
B1.7	Limit of detection	0.22 μgl^{-1} (n=9).
B1.8	Sensitivity	0.44 pg for 1% absorption.
B1.9	Bias	Not Known.
B1.10	Interferences	See Section B3 and Table B1.
B1.11	Spiking recoveries	See Table B2.
B1.12	Time required for analysis	The total analytical time for 20 pre-treated samples is approximately 2 hours. The corresponding operator time is approximately 45 minutes, assuming automatic data calculations.

*n = number of degrees of freedom.

Note: See the General Comments on Instrument Performance.

Data by Yorkshire WA Sheffield Laboratory.

Table B1 Effect of Other Substances on the Determination of Beryllium

Other Substances	Concentration of other substances (mgl^{-1})	Other Substance added as	Effect in μgl^{-1} Beryllium of other substances at a Beryllium concentration of (μgl^{-1})	
			0.0	3.2
Sodium	300	Sulphate	−0.01	−0.03
Calcium	300			
Magnesium	100	nitrate	−0.03	0.01
Iron	5			
Aluminium	5	nitrate	−0.02	−0.04
Manganese	5			
Calcium	50			
Magnesium	10	nitrate		
Sodium	50		0.01	0.03
Chloride	100			
Sulphate	150	acid		

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

0.00 ± 0.06 at 0 μgl^{-1} Be and
0.00 ± 0.14 at 3.2 μgl^{-1} Be

Table B2 Spiking Recoveries on Potable Water Samples (3.2 μgl^{-1} spike)

Sample	Ca mgl^{-1}	Mg mgl^{-1}	Na mgl^{-1}	Conductivity μScm^{-1}	Unspiked μgl^{-1}	Spiked μgl^{-1}	%Recovery
1	7.84	2.71	5.1	111	0.04	3.12	96.3
2	23.8	2.08	6.28	205	0.04	3.14	96.9
3	8.2	1.68	3.23	109	0.01	3.24	100.9
4	48.5	22.1	14.2	502	0.06	3.23	99.1
5	46.4	21.0	13.6	377	0.05	3.22	99.1
6	44.6	6.29	12.3	374	0.03	3.08	95.3

Table B3 Instrument Conditions

B3.1 *Instrument[1] Parameters*

Lamp Current (mA)	5
Slit Width (nm)	1.0
Slit Height	Reduced
Wavelength (nm)	234.9
Sample Introduction	Sampler Automixing
Measurement Time (sec)	4.5
Replicates	2
Background Correction	ON
Measurement Mode	Peak Area

B3.2 *Furnace[2] Parameters*

Step No.	Temperature (°C)	Time (sec)	Gas Flow (L min^{-1})	Read Command
1	100	5.0	3.0	No
2	200	10.0	3.0	No
3	250	45.0	3.0	No
4	1700	20.0	3.0	No
5	1700	10.0	3.0	No
6	1700	2.0	0.0	No
7	2650	0.5	0.0	Yes
8	2650	5.0	0.0	Yes
9	40	13.3	3.0	No

Tube Type — Pyrolytic coated L'vov platform
Sample Volume — 10 µl
Matrix Modifier — 5 µl of 10 gl^{-1} Mg $(NO_3)_2$ } inject together
Purge Gas — Argon

1 Varian Spectra AA-40 Atomic Absorption Spectrophotometer
2 Varian GTA-96 Graphite Tube Atomizer

B2 Principle

Beryllium in raw and potable waters is determined directly in acidified aqueous samples by electrothermal atomization atomic absorption spectrophotometry. Magnesium nitrate is added as a matrix modifer.

The conditions used are given in Table 3. It is essential that these conditions are used only as a guideline to determining optimum conditions for other instruments.

B3 Interferences

The effects of other substances vary considerably between electrothermal atomization atomic absorption spectrophotometers. It is essential that all analysts using this technique should check the interference effects of other substances for their particular instruments and decide whether any effects are important enough to consider means of overcoming the interference. For the instrument used in obtaining these performance characteristics (See Table B3), matrix modification was considered necessary (See Tables B1 and B2).

The effects of other substances on the determination of beryllium are shown in Table B1.

B4 Hazards

Beryllium compounds are highly toxic if inhaled or if they enter the blood stream. See also the Antimony method, Section A4.

B5 Reagents

All reagents and standard solutions may be kept in glass or polyethylene bottles (see Section B6.3). Analytical reagent grade chemicals are suitable unless otherwise stated.

B5.1 Water

See the Antimony method, Section A5.1.

B5.2 Nitric Acid (d_{20} 1.42), atomic spectroscopy grade

B5.3 10% V/V Nitric Acid

See the Antimony method, Section A5.3.

B5.4 50% V/V Nitric Acid

See the Antimony method, Section A5.4.

B5.5 Solution A: 1 ml contains 1 mg beryllium

This solution in commercially available as an atomic spectroscopy standard solution. Alternatively dissolve 20.7574 ± 0.005 g of pure beryllium nitrate trihydrate in 200 ml deionized water, and add 1.5 ml nitric acid ($d_{20} = 1.42$). Quantitatively transfer the solution to a 1 litre calibrated flask, dilute with water to the mark and mix well. The solution is stable for several months. Alternatively use a commercially available standard beryllium solution.

B5.6 Solution B: 1 ml is equivalent to 10 μg Be

Dilute 5 ± 0.01 ml of Solution A with water to 500 ml in a calibrated flask containing 10 ± 0.1 ml of 50% V/V nitric acid. This solution is stable for one month.

B5.7 Solution C: 1 ml is equivalent to 0.1 μg Be

Dilute 10.00 ± 0.01 ml of Solution B with water to 1,000 ml in a calibrated flask containing 20.0 ± 0.2 ml of 50% V/V nitric acid. This solution should be prepared immediately before use.

B5.8 Matric Modifier Solution: Magnesium Nitrate 10 gl^{-1}

Weigh out 17.3 ± 0.5 g of magnesium nitrate hexahydrate, dissolve in approximately 500 ml of water and make up to 1 litre ± 10 ml.

B6 Apparatus

See the Antimony method, Section A6.

B7 Sample Collection and Preservation

See the Antimony method, Section A7.

B8 Analytical Procedure

Read Section B4 on hazards before starting this procedure:

Step	Procedure	Notes
B8.1	**Pre-treatment Stage** Allow the acidified sample to stand for at least 24 hours (Note a).	(a) If the sample contains a significant amount of suspended matter, the bottle should be placed in an oven at 70°C for 24 hours. The bottle cap should be loosened slightly.
B8.2	**Blank Determination** A blank must be run with each batch (eg up to 10 samples) of determinations using the same batch of reagents as for the samples.	
B8.3	Add 2.0 ± 0.05 ml of 50% V/V nitric acid to 100 ml of water in a calibrated flask. Proceed with steps B8.5 to B8.11.	
B8.4	**Calibration Standards** Calibration standards must be run with each batch of determinations using the same batch of reagents as for the samples. In a series of 100 ml calibrated flasks dilute appropriate amounts of standard beryllium Solution C to cover the calibration range for the instrument (See Section B9). It is preferable to use at least five calibration standards, including the blank (Notes b and c).	(b) If the instrument can automatically prepare calibration standards, then this facility may be utilized. (c) It is advisable to analyse an AQC standard of a suitable concentration.

Step	Procedure	Notes
B8.5	**Electrothermal Atomization Atomic Absorption Stage** Set up the instrument according to the manufacturer's instructions for the determination of beryllium by electrothermal atomization (Note d). Each new tube should be conditioned as described in Section A6.2.	(d) Operating conditions are given for the instrument used for this work, however, it is essential that each operator obtains optimum conditions for the particular instrument.
B8.6	Inject an appropriate volume of a calibration standard and ensure that the instrument gives a satisfactory response (Note e).	(e) An appropriate volume or nebulization time is usually in the range 5–30 μl or 2–10 s respectively, depending on the particular instrument employed. The same volume or nebulization time should be used for all subsequent samples, standards and blanks.
B8.7	Inject the blank and calibration standards (Note f).	(f) All injections must be carried out in duplicate. Repeat the determination if satisfactory agreement is not achieved.
B8.8	Inject a standard, a spiked sample and an unspiked sample (See Section A12.4) and note the responses (Note g).	(g) The recovery of the spiked addition should meet the criteria given in Section A12. Any failure to do so should be investigated and overcome before proceeding with analysis of samples.
B8.9	Inject the sample and note the response (Note h).	(h) The preferred method of sample introduction is by automatic sampler. Manual techniques can be used, but are less precise.
B8.10	Instrument drift should be checked for at the end of each batch of samples (eg up to 10 samples). Inject both the blank and a suitable calibration standard.	
B8.11	**Calculation of Results** The preferred method of calculation is by use of data processing facilities in conjunction with a 5 point calibration graph and check standards (Note i).	(i) A suitable recorder can be used for manual calculation of results with appropriate adjustments for variations in sensitivity and blank value.

B9 Checking the linearity of the Calibration Curve

The procedure given in this section must be carried out on at least two independent occasions before application of this method to any samples and regularly thereafter.

B9.1 Into a series of 100 ml calibrated flasks, pipette 0.8, 1.6, 2.4, 3.2 and 4.0 ± 0.05 ml of standard beryllium solution C. Dilute to 100 ml with water. Add 2.0 ± 0.05 ml of 50% v/v nitric acid. Mix well. These solutions correspond to beryllium concentrations of 0.8, 1.6, 2.4, 3.2 and 4.0 μgl^{-1} respectively in the stabilized sample.

B9.2 The calibration curve is normally linear to 4 μgl^{-1} beryllium for the Varian Spectra AA-40 + GTA-96 instrument, however, the linearity of the curve may depend on the type of instrumentation used and therefore linearity must be checked. If the calibration curve significantly departs from linearity, the top calibration standard chosen for step B8.4 should be the highest concentration on the acceptable portion of the calibration curve and the concentration range of the method should be adjusted accordingly.

B10 Change of Concentration Range of the Method

See the Antimony method, Section A10; but using procedure B8.

B11 Sources of Error

See the Antimony method, Section A11.

B12 Checking the accuracy of Analytical Results

See the Antimony method, Section A12.

C Chromium in Raw and Potable Waters

C1 Performance Characteristics of the Method

(For further information on the determination and definition of performance characteristics see General Principle of Sampling and Accuracy of Results 1980, (4) also published in this series.)

C1.1	Substances determined	All forms of Chromium likely to occur dissolved in raw and potable waters.
C1.2	Type of sample	Raw and potable waters.
C1.3	Basis of the method	Direct analysis by electrothermal atomization atomic absorption spectrophotometry of samples pre-treated with acid. Calcium must be used as a matrix modifier with some instruments.
C1.4	Range of application	Perkin Elmer:— Up to 20 μgl^{-1} Cr. † Instrumentation Laboratory:— Up to 10 μgl^{-1} Cr.
C1.5	Calibration curve	Perkin Elmer:— typically linear to 12 μgl^{-1} Cr. Instrumentation Laboratory:— typically linear to 10 μgl^{-1} Cr.
C1.6	Standard deviation	Instrument / Chromium Concentration μgl^{-1} / Standard Deviation μgl^{-1} PE 2.0 0.07 (n=9)* 18.0 0.50 (n=9) IL 1.0 0.11 (n=9) 9.0 0.22 (n=9)
C1.7	Limit of detection	Perkin Elmer:— 0.44 μgl^{-1} Cr (n=9). Instrumentation Laboratory:— 0.62 μgl^{-1} Cr (n=9).
C1.8	Sensitivity	Perkin Elmer:— 5.5 pg for 1% absorption. Instrumentation Laboratory:— 1.37 pg for 1% absorption.
C1.9	Bias	Not Known.
C1.10	Interferences	See Section C3 and Table C1.
C1.11	Spiking recoveries	See Table C2.
C1.12	Time required for analysis	The total analytical time for 20 pre-treated samples is approximately 2½ hours for the Perkin Elmer and 2 hours for the Instrumentation Laboratory Instruments. The corresponding operator time is approximately 45 minutes, assuming automatic data calculation.

NOTE: See the General Comments on Instrument Performances

*n = number of degrees of freedom. † = now Thermo Electro Ltd.

Data by Yorkshire WA, Sheffield Laboratory.

Table C1 Effect of Other Substances on the Determination of Chromium

Other Substance	Concentration of other Substance (mgl^{-1})	Other Substance added as	Effect in μgl^{-1} Chromium of other substance at a Chromium concentration of (μgl^{-1})			
			PE		IL	
			0.0	10.0	0.0	9.0
Calcium	300	nitrate	−0.10	0.13	−0.18	−0.16
Magnesium	100	nitrate	−0.13	−0.08	−0.02	−0.29
Sodium	300	nitrate	0.04	0.45	−0.11	0.26
Potassium	20	nitrate	−0.13	−0.05	0.13	−0.16
Calcium + Magnesium	300 + 100	nitrate	−0.04	−0.04	0.03	0.26
Chloride	500	acid	−0.08	−0.11	−0.27	−0.02
Sulphate	300	acid	0.09	0.19	−0.21	−0.04
Silicon	30	ammonium fluorosilicate	0.01	0.13	0.23	0.10
Iron + Aluminium + Manganese	5 + 5 + 5	nitrate	0.08	−0.04	0.17	0.27
Copper + Zinc	20 + 20	nitrate	0.03	0.35	−0.10	0.05
Flouride	10	sodium fluoride	−0.11	−0.41	−0.17	0.09
Phosphate	10	acid	−0.14	−0.39	0.18	−0.16
Calcium + Magnesium + Sodium + Chloride + Sulphate	100 + 20 + 100 + 200 + 300	nitrate + acid	0.00	−0.41	−0.12	−0.06

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

Perkin Elmer:—
0.0 ± 0.14 at 0 μgl^{-1} Cr and
0.0 ± 0.30 at 10 μgl^{-1} Cr.

Instrumentation Laboratory:—
0.0 ± 0.28 at 0 μgl^{-1} Cr and
0.0 ± 0.28 at 9 μgl^{-1} Cr.

Table C2 Spiking Recoveries on Potable Water Samples (10 μgl^{-1} spike for PE and 9 μgl^{-1} spike for IL)

Sample	Ca	Mg	Na	Conductivity	Perkin Elmer Unspiked	Spiked	%Recovery
	mgl^{-1}	mgl^{-1}	mgl^{-1}	μScm^{-1}	μgl^{-1}	μgl^{-1}	
1	10.5	2.93	9.5	143	0.49	10.56	100.7
2	10.7	2.82	10.0	146	−0.13	9.97	101.0
3	10.7	2.85	9.3	142	−0.13	10.41	105.4
4	44.3	15.0	7.2	408	0.06	9.97	99.1
5	43.4	15.9	9.5	410	0.37	10.11	97.4
6	51.4	18.5	14.6	483	0.37	10.05	96.8

Sample	Ca	Mg	Na	Conductivity	Instrumentation Laboratory Unspiked	Spiked	%Recovery
	mgl^{-1}	mgl^{-1}	mgl^{-1}	μScm^{-1}	μgl^{-1}	μgl^{-1}	
1	44.0	18.0	10.9	405	0.04	8.98	99.2
2	45.0	18.6	13.6	456	−0.03	8.99	100.2
3	46.3	19.7	15.4	466	0.10	8.71	95.7
4	7.5	2.5	8.6	116	−0.20	9.09	103.2
5	8.2	1.4	6.4	105	−0.03	9.15	102.0
6	7.2	2.1	8.2	110	0.05	9.04	99.9

Table C3 Instrument Conditions

Perkin Elmer (1)

Step	1	2	3	4
Temp °C	140	1550	2300	2600
Ramp (s)	10	10	0	0
Hold (s)	20	20	7	5
Read			/	

Internal flow (ml min^{-1}) = 50

Integration Time (s) = 4
Sample volume (μl) = 20
Tube Type = Pyro-coated
Mode = Peak Area
Matrix Modification = 5 μl of 5000 mgl^{-1} Ca
(inject with sample)
Injection = Auto:—AS40
Wavelength (nm) = 357.9
Band Width (nm) = 0.7
Lamp Current (mA) = 8.0
Deuterium Arc
Background Correction = No*

Instrumentation Laboratories (2)

Step	1	2	3	4	5	6
Temp °C	0	175	750	1200	2400	2400
Time (s)	0	5	15	15	0	10
Read					/	

Internal flow (l min^{-1}) = 1.3

Integration Time (s) = 6
Delay (s) = 7
Deposit = 8
Tube Type = Delayed Atomization Cuvette (DAC)
Mode = Peak Area
Matrix Modification = None
Injection = Auto:— IL254 (Fastac 2)
Wavelength (nm) = 357.9
Band Width (nm) = 1.0
Lamp Current (mA) = 3.0
High Voltage (V) = 530
Deuterium Arc
Background Correction = Yes

(1) Atomic Absorption Spectrophotometer: PE 272 (single beam)
Electrothermal Atomizer: HGA 500

(2) Atomic Absorption Spectrophotometer: IL 451 (double beam)
Electrothermal Atomizer: IL 655

*See section A11.5.

C2 Principle

Chromium in raw and potable waters is determined directly in acidified aqueous samples by electrothermal atomization atomic absorption spectrophotometry.

A calcium matrix modifer has been found to be necessary with one instrument but not for another of different manufacture.

The conditions used are given for both instruments in Table 3. It is essential that these conditions are used only as a guideline to determining optimum conditions for other instruments.

C3 Interferences

The effects of other substances vary considerably between electrothermal atomization atomic absorption spectrophotometers. It is essential that all analysts using this technique should check the interference effects of other substances for their particular instruments and decide whether any effects are important enough to require means of overcoming the interference. For the two instruments used to obtain the test data (see Table C3), matrix modification was considered necessary only for the Perkin Elmer (see Table 1 and C2). No significant interferences were observed on the Instrumentation Laboratory instrument, thus no matrix modifier was employed.

The effects of other substances on the determination of chromium are shown in Table C1.

C4 Hazards

See the Antimony method, Section A4.

C5 Reagents

All reagents and standard solutions may be kept in glass or polyethylene bottles (see Section A6.3). Analytical reagent grade chemicals are suitable unless otherwise stated.

C5.1 Water

See the Antimony method, Section A5.1.

C5.2 Nitric Acid (d_{20} 1.42), atomic spectroscopy grade

C5.3 10% V/V Nitric Acid

See the Antimony method, Section A5.3.

C5.4 50% V/V Nitric Acid

See the Antimony method, Section A5.4.

C5.5 Solution A: 1 ml contains 1 mg chromium

Dissolve 2.828 ± 0.001 g of anhydrous potassium dichromate (previously dried in an oven at 105°C for 2 hours) in about 200 ml of water. Quantitatively transfer the solution to a 1 litre calibrated flask, add 1.5 ml of nitric acid (d_{20} 1.42), dilute to the mark with water and mix well. The solution is stable for at least several months. Alternatively use a commercially available standard chromium solution.

C5.6 Solution B: 1 ml is equivalent to 10 μg Cr

Dilute 5 ± 0.01 ml of Solution A with water to 500 ml in a calibrated flask containing 10 ± 0.1 ml of 50% V/V nitric acid. This solution is stable for at least one month.

C5.7 Solution C: 1 ml is equivalent to 0.1 μg Cr

Dilute 10 ± 0.01 ml of Solution B with water to 1 litre in a calibrated flask containing 20.0 ± 0.2 ml of 50% V/V nitric acid. Prepare immediately before use.

C5.8 Matrix Modifier: 1 ml contains 5 mg calcium

Dissolve 12.5 ± 0.5 g of Aristar calcium carbonate in the minimum volume of nitric acid (d_{20} 1.42). Quantitatively transfer the solution to a 1 litre calibrated flask, dilute to the mark with water and mix well.

C6 Apparatus Refer to section A.6 of the Antimony Method but note that background correction was found to be necessary for the IL instrument, but not for the Perkin Elmer.

C7 Sample Collection and Preservation See the Antimony method, Section A7.

C8 Analytical Procedure

Read Section A4 on hazards starting this procedure:

Step	Procedure	Notes
C8.1	**Pre-treatment Stage** Allow the acidified sample to stand for at least 24 hours (Note a).	(a) If the sample contains a significant amount of suspended matter, the bottle should be placed in an oven at 70°C for 24 hours. The bottle cap should be loosened slightly.
C8.2	**Blank Determination** A blank must be run with each batch (eg up to 10 samples) of determinations using the same batch of reagents as for the samples.	
C8.3	Add 2.0 ± 0.05 ml of 50% V/V nitric acid to 100 ml of water in a calibrated flask. Proceed with steps C8.5 to C8.11.	
C8.4	**Calibration Standards** Calibration standards must be run with each batch of determinations using the same batch of reagents as for the samples. In a series of 100 ml calibrated flasks dilute appropriate amounts of standards chromium Solution C to cover the calibration range for the instrument (See Section C9). It is preferable to use at least five calibration standards, including the blank (Notes b and c).	(b) If the instrument can automatically prepare calibration standards, then this facility may be utilized. (c) It is advisable to analyse an AQC standard of a suitable concentration.
C8.5	**Electrothermal Atomization Atomic Absorption Stage** Set up the instrument according to the manufacturer's instructions for the determination of chromium by electrothermal atomization (Note d). Each new tube should be conditioned as described in Section A6.2.	(d) Operating conditions are given for the two instruments used for this work, however, it is essential that each operator obtains optimum conditions for the particular instrument.
C8.6	Inject an appropriate volume of a calibration standard and ensure that the instrument gives a satisfactory response (Note e).	(e) An appropriate volume or nebulization time is usually in the range 5–30 μl or 2–10 s respectively, depending on the particular instrument employed. The same volume or nebulization time should be used for all subsequent samples, standards and blanks.
C8.7	Inject the blank and calibration standards (Note f).	(f) All injections must be carried out in duplicate. Repeat the determination if satisfactory agreement is not achieved.
C8.8	Inject a standard, a spiked sample and an unspiked sample (See Section A12.4) and note the responses (Note g).	(g) The recovery of the spiked addition should meet the criteria given in Section A12. Any failure to do so should be investigated and overcome before proceeding with analysis of samples.

Step	Procedure	Notes
C8.9	Inject the samples and note the response (Note h).	(h) The preferred method of sample injection is by automatic sampler. Manual techniques can be used, but are considered less precise.
C8.10	Instrument drift should be checked for at the end of each batch of samples (eg up to 10 samples). Inject both the blank and a suitable calibration standard.	
C8.11	**Calculation of Results** The preferred method of calculation is by use of data processing facilities in conjunction with a 5 point calibration graph and check standards. (Note i).	(i) A suitable recorder can be used for manual calculation of results with appropriate adjustments for variations in sensitivity and blank value.

C9 Checking the linearity of the Calibration Curve

The procedure given in this section must be carried out on at least two independent occasions before application of this method to any samples and regularly thereafter. The standards required will vary slightly with the usable range of the instrument. Thus the calibration curve is normally linear to 12 μgl^{-1} chromium for the Perkin Elmer instrument used to obtain the test data provided, and 10 μgl^{-1} chromium for the Instrumentation Laboratory instrument, however, the linearity of the curve may depend on the type of instrumentation used and therefore linearity must be checked. If the calibration curve significantly departs from linearity, the top calibration standard chosen for step C8.4 should be the highest concentration on the acceptable portion of the calibration curve and the concentration range of the method should be adjusted accordingly. Two examples are given:

C9.1 Into a series of 100 ml calibrated flasks, pipette 4.0, 8.0, 12.0, 16.0 and 20.0 ml all ± 0.05 ml of standard chromium solution C. Dilute to 100 ml with water. Add 2.0 ± 0.05 ml of 50% v/v nitric acid and mix well. These solutions correspond to chromium concentrations of 4, 8, 12, 16 and 20 μgl^{-1} respectively in the stabilized sample.

C9.2 Prepare a series as in Section C9.1 above but using 2.0, 4.0, 6.0, and 10.0 ml all ± 0.05 ml of standard chromium solution C. Dilute, acidify and mix in the same way. These solutions will have half the concentrations quoted in Section C9.1.

C10 Change of Concentration Range of the Method

See the Antimony method, Section A10; but using procedure C8.

C11 Sources of Error

See the Antimony method, Section A11.

C12 Checking the accuracy of Analytical Results

See the Antimony method, Section A12.

D. Cobalt in Raw and Potable Waters

D1 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, (4) also published in this series).

D1.1	Substances determined	All forms of Cobalt likely to occur in raw and potable waters.
D1.2	Type of sample	Raw and potable waters.
D1.3	Basis of the method	Direct analysis by electrothermal atomization atomic absorption spectrophotometry of samples pre-treated with acid.
D1.4	Range of application	Up to 20 μgl^{-1} Co.
D1.5	Calibration Curve	Perkin Elmer:- typically linear to 20 μgl^{-1} Co. †Instrumentation Laboratory:- typically linear to 20 μgl^{-1} Co.
D1.6	Standard deviation	See table below
D1.7	Limit of detection	Perkin Elmer:- 1.48 μgl^{-1} Co (n = 9). Instrumentation Laboratory:- 1.03 μgl^{-1} Co (n = 10).
D1.8	Sensitivity	Perkin Elmer:- 11.0 pg for 1% absorption. Instrumentation Laboratory:- 12.6 pg for 1% absorption.
D1.9	Bias	Not Known.
D1.10	Interferences	See Section D3 and Table D1.
D1.11	Spiking recoveries	See Table A2.
D1.12	Time required for analysis	The total analytical time for 20 pre-treated samples is approximately 2 hours for both instruments. The corresponding operator time is approximately 45 minutes, assuming automatic data calculation.

Instrument	Cobalt Concentration μgl^{-1}	Standard Deviation μgl^{-1}
P.E.	2	0.12 (n = 9)*
	18	0.33 (n = 9)
I.L.	2	0.19 (n = 9)
	18	0.29 (n = 13)

Note: See the General Comment on Instrument Performances

*n = number of degrees of freedom.
† = now Thermo Electron Ltd.

Data by Yorkshire WA Sheffield Laboratory.

Table D1 Effect of Other Substances on the Determination of Cobalt

Other Substance	Concentration of other Substance (mgl^{-1})	Other Substance added as	Effect in μgl^{-1} Cobalt of other substance at a Cobalt concentration of (μgl^{-1})			
			PE		IL	
			0.0	10.0	0.0	10.0
Calcium	300	nitrate	−0.32	−0.40	−0.18	−0.26
Magnesium	100	nitrate	0.23	0.25	0.00	−0.60
Sodium	300	nitrate	−0.05	−0.24	0.12	−0.01
Potassium	20	nitrate	0.20	−0.18	−0.19	−0.27
Calcium	300	nitrate	0.23	−0.17	−0.03	−0.27
Magnesium	100					
Chloride	500	acid	−0.32	−0.07	−0.12	0.41
Sulphate	300	acid	0.61	−0.35	−0.12	−0.08
Silicon	30	ammonium fluorosilicate	−0.28	−0.19	0.14	0.14
Iron	5	nitrate	−0.13	0.16	0.03	−0.08
Aluminium	5					
Manganese	5					
Copper	20	nitrate	0.00	0.00	0.06	0.00
Zinc	20					
Flouride	10	sodium fluoride	−0.10	0.02	−0.03	0.34
Phosphate	10	acid	0.20	0.17	−0.26	−0.18
Calcium	100	nitrate	0.30	0.83	−0.31	−0.38
Magnesium	20					
Sodium	100					
Chloride	200	acid				
Sulphate	300					

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

Perkin Elmer:—
0.0 ± 0.61 at 0 μgl^{-1} Co and
0.0 ± 0.42 at 10 μgl^{-1} Co.

Instrumentation Laboratory:—
0.0 ± 0.54 at 0 μgl^{-1} Co and
0.0 ± 0.61 at 10 μgl^{-1} Co.

Table D2 Spiking Recoveries on Potable Water Samples (10 μgl^{-1} spikes for P.E. and I.L)

Sample	Ca mgl^{-1}	Mg mgl^{-1}	Na mgl^{-1}	Conductivity μScm^{-1}	Perkin Elmer Unspiked μgl^{-1}	Spiked μgl^{-1}	%Recovery
1	44.0	18.0	10.9	405	0.23	10.26	100.3
2	45.0	18.6	13.6	456	0.59	10.42	98.3
3	46.3	19.7	15.4	466	0.05	9.67	96.2
4	7.5	2.5	8.6	116	−0.08	9.76	98.4
5	8.2	1.4	6.4	105	0.06	9.71	96.5
6	7.2	2.1	8.2	110	0.28	9.77	94.9

Sample	Ca mgl^{-1}	Mg mgl^{-1}	Na mgl^{-1}	Conductivity μScm^{-1}	Instrumentation Laboratory Unspiked μgl^{-1}	Spiked μgl^{-1}	%Recovery
1	55.0	19.0	12.9	488	0.06	10.01	99.5
2	57.0	22.4	10.8	476	−0.06	9.83	98.9
3	56.3	22.4	10.7	485	−0.03	10.03	100.6
4	11.8	3.18	8.30	145	0.78	10.91	101.3
5	12.1	3.38	8.37	146	0.56	10.72	101.6
6	13.8	3.04	8.64	153	0.44	10.34	99.0

Table D3 Instrument Conditions

Perkin Elmer (1)

Step	1	2	3	4
Temp °C	130	1000	2400	2600
Ramp (s)	15	10	0	0
Hold (s)	25	20	8	5
Read			/	

Internal flow (ml min^{-1}) = 10
Integration Time (s) = 6
Sample volume (μl) = 25
Tube Type = Pyro-coated L'vov platform
Mode = Peak Area
Matrix Modification = None
Injection = Auto:— AS40
Wavelength (nm) = 240.7
Band Width (nm) = 0.7 Alt
Lamp Current (mA) = 8.0
Deuterium Arc
Background Correction = Yes

Instrumentation Laboratories (2)

Step	1	2	3	4	5	6
Temp °C	0	180	500	1000	2500	2500
Time (s)	0	5	15	15	15	10
Read					/	

Internal flow (1 min^{-1}) = 1.3
Integration Time (s) = 6
Delay (s) = 7
Deposit = 5
Tube Type = DAC
Mode = Peak Area
Matrix Modification = None
Injection = Auto:— IL254
Wavelength (nm) = 240.7
Band Width (nm) = 0.3
Lamp Current (mA) = 8.0
High Voltage = 620
Deuterium Arc
Background Correction = Yes

(1) Atomic Absorption Spectrophotometer : PE 272 (single beam)
Electrothermal Atomizer : HGA 500

(2) Atomic Absorption Spectrophotometer : IL 451 (double beam)
Electrothermal Atomizer : IL 655

D2 Principle

Cobalt in raw and potable waters is determined directly in acidified aqueous samples by electrothermal atomization atomic absorption spectrophotometry.

Matrix modification has not been found to be necessary.

The conditions for both the instruments used are given in Table D3. It is essential that these conditions are used only as a guideline for determining the optimum conditions for other instruments.

D3 Interferences

The effects of other substances vary considerably between electrothermal atomization atomic absorption spectrophotometers. It is essential that all analysts using this technique should check the interference effects of other substances for their particular instruments and decide whether any effects are important enough to consider means of overcoming the interference. For the two instruments used to obtain this test data (see Table D3), no matrix modification was considered necessary (See Tables D1 and D2).

The effects of other substances on the determination of cobalt are shown in Table D1.

D4 Hazards

See the Antimony method, Section A4.

D5 Reagents

All reagents and standard solutions may be kept in glass or polyethylene bottles (See Section A6.3). Analytical reagent grade chemicals are suitable unless otherwise stated.

D5.1 Water

See the Antimony method, Section A5.1.

D5.2 Nitric Acid (d_{20}1.42), atomic spectroscopy grade.

D5.3 10% V/V Nitric Acid (wash solution)

See the Antimony method, Section A5.3.

D5.4 50% V/V Nitric Acid

See the Antimony method, Section A5.4

D5.5 Solution A: 1 ml contains 1 mg cobalt

Weigh 1.4070 ± 0.005 g of cobalt II oxide, and dissolve it in a mixture of 65 ± 2 ml of nitric acid (d_{20} 1.42) and 65 ml of water, carrying out the operation in a fume cupboard. Quantitatively transfer the solution to a 1 litre calibrated flask, dilute with water to the mark and mix well. The solution is stable for several months. Alternatively use a commercially available standard cobalt solution.

D5.6 Solution B: 1 ml is equivalent to 10 μg Co

Dilute 5 ± 0.01 ml of Solution A with water to 500 ml in a calibrated flask containing 10 ± 0.1 ml of 50% V/V nitric acid. This solution is stable for at least one month.

D5.7 Solution C: 1 ml is equivalent to 0.1 μg Co

Dilute 10 ± 0.01 ml of Solution B with water to 1 litre in a calibrated flask containing 20.0 ± 0.2 ml of 50% V/V nitric acid. Prepare immediately before use.

D6 Apparatus

See the Antimony method, Section A6.

D7 Sample Collection and Preservation

See the Antimony method, Section A7.

D8 Analytical Procedure

Read Section A4 on hazards before starting this procedure:

Step	Procedure	Notes
D8.1	**Pre-treatment Stage** Allow the acidified sample to stand for at least 24 hours (Note a).	(a) If the sample contains a significant amount of suspended matter, the bottle should be placed in an oven at 70 °C for 24 hours. The bottle cap should be loosened slightly.
D8.2	**Blank Determination** A blank must be run with each batch (e.g. up to 10 samples) of determinations using the same batch of reagents as for the samples.	
D8.3	Add 2.0 ml ± 0.05 ml of 50% V/V nitric acid to 100 ml of water in a calibrated flask. Proceed with steps D8.5 to D8.11.	
D8.4	**Calibration Standards** Calibration standards must be run with each batch of determinations using the same batch of reagents as for samples. In a series of 100 ml calibrated flasks dilute appropriate amounts of standard cobalt Solution C to cover the calibration range for the instrument (See Section D9). It is preferable to use at least five calibration standards, including the blank. (notes b and c).	(b) If the instrument can automatically prepare calibration standards, then this facility may be utilized. (c) It is advisable to analyse an AQC standard of a suitable concentration.
D8.5	**Electrothermal Atomization Atomic Absorption Stage** Set up the instrument according to the manufacturer's instructions for the determination of cobalt by electrothermal atomization. (Note d). Each new tube should be conditioned as described in Section A6.2.	(d) Operating conditions are given for the two instruments used for this work, however, it is essential that each operator obtains optimum conditions for the particular instrument.
D8.6	Inject an appropriate volume of a calibration standard and ensure that the instrument gives a satisfactory response (Note e).	(e) An appropriate volume or nebulization time is usually in the range 5–30 μl or 2–10 s respectively, depending on the particular instrument employed. The same volume or nebulization time should be used for all subsequent samples, standards and blanks.
D8.7	Inject the blank and calibration standards (Note f).	(f) All injections must be carried out in duplicate. Repeat the determination if satisfactory agreement is not achieved.
D8.8	Inject a standard, a spiked sample and an unspiked sample (See Section A12.4) and note the responses (Note g).	(g) The recovery of the spike addition should meet the criteria given in Section A12. Any failure to do so should be investigated and overcome before proceeding with analysis of samples.
D8.9	Inject the samples and note the response (Note h).	(h) The preferred method of sample injection is by automatic sampler. Manual techniques can be used but are considered less precise.
D8.10	Instrument drift should be checked for at the end of each batch of samples (e.g. up to 10 samples). Inject both the blank and a suitable calibration standard.	

Step	Procedure	Notes
D8.11	**Calculation of Results** The preferred method of calculation is by use of data processing facilities in conjunction with a 5 point calibration graph and check standards. (Note i).	(i) A suitable recorder can be used for manual calculation of results with appropriate adjustments for variations in sensitivity and blank value.

D9 Checking the Linearity of the Calibration Curve

The procedure given in this section must be carried out on at least two independent occasions before application of this method to any samples and regularly thereafter.

D9.1 Into a series of 100 ml calibrated flasks, pipette 4.0, 8.0, 12.0, 16.0 and 20.0 ml all ± 0.05 ml of standard cobalt solution C. Dilute to 100 ml with water, add 2.0 ± 0.05 ml of 50% V/V nitric acid. Mix well. These solutions correspond to cobalt concentrations of 4, 8, 12, 16 and 20 $\mu g l^{-1}$ respectively in the stabilized sample.

D9.2 The calibration curve is normally linear to 20 $ug l^{-1}$ cobalt (see Section D1.5) however, the linearity of the curve may depend on the type of instrumentation used and therefore linearity must be checked. If the calibration curve significantly departs from linearity, the top calibration standard chosen for step D8.4 should be the highest concentration on the acceptable portion of the calibration curve and the concentration range of the method should be adjusted accordingly.

D10 Change of Concentration Range of the Method

See the Antimony method, Section A10; but using procedure D8.

D11 Sources of Error

See the Antimony method, Section A11.

D12 Checking the accuracy of Analytical Results

See the Antimony Method, Section A12

E. Copper in Raw and Potable Waters

E1 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, (4) also published in this series).

E1.1	Substances determined	All forms of Copper likely to occur in raw and potable waters.
E1.2	Type of sample	Raw and potable waters.
E1.3	Basis of the method	Direct analysis by electrothermal atomization atomic absorption spectrophotometry of samples pre-treated with acid.
E1.4	Range of application	Up to 25 μgl^{-1} Cu.
E1.5	Calibration Curve	Perkin Elmer:— typically linear to 25 μgl^{-1} Cu. †Instrumentation Laboratory:— typically linear to 15 μgl^{-1} Cu.
E1.6	Standard deviation	Instrument / Copper Concentration μgl^{-1} / Standard Deviation μgl^{-1} PE / 2.5 / 0.08 (n = 9)* 22.5 / 0.17 (n = 9) IL / 2.5 / 0.15 (n = 10) 22.5 / 0.80 (n = 10)
E1.7	Limit of detection	Perkin Elmer:— 0.52 μgl^{-1} Cu (n = 9). Instrumentation Laboratory:— 0.74 μgl^{-1} Cu (n = 10).
E1.8	Sensitivity	Perkin Elmer:— 5.4 pg for 1% absorption. Instrumentation Laboratory:— 9.52 pg for 1% absorption.
E1.9	Bias	Not Known.
E1.10	Interferences	See Section E3 and Table E1.
E1.11	Spiking recoveries	See Table E2.
E1.12	Time required for analysis	The total analytical time for 20 pre-treated samples is approximately 2 hours for both instruments. The corresponding operator time is approximately 45 minutes, assuming automatic data calculation.

Note: See the General Comment on Instrument Performance

*n = number of degrees of freedom.
† = now Thermo Electron Ltd.

Data by Yorkshire WA Sheffield Laboratory.

Table E1 Effect of Other Substances on the Determination of Copper

Other Substance	Concentration of other Substance (mgl^{-1})	Other Substance added as	Effect in μgl^{-1} Copper of other substance at a Copper concentration of (μgl^{-1})			
			PE		IL	
			0.0	22.5	0.0	22.5
Calcium	300	nitrate	0.02	0.33	−0.06	−1.29
Magnesium	100	nitrate	0.15	0.12	−0.02	−0.15
Sodium	300	nitrate	−0.11	−0.42	0.02	0.56
Potassium	20	nitrate	0.04	−0.50	0.03	0.11
Calcium + Magnesium	300 + 100	nitrate	−0.01	0.44	−0.16	−0.34
Chloride	500	acid	−0.11	0.28	0.12	−0.15
Sulphate	300	acid	−0.14	−0.07	0.12	0.72
Silicon	30	ammonium metasilicate	−0.11	−0.40	0.07	−0.25
Iron + Aluminium + Manganese	5 + 5 + 5	nitrate	−0.03	0.04	0.22	−0.11
Copper + Zinc	20 + 20	nitrate	0.09	−0.09	0.04	0.35
Flouride	10	sodium fluoride	−0.15	−0.38	−0.05	−0.48
Phosphate	10	acid	0.01	−0.12	0.00	0.09
Calcium + Magnesium + Sodium	100 + 20 + 100	nitrate	−0.06	−0.98	0.13	−0.12
Chloride + Sulphate	200 + 300	acid				

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

Perkin Elmer:—
0.0 ± 0.15 at 0 μgl^{-1} Cu and
0.0 ± 0.51 at 22.5 μgl^{-1} Cu.

Instrumentation Laboratory:—
0.0 ± 0.46 at 0 μgl^{-1} Cu and
0.0 ± 0.86 at 22.5 μgl^{-1} Cu.

Table E2 Spiking Recoveries on Potable Water Samples (10 μgl^{-1} spikes for P.E. and I.L)

Sample	Ca mgl^{-1}	Mg mgl^{-1}	Na mgl^{-1}	Conductivity μScm^{-1}	Perkin Elmer Unspiked μgl^{-1}	Spiked μgl^{-1}	%Recovery
1	55.0	19.0	12.9	488	6.56	16.80	102.4
2	57.0	22.4	10.8	476	9.28	19.37	100.9
3	56.3	22.4	10.7	485	3.21	13.54	103.3
4	11.8	3.18	8.30	145	1.33	11.46	101.3
5	12.1	3.38	8.37	146	1.44	11.76	103.2
6	13.8	3.04	8.64	153	0.92	11.26	103.4

Sample	Ca mgl^{-1}	Mg mgl^{-1}	Na mgl^{-1}	Conductivity μScm^{-1}	Instrumentation Laboratory Unspiked μgl^{-1}	Spiked μgl^{-1}	%Recovery
1	49.5	19.8	10.7	487	3.01	13.22	102.1
2	51.5	20.6	12.3	498	5.68	15.45	97.7
3	48.7	19.9	9.92	451	4.92	15.05	101.3
4	11.3	3.42	8.52	151	2.75	12.81	100.6
5	9.6	3.18	7.36	145	2.00	11.94	99.4
6	10.2	3.51	8.04	141	3.66	13.69	100.3

Table E3 Instrument Conditions

Perkin Elmer [1]

Step	1	2	3	4
Temp °C	140	1050	2350	2600
Ramp (s)	15	10	0	1
Hold (s)	25	20	5	5
Read			/	

Internal flow (ml min^{-1}) = 10
Integration Time (s) = 5
Sample volume (μl) = 30
Tube Type = L'vov (pyro-coated)
Mode = Peak Area
Matrix Modification = None
Injection = Auto:— AS40
Wavelengh (nm) = 324.7
Band Width (nm) = 0.7 Alt
Lamp Current (mA) = 4.5
Deuterium Arc
Background Correction = Yes

Instrumentation Laboratories [2]

Step	1	2	3	4	5	6
Temp °C	0	180	300	550	2000	2000
Time (s)	0	5	15	15	0	5
Read					/	

Internal flow (1 min^{-1}) = 1.3
Integration Time (s) = 4
Delay (s) = 7
Deposit (s) = 5
Tube Type = DAC (pyro-coated)
Mode = Peak Area
Matrix Modification = None
Injection = Auto:— IL254
Wavelength (nm) = 324.7
Band Width (nm) = 1.0
Lamp Current (mA) = 2
High Voltage = 460
Deuterium Arc
Background Correction = Yes

[1] Atomic Absorption Spectrophotometer : PE 272 (single beam)
Electrothermal Atomizer : HGA 500

[2] Atomic Absorption Spectrophotometer : IL 451 (double beam)
Electrothermal Atomizer : IL 655

E2 Principle

Copper in raw and potable waters is determined directly in acidified aqueous samples by electrothermal atomization atomic absorption spectrophotometry. Matrix modification has not been found to be necessary. (See also Note N)

The conditions used are given for both instruments in Table 3. It is essential that these conditions are used only as a guideline to determining optimum conditions for other instruments.

E3 Interferences

The effects of other substances vary considerably between electrothermal atomization atomic absorption spectrophotometers. It is essential that all analysts using this technique should check the interference effects of other substances for their particular instruments and decide whether any effects are important enough to consider means of overcoming the interference. For the two instruments used to obtain the test data (see Table E3), no matrix modification was considered necessary (See Tables E1 and E2).

The effects of other substances on the determination of copper are shown in Table E1.

E4 Hazards

See the Antimony method, Section A4.

E5 Reagents

All reagents and standard solutions may be kept in glass or polyethylene bottles (See Section A6.3). Analytical reagent grade chemicals are suitable unless otherwise stated.

E5.1 Water

See the Antimony method, Section A5.1

E5.2 Nitric Acid (d_{20} 1.42), atomic spectroscopy grade.

E5.3 10% V/V Nitric Acid (wash solution)

See the Antimony method Section A5.3.

E5.4 50% V/V Nitric Acid

See the Antimony method, Section A5.4.

E5.5 Solution A: 1 ml contains 1 mg copper

Weigh 1.000 ± 0.005 g of copper foil (greater than 99% purity), and dissolve it in a mixture of 65 ± 2 ml of nitric acid (d_{20} 1.42) and 65 ml of water, carrying out the operation in a fume cupboard. Quantitatively transfer the solution to a 1 litre calibrated flask, dilute with water to the mark and mix well. The solution is stable for several months. Alternatively use a commercially available standard copper solution.

E5.6 Solution B: 1 ml is equivalent to 10 μg Cu

Dilute 5 ± 0.01 ml of Solution A with water to 500 ml in a calibrated flask containing 10 ± 0.1 ml of 50% V/V nitric acid. This solution is stable for at least one month.

E5.7 Solution C: 1 ml is equivalent to 0.1 μg Cu

Dilute 10 ± 0.01 ml of Solution B with water to 1 litre in a calibrated-flask containing 20 ± 0.2 ml of 50% V/V nitric acid. Prepare immediately before use.

E6 Apparatus

See the Antimony method Section A6.

E7 Sample Collection and Preservation

See the Antimony method, Section A7.

E8 Analytical Procedure Read Section A4 on hazards before starting this procedure:

Step	Procedure	Notes
E8.1	**Pre-treatment Stage** Allow the acidified sample to stand for at least 24 hours (Note a).	(a) If the sample contains a significant amount of suspended matter, the bottle should be placed in an oven at 70°C for 24 hours. The bottle cap should be loosened slightly.
E8.2	**Blank Determination** A blank must be run with each batch (e.g. up to 10 samples) of determinations using the same batch of reagents as for the samples.	
E8.3	Add 2.0 ml ± 0.05 ml of 50% V/V nitric acid to 100 ml of water in a calibrated flask. Proceed with steps E8.15 to E8.11.	
E8.4	**Calibration Standards** Calibration standards must be run with each batch of determinations using the same batch of reagents as for samples. In a series of 100 ml calibrated flasks dilute appropriate amounts of standard copper Solution C to cover the calibration range for the instrument (See Section E9). It is preferable to use at least five calibration standards, including the blank. (notes b and c).	(b) If the instrument can automatically prepare calibration standards, then this facility may be utilized. (c) It is advisable to analyse an AQC standard of a suitable concentration.
E8.5	**Electrothermal Atomization Atomic Absorption Stage** Set up the instrument according to the manufacturer's instructions for the determination of copper by electrothermal atomisation. (Note d). Each new tube should be conditioned as described in Section A6.2.	(d) Operating conditions are given for the two instruments used for this work, however, it is essential that each operator obtains optimum conditions for the particular instrument.
E8.6	Inject an appropriate volume of a calibration standard and ensure that the instrument gives a satisfactory response (Note e).	(e) An appropriate volume or nebulization time is usually in the range 5–30 µl or 2–10 s respectively, depending on the particular instrument employed. The same volume or nebulization time should be used for all subsequent samples, standards and blanks.
E8.7	Inject the blank and calibration standards (Note f).	(f) All injections must be carried out in duplicate. Repeat the determination if satisfactory agreement is not achieved.
E8.8	Inject a standard, a spiked sample and an unspiked sample (See Section A12.4) and note the responses (Note g).	(g) The recovery of the spike addition should meet the criteria given in Section A12. Any failure to do so should be investigated and overcome before proceeding with analysis of samples.
E8.9	Inject the samples and note the response (Note h).	(h) The preferred method of sample injection is by automatic sampler. Manual techniques can be used but are considered less precise.

Step	Procedure	Notes
E8.10	Instrumental drift should be checked at the end of each batch of samples (e.g. up to 10 samples). Inject both the blank and a suitable calibration standard.	
E8.11	Calculation of Results. The preferred method of calculation is by use of data processing facilities in conjunction with a 5 point calibration graph and check standards. (Note i).	(i) A suitable recorder can be used for manual calculation of results with appropriate adjustments for variations in sensitivity and blank value.

E9 Checking the Linearity of the Calibration Curve

The procedure given in this section must be carried out on at least two independent occasions before application of this method to any samples and regularly thereafter.

E9.1 Into a series of 100 ml calibrated flasks, pipette 5.0, 10.0, 15.0, 20.0 and 25.0 ml all ± 0.05 ml of standard copper solution C. Dilute to 100 ml with water and add 2.0 ± 0.05 ml of 50% V/V nitric acid and mix well. These solutions correspond to copper concentrations of 5, 10, 15, 20 and 25 μgl^{-1} respectively. Mix well.

E9.2 The calibration curve is normally linear to 25 μgl^{-1} copper (see Section 1.5) however, the linearity of the curve may depend on the type of instrumentation used and therefore linearity must be checked. If the calibration curve significantly departs from linearity, the top calibration standard chosen for step E8.4 should be the highest concentration on the acceptable portion of the calibration curve and the concentration range of the method should be adjusted accordingly.

E10 Change of Concentration Range of the Method

See the Antimony method, Section A10; but using Procedure E8.

E11 Sources of Error

See the Antimony method, Section A11.

E12 Checking the accuracy of Analytical Results

See the Antimony Method, Section A12.

F. Gallium in Raw and Potable Waters by Electrothermal Atomization Atomic Absorption Spectrophotometry

F1 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, (4) also published in this series).

F1.1	Substances determined	All forms of Gallium likely to occur in raw and potable waters.
F1.2	Type of sample	Raw and potable waters.
F1.3	Basis of the method	Direct analysis by electrothermal atomization atomic absorption spectrophotometry of sample pre-treated with acid. Magnesium nitrate is used as a matrix modifier.
F1.4	Range of applications	Up to 50 μgl^{-1}Ga
F1.5	Calibration curve	Typically linear to 50 μgl^{-1}
F1.6	Standard deviation	Gallium Concentration μgl^{-1}: 5; 45 Standard Deviation μgl^{-1}: 0.37 (n = 9)*; 0.43 (n = 9)
F1.7	Limit of detection	1.6 μgl^{-1} (n = 9)*.
F1.8	Sensitivity	12.6 pg for 1% absorption.
F1.9	Bias	Not Known.
F1.10	Interferences	See Section F3 and Table F1.
F1.11	Spiking recoveries	See Table F2.
F1.12	Time required for analysis	The total analytical time for 20 pretreated samples is approximately 2 hours. The corresponding operator time is approximately 45 minutes, assuming automatic data calculations.

*n = number of degrees of freedom

Note: See the General Comments on Instrument Performance.

Data obtained by the Yorkshire WA Sheffield Laboratory

Table F1 Effect of Other Substances on the Determination of Gallium

Other Substances	Concentration of other substances (mgl^{-1})	Other Substance added as	Effect in μgl^{-1} Gallium of other substances at a Gallium concentration of (μgl^{-1})	
			0.0	30.0
Sodium	300	sulphate	−0.35	−0.85
Calcium	300	nitrate	0.07	−1.23
Magnesium	100			
Iron	5	nitrate	0.50	−0.15
Aluminium	5			
Manganese	5			
Calcium	50	nitrate	0.22	−0.13
Magnesium	10			
Sodium	50	sulphate		
Chloride	100	acid		
Sulphate	150			

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

0.0 ± 0.70 at 0 $\mu g/l^{-1}$ Ga and
0.0 ± 0.91 at 30 $\mu g/l^{-1}$ Ga

Table F2 Spiking Recoveries on Potable Water Samples (30 μgl^{-1} spike)

Sample	Ca mgl^{-1}	Mg mgl^{-1}	Na mgl^{-1}	Conductivity μScm^{-1}	Unspiked μgl^{-1}	Spiked μgl^{-1}	%Recovery
1	7.84	2.71	5.10	111	−0.57	29.49	100.2
2	23.8	2.08	6.28	205	−0.34	29.02	97.9
3	8.20	1.68	3.23	109	−0.68	29.35	100.1
4	48.5	22.1	14.2	502	−0.14	29.35	98.3
5	46.4	21.0	13.6	377	0.14	29.35	97.4
6	44.6	6.29	12.3	374	−0.29	29.67	99.9

Table F3 Instrument Conditions

F3.1 *Instrument[1] Parameters*

Lamp Current (mA)	5
Slit Width (nm)	0.5
Slit Height	Reduced
Wavelength (nm)	287.4
Sample Introduction	Sampler Automixing
Measurement Time (sec)	2.0
Replicates	2
Background Correction	ON
Measurement Mode	Peak Area

F3.2 *Furnace[2] Parameters*

Step No.	Temperature (°C)	Time (sec)	Gas Flow (L min^{-1})	Read Command
1	100	5.0	3.0	No
2	250	10.0	3.0	No
3	350	45.0	3.0	No
4	1050	20.0	3.0	No
5	1050	10.0	3.0	No
6	1050	2.0	0.0	No
7	2600	0.8	0.0	Yes
8	2600	3.0	0.0	Yes
9	40	13.3	3.0	No

Tube Type	Pyrolytic coated L'vov platform
Sample Volume	20 µl
Matrix Modifier	5 µl of 10 gl^{-1} $Mg(NO_3)_2$ coinjected with the sample
Purge Gas	Argon

[1]Varian Spectra AA-40 Atomic Absorption Spectrophotometer
[2]Varian GTA-96 Graphite Tube Atomizer

F2 Principle

Gallium in potable waters is determined directly in acidified aqueous samples by electrothermal atomization atomic absorption spectrophotometry. Magnesium nitrate is used as a matrix modifier.

The conditions used are given in Table 3. It is essential that these conditions are used only as a guideline to determining optimum conditions for other instruments.

F3 Interferences

The effects of other substances vary considerably between electrothermal atomization atomic absorption spectrophotometers. It is essential that all analysts using this technique should check the interference effects of other substances for their particular instruments and decide whether any interference effects are important enough to consider means of overcoming the interference. For the instrument used in obtaining these performance characteristics (See Table F3), matrix modification was considered necessary (See Tables F1 and F2).

The effects of other substances on the determination of gallium are shown in Table F1.

F4 Hazards

See the Antimony Method, Section A4.

F5 Reagents

All reagents and standard solutions may be kept in glass or polyethylene bottles (see Section A6.3). Analytical reagent grade chemicals are suitable unless otherwise stated.

F5.1 Water

See the Antimony method, Section A5.1.

F5.2 Nitric Acid (d_{20} 1.42), atomic spectroscopy grade.

F5.3 10% V/V Nitric Acid

See the Antimony method, Section A5.3.

F5.4 50% V/V Nitric Acid

See the Antimony method, Section A5.4.

F5.5 Solution A: 1 ml contains 1 mg gallium

Dissolve 1 ± 0.005 g of gallium (99.9%) in 50 ml nitric acid (5 M) and 50 ml of water. Quantitatively transfer the solution to a 1 litre calibrated flask, dilute with water to the mark and mix well. The solution is stable for several months. Alternatively use a commercially available standard gallium solution.

F5.6 Solution B: 1 ml is equivalent to 10 μg Ga

Dilute 5 ± 0.01 ml of Solution A with water to 500 ml in a calibrated flask containing 10 ± 0.1 ml of 50% V/V nitric acid. This solution is stable for at least one month.

F5.7 Solution C: 1 ml is equivalent to 1 μg Ga

Dilute 10 ± ml of Solution B with water to 100 ml in a calibrated flask containing 2.0 ± 0.2 ml of 50% V/V nitric acid. This solution should be prepared immediately before use.

F5.8 Matrix Modifier Solution: Magnesium nitrate 10gl^{-1}

Weigh out 17.3 ± 0.5 g of magnesium nitrate hexahydrate, dissolve in approximately 500 ml of water and make up to 1 litre in a volumetric flask.

F6 Apparatus

See the Antimony method, Section A6.

F7 Sample Collection and Preservation

See the Antimony method, Section A7.

F8 Analytical Procedure

Read Section A4 on hazards before starting this procedure:

Step	Procedure	Notes
F8.1	**Pre-treatment Stage** Allow the acidified sample to stand for at least 24 hours (Note a).	(a) If the sample contains a significant amount of suspended matter, the bottle should be placed in an oven at 70°C for 24 hours. The bottle cap should be loosened slightly.
F8.2	**Blank Determination** A blank must be run with each batch (eg up to 10 samples) of determinations using the same batch of reagents as for the samples.	
F8.3	Add 2.0 ml ± 0.05 ml of 50% V/V nitric acid to 100 ml of water in a calibrated flask. Proceed with steps F8.5 to F8.11.	
F8.4	**Calibration Standards** Calibration standards must be run with each batch of determinations using the same batch of reagents as for the samples. In a series of 100 ml calibrated flasks dilute appropriate amounts of standard gallium Solution C to cover the calibration range for the instrument (See Section F9). It is preferable to use at least five calibration standards, including blank (Notes b and c).	(b) If the instrument can automatically prepare calibration standards, then this facility may be utilized. (c) It is advisable to analyse an AQC standard of a suitable concentration.

Step	Procedure	Notes
F8.5	**Electrothermal Atomization Atomic Absorption Stage** Set up the instrument according to the manufacturer's instructions for the determination of gallium by electrothermal atomization. (Note d). Each new tube should be conditioned as described in Section A6.2.	(d) Operating conditions are given for the instrument used for this work, however, it is essential that each operator obtains optimum conditions for the particular instrument.
F8.6	Inject an appropriate volume of a calibration standard and ensure that the instrument gives a satisfactory response (Note e).	(e) An appropriate volume or nebulization time is usually in the range 5–30 μl or 2–10 s respectively, depending on the particular instrument employed. The same volume or nebulization time should be used for all subsequent samples, standards and blanks.
F8.7	Inject the blank and calibration standards (Note f).	(f) All injections must be carried out in duplicate. Repeat the determination if satisfactory agreement is not achieved.
F8.8	Inject a standard, a spiked sample and an unspiked sample (See Section A12.4) and note the responses (Note g).	(g) The recovery of the spiked addition should meet the criteria given in Section A12. Any failure to do so should be investigated and overcome before proceeding with analysis of samples.
F8.9	Inject the samples and note the response (Note h).	(h) The preferred method of sample introduction is by automatic sampler. Manual techniques can be used but are considered less precise.
F8.10	Instrument drift should be checked for at the end of each batch of samples (eg up to 10 samples). Inject both the blank and a suitable calibration standard.	
F8.11	**Calculation of Results** The preferred method of calculation is by use of data processing facilities in conjunction with a 5 point calibration graph and check standards (Note i).	(i) A suitable recorder can be used for manual calculation of results with appropriate adjustments for variations in sensitivity and blank value.

F9 Checking the linearity of the Calibration Curve

The procedure given in this section must be carried out on at least two independent occasions before application of this method to any samples and regularly thereafter.

F9.1 Into a series of 100 ml calibrated flasks, pipette 1.0, 2.0, 3.0, 4.0 and 5.0 ml a 11 ± 0.05 ml of standard gallium solution C. Dilute to 100 ml with water. Mix well. Add 2.0 ± 0.05 ml of 50% v/v nitric acid. These solutions correspond to gallium concentrations of 10, 20, 30, 40 and 50 $\mu g l^{-1}$ respectively in the stabilized sample.

F9.2 The calibration curve is normally linear to 50 $\mu g l^{-1}$ gallium with the Varian Spectra AA-40 + GTA-96 instrument, however, the linearity of the curve may depend on the type of instrumentation used and therefore linearity must be checked. If the calibration curve significantly departs from linearity, the top calibration standard chosen for step F8.4 should be the highest concentration on the acceptable portion of the calibration curve and the concentration range of the method should be adjusted accordingly.

F10 Change of Concentration Range of the Method

See the Antimony method, Section A10; but using Procedure F8.

F11 Sources of Error

See the Antimony method, Section A11.

F12 Checking the accuracy of Analytical Results

See the Antimony method, Section A12.

G. Germanium in Raw and Potable Waters

G0 Note on the Determination and Occurrence of Germanium in Waters

Germanium compounds are very rarely found in natural waters, and then only at extremely low concentrations usually as mono or dimethyl substituted halides or oxides. These can be determined by extraction into organic solvents followed by gas chromatography and atomic absorption spectrophotometry similar to the determination of organotin compounds (Ref 12). The method which follows is intended for monitoring effluents from germanium producers of users and potable waters which might be abstracted below such a discharge.

G1 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, (4) also published in this series).

G1.1	Substances determined	All forms of germanium likely to occur in raw and potable waters. (But see note above)
G1.2	Type of sample	Raw and potable waters.
G1.3	Basis of the method	Direct analysis by electrothermal atomization atomic absorption spectrophotometry of sample pre-treated with acid. Calcium is added as a matrix modifier.
G1.4	Range of applications	Up to 100 $\mu g l^{-1}$ Ge
G1.5	Calibration curve	Typically linear to 100 $\mu g l^{-1}$
G1.6	Standard deviation	Germanium Concentration $\mu g l^{-1}$: 10 — Standard Deviation $\mu g l^{-1}$: 0.96 (n = 9)*; 90 — 2.26 (n = 9)
G1.7	Limit of detection	8.13 $\mu g l^{-1}$ (n = 9).
G1.8	Sensitivity	29.5 pg for 1% absorption.
G1.9	Bias	Not Known.
G1.10	Interferences	See Section G3 and Table G1.
G1.11	Spiking recoveries	See Table G2.
G1.12	Time required for analysis	The total analytical time for 20 pre-treated samples is approximately 2 hours. The corresponding operator time is approximately 45 minutes, assuming automatic data calculations.

*n = number of degrees of freedom.

Note: See the General Comments on Instrument Performance.

Data obtained by Yorkshire WA, Sheffield Laboratory.

Table G1 Effect of Other Substances on the Determination of Germanium

Other Substances	Concentration of other substances (mgl^{-1})	Other Substance added as	Effect in μgl^{-1} Germanium of other substances at a Germanium concentration of (μgl^{-1})	
			0.0	70.0
Sodium	300	sulphate	−0.17	−6.98
Calcium	300	nitrate	−0.34	−2.34
Magnesium	100	nitrate		
Iron	5			
Aluminium	5	nitrate	−0.84	−5.11
Manganese	5			
Calcium	50	nitrate		
Magnesium	10			
Sodium	50	sulphate	0.85	−32.79
Chloride	100	acid		
Sulphate	150			

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

0.0 ± 1.71 at 0 $\mu g/l^{-1}$ Ge and
0.0 ± 2.71 at 70 $\mu g/l^{-1}$ Ge

Table G2 Spiking Recoveries on Potable Water Samples (70 μgl^{-1} spike)

Sample	Ca mgl^{-1}	Mg mgl^{-1}	Na mgl^{-1}	Conductivity μScm^{-1}	Unspiked μgl^{-1}	Spiked μgl^{-1}	%Recovery
1	7.84	2.71	5.10	111	0.00	74.1	105.9
2	23.8	2.08	6.28	205	−0.41	72.1	103.6
3	8.20	1.68	3.23	109	0.82	73.7	104.1
4	48.5	22.1	14.2	502	0.82	72.9	103.0
5	46.4	21.0	13.6	377	−0.41	73.7	105.9
6	44.6	6.29	12.3	374	−0.82	70.8	102.3

Table G3 Instrument Conditions

G3.1 *Instrument[1] Parameters*

Lamp Current (mA)	6
Slit Width (nm)	0.5
Slit Height	Reduced
Wavelength (nm)	265.2
Sample Introduction	Sampler Automixing
Measurement Time (sec)	2.5
Replicates	2
Background Correction	ON
Measurement Mode	Peak Area

G3.2 *Furnace[2] Parameters*

Step No.	Temperature (°C)	Time (sec)	Gas Flow (L min^{-1})	Read Command
1	100	5.0	3.0	No
2	250	10.0	3.0	No
3	300	45.0	3.0	No
4	1250	20.0	3.0	No
5	1250	10.0	3.0	No
6	1250	2.0	0.0	No
7	2650	0.7	0.0	Yes
8	2650	4.0	0.0	Yes
9	40	13.3	3.0	No

Tube Type	Pyrolytic coated L'vov platform
Sample Volume	20 µl
Matrix Modifier	5 µl of 10 gl^{-1} $Ca(NO_3)_2$ (coinject with the sample)
Purge Gas	Argon

[1]Varian Spectra AA-40 Atomic Absorption Spectrophotometer
[2]Varian GTA-96 Graphite Tube Atomizer

G2 Principle

Germanium in raw and potable waters is determined directly in acidified aqueous samples by electrothermal atomization atomic absorption spectrophotometry.

The conditions used are given in Table G3. It is essential that these conditions are used only as a guideline to determining optimum conditions for other instruments.

G3 Interferences

The effects of other substances vary considerably between electrothermal atomization atomic absorption spectrophotometers. It is essential that all analysts using this technique should check the interference effects of other substances for their particular instruments and decide whether any interference effects are important enough to consider means of overcoming the interference. For the instrument used in obtaining these performance characteristics (See Table G3), matrix modification was considered necessary (See Tables G1 and G2).

The effects of other substances on the determination of germanium are shown in Table G1.

G4 Hazards

See the Antimony method, Section A4.

G5 Reagents

All reagents and standard solutions may be kept in glass or polyethylene bottles (see Section A6.3). Analytical reagent grade chemicals are suitable unless otherwise stated.

G5.1 Water

See the Antimony method, Section A5.1

G5.2 Nitric Acid (d_{20} 1.42), atomic spectroscopy grade.

G5.3 10% V/V Nitric Acid (wash solution)

See the Antimony method, Section A5.3

G5.4 50% V/V Nitric Acid

See the Antimony method, Section A5.4

G5.5 Solution A: 1 ml contains 1 mg germanium

Dissolve 144.0 ± 40.1 mg of germanium dioxide in 25 ± 0.5 ml sodium hydroxide (1 M). Quantitatively transfer the solution to a 100 ml calibrated flask, dilute with water to the mark and mix well. The solution is stable for at least several months. Alternatively, use a commercially available standard germanium solution.

G5.6 Solution B: 1 ml is equivalent to 10 μg Ge

Dilute 5 ± 0.01 ml of Solution A with water to 500 ml in a calibrated flask containing 10 ± 0.1 ml of 50% V/V nitric acid. This solution is stable for at least one month.

G5.7 Solution C: 1 ml is equivalent to 1 μg Ge

Dilute 10 ± 0.01 ml of Solution B with water to 100 ml in a calibrated flask containing 2.0 ± 0.2 ml of 50% V/V nitric acid. This solution should be prepared immediately before use.

G5.8 Matrix Modifier: 1 ml contains 10 mg calcium

Dissolve 59.0 ± 0.1 g of calcium nitrate, $Ca(NO_3)_2$, $4H_20$, in approximately 200 ml of water. Quantitatively transfer the solution to a 1 litre calibrated flask, dilute to the mark with water and mix well.

G6 Apparatus

See the Antimony method, Section A6.

G7 Sample Collection and Preservation

See the Antimony method, Section A7.

G8 Analytical Procedure

Read Section A4 on hazards before starting this procedure:

Step	Procedure	Notes
G8.1	**Pre-treatment Stage** Allow the acidified sample to stand for at least 24 hours (Note a).	(a) If the sample contains a significant amount of suspended matter, the bottle should be placed in an oven at 70°C for 24 hours. The bottle cap should be loosened slightly.
G8.2	**Blank Determination** A blank must be run with each batch (eg up to 10 samples) of determinations using the same batch of reagents as for the samples.	
G8.3	Add 2.0 ml ± 0.05 ml of 50% V/V nitric acid to 100 ml of water in a calibrated flask. Proceed with steps G8.5 to G8.11.	
G8.4	**Calibration Standards** Calibration standards must be run with each batch of determinations using the same batch of reagents as for the samples. In a series of 100 ml calibrated flasks dilute appropriate amounts of standard germanium Solution C to cover the calibration range for the instrument (See Section G9). It is preferable to use at least five calibration standards, including the blank (Notes b and c).	(b) If the instrument can automatically prepare calibration standards, then this facility may be utilized. (c) It is advisable to analyse an AQC standard of a suitable concentration.

Step	Procedure	Notes
G8.5	**Electrothermal Atomization Atomic Absorption Stage** Set up the instrument according to the manufacturer's instructions for the determination of germanium by electrothermal atomization. (Note d). Each new tube should be conditioned as described in Section A6.2.	(d) Operating conditions are given for the instrument used for this work, however, it is essential that each operator obtains optimum conditions for the particular instrument.
G8.6	Inject an appropriate volume of a calibration standard and ensure that the instrument gives a satisfactory response (Note e).	(e) An appropriate volume or nebulization time is usually in the range 5–30 μl or 2–10 s respectively, depending on the particular instrument employed. The same volume or nebulization time should be used for all subsequent samples, standards and blanks.
G8.7	Inject the blank and calibration standards (Note f).	(f) All injections must be carried out in duplicate. Repeat the determination if satisfactory agreement is not achieved.
G8.8	Inject a standard, a spiked sample and an unspiked sample (See Section A12.4) and note the responses (Note g).	(g) The recovery of the spiked addition should meet the criteria given in Section A12. Any failure to do so should be investigated and overcome before proceeding with analysis of samples.
G8.9	Inject the samples and note the response (Note h).	(h) The preferred method of sample injection is by automatic sampler. Manual techniques can be used but are less precise.
G8.10	Instrument drift should be checked for at the end of each batch of samples (eg up to 10 samples). Inject both the blank and a suitable calibration standard. (Note h).	
G8.11	**Calculation of Results** The preferred method of calculation is by use of data processing facilities in conjunction with a 5 point calibration graph and check standards (Note i).	(i) A suitable recorder can be used for manual calculation of results with appropriate adjustments for variations in sensitivity and blank value.

G9 Checking the linearity of the Calibration Curve

The procedure given in this section must be carried out on at least two independent occasions before application of this method to any samples and regularly thereafter.

G9.1 Into a series of 100 ml calibrated flasks, pipette 2.0, 4.0, 6.0, 8.0 and 10.0 ml all ± 0.05 ml of standard germanium solution C. Dilute to 100 ml with water.

Add 2.0 ± 0.05 ml of 50% v/v nitric acid. Mix well. These solutions correspond to germanium concentrations of 20, 40, 60, 80 and 100 μgl^{-1} respectively in the stabilized sample.

G9.2 The calibration curve is normally linear to 100 μgl^{-1} germanium for the Varian Spectra AA–40 + GTA–96 instrument, however, the linearity of the curve may depend on the type of instrumentation used and therefore linearity must be checked. If the calibration curve significantly departs from linearity, the top calibration standard chosen for step G8.4 should be the highest concentration on the acceptable portion of the calibration curve and the concentration range of the method should be adjusted accordingly.

G10 Change of Concentrations Range of the Method

See the Antimony method, Secton A10; but use procedure G8.

G11 Sources of Error

See the Antimony method, Section A11.

G12 Checking the accuracy of Analytical Results

See the Antimony method, Section A12.

H. Indium in Raw and Potable Waters

H1 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, (4) also published in this series).

H1.1	Substances determined	All forms of indium likely to occur in raw and potable waters.
H1.2	Type of sample	Raw and potable waters.
H1.3	Basis of the method	Direct analysis by electrothermal atomization atomic absorption spectrophotometry of sample pre-treated with acid. Magnesium nitrate is used as a matrix modifer
H1.4	Range of applications	Up to 50 μgl^{-1} In
H1.5	Calibration curve	Typically linear to 50 μgl^{-1}
H1.6	Standard deviation	Indium Concentration μgl^{-1}: 5; 45 Standard Deviation μgl^{-1}: 0.22 (n = 9)*; 0.67 (n = 9)
H1.7	Limit of detection	1.67 μgl^{-1} (n = 9).
H1.8	Sensitivity	13.8 pg for 1% absorption.
H1.9	Bias	Not Known.
H1.10	Interferences	See Section H3 and Table H1.
H1.11	Spiking recoveries	See Table H2.
H1.12	Time required for analysis	The total analytical time for 20 pre-treated samples is approximately 2 hours. The corresponding operator time is approximately 45 minutes, assuming automatic data calculations.

*n = number of degrees of freedom.

Note: See the General Comments on Instrument Performance.

Data obtained by Yorkshire WA Sheffield Laboratory

Table H1 Effect of Other Substances on the Determination of Indium

Other Substances	Concentration of other substances (mgl^{-1})	Other Substance added as	Effect in μgl^{-1} Indium of other substances at a Indium concentration of (μgl^{-1})	
			0.0	30.0
Sodium	300	Sulphate	0.70	−0.65
Calcium	300	nitrate	0.00	−1.10
Magnesium	100			
Iron	5			
Aluminium	5	nitrate	−0.70	−0.22
Manganese	5			
Calcium	50	nitrate		
Magnesium	10		0.08	−0.93
Sodium	50	Sulphate		
Chloride	100	acid		
Sulphate	150			

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

0.0 ± 0.72 at 0 μgl^{-1} In and
0.0 ± 0.96 at 30 μgl^{-1} In

Table H2 Spiking Recoveries on Potable Water Samples (30 $\mu g1^{-1}$ spike)

Sample	Ca mgl^{-1}	Mg mgl^{-1}	Na mgl^{-1}	Conductivity μScm^{-1}	Unspiked μgl^{-1}	Spiked μgl^{-1}	%Recovery
1	7.84	2.71	5.10	111	−0.47	29.53	100.0
2	23.8	2.08	6.28	205	−0.31	30.00	101.0
3	8.20	1.68	3.23	109	−0.63	29.85	101.6
4	48.5	22.1	14.2	502	0.00	30.00	100.0
5	46.4	21.0	13.6	377	0.16	29.40	97.5
6	44.6	6.29	12.3	374	−0.16	29.40	98.5

Table H3 Instrument Conditions

H3.1 Instrument[1] Parameters

Lamp Current (mA)	5
Slit Width (nm)	0.5
Slit Height	Reduced
Wavelength (nm)	303.9
Sample Introduction	Sampler Automixing
Measurement Time (sec)	2.0
Replicates	2
Background Correction	ON
Measurement Mode	Peak Area

H3.2 Furnace[2] Parameters

Step No.	Temperature (°C)	Time (sec)	Gas Flow (L/min^{-1})	Read Command
1	100	5.0	3.0	No
2	250	10.0	3.0	No
3	300	45.0	3.0	No
4	1050	20.0	3.0	No
5	1050	10.0	3.0	No
6	1050	2.0	0.0	No
7	2200	0.7	0.0	Yes
8	2200	4.0	0.0	Yes
9	2600	2.0	3.0	No
10	40	13.3	3.0	No

Tube Type Pyrolytic coated L'vov platform
Sample Volume 20 µl
Matrix Modifier 5 µl of 10 gl^{-1} $Mg(NO_3)_2$
Purge Gas Argon

1 Varian Spectra AA-40 Atomic Absorption Spectrophotometer
2 Varian GTA-96 Graphite Tube Atomizer

H2 Principle

Indium in raw and potable waters is determined directly in acidified aqueous samples by electrothermal atomization atomic absorption spectrophotometry. Magnesium nitrate is used as a matrix modifier.

The conditions used are given in Table H3. It is essential that these conditions are used only as a guideline to determining optimum conditions for other instruments.

H3 Interferences

The effects of other substances vary considerably between electrothermal atomization atomic absorption spectrophotometers. It is essential that all analysts using this technique should check the interference effects of other substances for their particular instruments and decide whether any interference effects are important enough to consider means of overcoming the interference. For the instrument used in obtaining these performance characteristics (See Table H3), matrix modification was considered necessary (See Tables H1 and H2).

The effects of other substances on the determination of indium are shown in Table H1.

H4 Hazards

See the Antimony method, Section A4.

H5 Reagents

All reagents and standard solutions may be kept in glass or polyethylene bottles (see Section A6.3). Analytical reagent grade chemicals are suitable unless otherwise stated.

H5.1 Water

See the Antimony Method, Section A5.1.

H5.2 Nitric Acid (d_{20} 1.42), atomic spectroscopy grade.

H5.3 10% V/V Nitric Acid (wash solution)

See the Antimony method, Section A5.3.

H5.4 50% V/V Nitric Acid

See the Antimony method, Section A5.4

H5.5 Solution A: 1 ml contains 1 mg indium

Dissolve 1.000 ± 0.005 g of indium metal in 20 ml nitric acid (d_{20} 1.42) and 30 ml of water. Quantitatively transfer the solution to a 1 litre calibrated flask, dilute with water to the mark and mix well. The solution is stable for several months. Alternatively use a commercially available standard indium solution.

H5.6 Solution B: 1 ml is equivalent to 10 μg In

Dilute 5 ± 0.01 ml of Solution A with water to 500 ml in a calibrated flask containing 10 ± 0.1 ml of 50% V/V nitric acid. This solution is stable for one month.

H5.7 Solution C: 1 ml is equivalent to 1 μg In

Dilute 10 ± 0.01 ml of Solution B with water to 100 ml in a calibrated flask containing 2.0 ± 0.2 ml of 50% V/V nitric acid. This solution should be prepared immediately before use.

H5.8 Matrix Modifier: magnesium Nitrate $10gl^{-1}$

Weigh out 17.3 ± 0.5 g of magnesium nitrate hexahydrate, dissolve in approximately 500 ml of water and make up to 1 litre in a volumetric flask.

H6 Apparatus

See the Antimony method, Section A6.

H7 Sample Collection and Preservation

See the Antimony method, Section A7.

H8 Analytical Procedure

Read Section A4 on hazards before starting this procedure:

Step	Procedure	Notes
H8.1	**Pre-treatment Stage** Allow the acidified sample to stand for at least 24 hours (Note a).	(a) If the sample contains a significant amount of suspended matter, the bottle should be placed in an oven at 70°C for 24 hours. The bottle cap should be loosened slightly.
H8.2	**Blank Determination** A blank must be run with each batch (eg up to 10 samples) of determinations using the same batch of reagents as for the samples.	
H8.3	Add 2.0 ml ± 0.05 ml of 50% V/V nitric acid to 100 ml of water in a calibrated flask. Proceed with steps H8.5 to H8.11.	
H8.4	**Calibration Standards** Calibration standards must be run with each batch of determinations using the same batch of reagents as for the samples. In a series of 100 ml calibrated flasks dilute appropriate amounts of standard indium Solution C to cover the calibration range for the instrument (See Section H9). It is preferable to use at least five calibration standards, including the blank (Notes b and c).	(b) If the instrument can automatically prepare calibration standards, then this facility may be utilized. (c) It is advisable to analyse an AQC standard of a suitable concentration.

Step	Procedure	Notes
H8.5	**Electrothermal Atomization Atomic Absorption Stage** Set up the instrument according to the manufacturer's instructions for the determination of indium by electrothermal atomization. (Note d). Each new tube should be conditioned as described in Section A6.2.	(d) Operating conditions are given for the instrument used for this work, however, it is essential that each operator obtains optimum conditions for the particular instrument.
H8.6	Inject an appropriate volume of a calibration standard and ensure that the instrument gives a satisfactory response (Note e).	(e) An appropriate volume or nebulization time is usually in the range 5–30 μl or 2–10 s respectively, depending on the particular instrument employed. The same volume or nebulization time should be used for all subsequent samples, standards and blanks.
H8.7	Inject the blank and calibration standards (Note f).	(f) All injections must be carried out in duplicate. Repeat the determination if satisfactory agreement is not achieved.
H8.8	Inject a standard, a spiked sample and an unspiked sample (See Section A12.4) and note the responses (Note g).	(g) The recovery of the spiked addition should meet the criteria given in Section A12. Any failure to do so should be investigated and overcome before proceeding with analysis of samples.
H8.9	Inject the samples and note the responses (Note h).	(h) The preferred method of sample injection is by automatic sampler. Manual techniques can be used but are less precise.
H8.10	Instrument drift should be checked for at the end of each batch of samples (eg up to 10 samples). Inject both the blank and a suitable calibration standard. (Note h).	
H8.11	**Calculation of Results** The preferred method of calculation is by use of data processing facilities in conjunction with a 5 point calibration graph and check standards (Note i).	(i) A suitable recorder can be used for manual calculation of results with appropriate adjustments for variations in sensitivity and blank value.

H9 Checking the linearity of the Calibration Curve

The procedure given in this section must be carried out on at least two independent occasions before application of this method to any samples and regularly thereafter.

H9.1 Into a series of 100 ml calibrated flasks, pipette 1.0, 2.0, 3.0, 4.0 and 5.0 ml all ± 0.05 ml of standard indium solution C. Dilute to 100 ml with water. Mix well. Add 2.0 ± 0.05 ml of 50% v/v nitric acid. These solutions correspond to indium concentrations of 10, 20, 30, 40 and 50 $\mu g l^{-1}$ respectively in the stabilized sample.

H9.2 The calibration curve is normally linear to 50 $\mu g l^{-1}$ indium for the Varian Spectra AA-40 + GTA-96 instrument, however, the linearity of the curve may depend on the type of instrumentation used and therefore linearity must be checked. If the calibration curve significantly departs from linearity, the top calibration standard chosen for step H8.4 should be the highest concentration on the acceptable portion of the calibration curve and the concentration range of the method should be adjusted accordingly.

H10 Change of Concentrations Range of the Method

See the Antimony method, Section A10; but use procedure H8.

H11 Sources of Error

See the Antimony method, Section H11.

H12 Checking the accuracy of Analytical Results

See the Antimony Method, Section A12.

I Nickel in Raw and Potable Waters

I1 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, (4) also published in this series).

I1.1	Substances determined	All forms of Nickel likely to occur in raw and potable waters.
I1.2	Type of sample	Raw and potable waters.
I1.3	Basis of the method	Direct analysis by electrothermal atomization atomic absorption spectrophotometry of samples pre-treated with acid.
I1.4	Range of application	Up to 20 μgl^{-1} Ni.
I1.5	Calibration curve	Perkin Elmer:— typically linear to 20 μgl^{-1} Ni. †Instrumentation Laboratory:— typically linear to 16 μgl^{-1} Ni.
I1.6	Standard deviation	See table below
I1.7	Limit of detection	Perkin Elmer:— 1.62 μgl^{-1} Ni (n = 9). Instrumentation Laboratory:— 0.82 μgl^{-1} Ni (n = 9).
I1.8	Sensitivity	Perkin Elmer:— 13 pg for 1% absorption. Instrumentation Laboratory:— 2.3 pg for 1% absorption.
I1.9	Bias	Not known.
I1.10	Interferences	See Section I3 and Table I1.
I1.11	Spiking recoveries	See Table I2.
I1.12	Time required for analysis	The total analytical time for 20 pre-treated samples is approximately 2 hours for both instruments. The corresponding operator time is approximately 45 minutes, assuming automatic data calculation.

Instrument	Nickel Concentration μgl^{-1}	Standard Deviation μgl^{-1}
PE	2	0.34 (n = 9)*
	18	0.25 (n = 9)
IL	2	0.13 (n = 11)
	18	0.43 (n = 13)

Note See the General Comment on Instrument Performancce

*n = number of degrees of freedom.
† = now Thermo Electron Ltd.

Data obtained by Yorkshire WA, Sheffield Laboratory.

Table I1 Effect of Other Substances on the Determination of Nickel

Other Substance	Concentration of other Substance (mgl^{-1})	Other Substance added as	Effect in μgl^{-1} Nickel of other substance at a Nickel concentration of (μgl^{-1})			
			PE		IL	
			0.0	12.0	0.0	10.0
Calcium	300	nitrate	−0.15	−1.06	−0.14	0.09
Magnesium	100	nitrate	−0.20	−0.28	−0.17	1.01
Sodium	300	nitrate	−0.06	−0.52	−0.03	0.23
Potassium	20	nitrate	−0.17	−0.13	0.20	0.30
Calcium + Magnesium	300 + 100	nitrate	0.06	−0.16	0.00	1.28
Chloride	500	acid	−0.26	−0.12	0.22	0.24
Sulphate	300	acid	−0.16	−0.14	0.19	0.06
Silicon	30	ammonium fluorosilicate	−0.12	0.02	−0.33	0.10
Iron + Aluminium + Manganese	5 + 5 + 5	nitrate	−0.14	0.19	0.00	0.24
Copper + Zinc	20 + 20	nitrate	0.14	0.27	0.37	0.90
Flouride	10	sodium fluoride	−0.10	−0.22	−0.36	−0.34
Phosphate	10	acid	−0.13	0.07	0.00	0.01
Calcium + Magnesium + Sodium + Chloride + Sulphate	100 + 20 + 100 + 200 + 300	nitrate + acid	−0.06	−0.29	−0.10	0.07

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

Perkin Elmer:—
0.0 ± 0.26 at 0 μgl^{-1} Ni and
0.0 ± 0.32 at 12 μgl^{-1} Ni.

Instrumentation Laboratory:—
0.0 ± 0.41 at 0 μgl^{-1} Ni and
0.0 ± 0.31 at 10 μgl^{-1} Ni.

Table I2 Spiking Recoveries on Potable Water Samples (12 μgl^{-1} spike for PE and 10 μgl^{-1} spike for IL)

Sample	Ca mgl^{-1}	Mg mgl^{-1}	Na mgl^{-1}	Conductivity μScm^{-1}	Perkin Elmer Unspiked μgl^{-1}	Spiked μgl^{-1}	%Recovery
1	55.0	19.0	12.9	488	2.48	14.6	101.0
2	57.0	22.4	10.8	476	2.53	15.01	104.0
3	56.3	22.4	10.7	485	1.86	13.7	98.7
4	11.8	3.18	8.30	145	0.09	12.0	99.3
5	12.1	3.38	8.37	146	0.56	12.8	102.0
6	13.8	3.04	8.64	153	0.36	12.1	97.8

Sample	Ca mgl^{-1}	Mg mgl^{-1}	Na mgl^{-1}	Conductivity μScm^{-1}	Instrumentation Laboratory Unspiked μgl^{-1}	Spiked μgl^{-1}	%Recovery
1	44.0	18.0	10.9	405	0.50	10.6	101.0
2	45.0	18.6	13.6	456	0.87	10.8	99.3
3	46.3	19.7	15.4	466	0.82	10.9	100.8
4	7.5	2.5	8.6	116	0.16	10.1	99.4
5	8.2	1.4	6.4	105	0.34	10.3	99.6
6	7.2	2.1	8.2	110	0.05	10.2	101.5

Table I3 Instrument Conditions

Perkin Elmer [1]

Step	1	2	3	4
Temp °C	140	1000	2300	2500
Ramp (s)	10	10	0	0
Hold (s)	20	20	5	5
Read			/	

Internal flow (ml min^{-1}) = 50
Integration Time (s) = 4
Sample volume (μl) = 25
Tube Type = Pyro-coated
Mode = Peak Height
Matrix Modification = None
Injection = Auto:— AS40
Wavelengh (nm) = 232.0
Band Width (nm) = 0.2
Lamp Current (mA) = 7
Deuterium Arc
Background Correction = Yes

Instrumentation Laboratories [2]

Step	1	2	3	4	5	6
Temp °C	0	120	800	1200	2400	2400
Time (s)	0	5	15	15	0	10
Read					/	

Internal flow (1 min^{-1}) = 1.3
Integration Time (s) = 5
Delay (s) = 10
Deposit (s) = 5
Tube Type = DAC
Mode = Peak Area
Matrix Modification = None
Injection = Auto:— IL254
Wavelength (nm) = 232.0
Band Width (nm) = 0.3
Lamp Current (mA) = 3
High Voltage = 700
Deuterium Arc
Background Correction = Yes

[1] Atomic Absorption Spectrophotometer : PE 272 (single beam)
Electrothermal Atomizer : HGA 500

[2] Atomic Absorption Spectrophotometer : IL 451 (double beam)
Electrothermal Atomizer : IL 655

I2 Principle

Nickel in raw and potable waters is determined directly in acidified aqueous samples by electrothermal atomization atomic absorption spectrophotometry. Matrix modification has not been found to be necessary.

The conditions used are given for both instruments in Table I3. It is essential that these conditions are used only as a guideline to determining optimum conditions for other instruments.

I3 Interferences

The effects of other substances vary considerably between electrothermal atomization atomic absorption spectrophotometers. It is essential that each analyst using this technique should check the interference effects of other substances for his particular instrument and decide whether any effects are important enough to consider means of overcoming the interference. For the two instruments used to obtain the test data (See Table I3), no matrix modification was considered necessary (See Tables I1 and I2).

The effects of other substances on the determination of nickel are shown in Table I1.

I4 Hazards

See the Antimony method, Section A4.

I5 Reagents

All reagents and standard solutions may be kept in glass or polyethylene bottles (See Section A6.3). Analytical reagent grade chemicals are suitable unless otherwise stated.

I5.1 Water

See the Antimony method, Section A5.1.

I5.2 Nitric Acid (d_{20} 1.42), atomic spectroscopy grade.

I5.3 10% V/V Nitric Acid (wash solution)

See the Antimony method, Section A5.3

I5.4 50% V/V Nitric Acid

See the Antimony method, Section A5.4.

I5.5 Solution A: 1 ml contains 1 mg nickel

Weigh 1.000 ± 0.005 g of nickel foil (greater that 99.9% purity), and dissolve it in a mixture of 65 ± 2 ml of nitric acid (d_{20} 1.42) and 65 ml of water, carrying out the operation in a fume cupboard. Quantitatively transfer the solution to a 1 litre calibrated flask, dilute with water to the mark and mix well. The solution is stable for several months. Alternatively, use a commercially available standard nickel solution.

I5.6 Solution B: 1 ml is equivalent to 10 μg Ni

Dilute 5 ± 0.01 ml of Solution A with water to 500 ml in a calibrated flask containing 10 ± 0.1 ml of 50% V/V nitric acid. This solution is stable for at least one month.

I5.7 Solution C: 1 ml is equivalent to 0.1 μg Ni

Dilute 10 ± 0.01 ml of Solution B with water to 1 litre in a calibrated flask containing 20 ± 0.2 of 50% V/V nitric acid. Prepare immediately before use.

I6 Apparatus

See the Antimony method, Section A6.

I7 Sample Collection and Preservation

See the Antimony method, Section A7. See also Ref 6.

Read Section A4 on hazards before starting this procedure:

Step	Procedure	Notes
I8.1	**Pre-treatment Stage** Allow the acidified sample to stand for at least 24 hours (Note a).	(a) If the sample contains a significant amount of suspended matter, the bottle should be placed in an oven at 70°C for 24 hours. The bottle cap should be loosened slightly.
I8.2	**Blank Determination** A blank must be run with each batch (eg up to 10 samples) of determinations using the same batch of reagents as for the samples.	
I8.3	Add 2.0 ml ± 0.05 ml of 50% V/V nitric acid to 100 ml of water in a calibrated flask. Proceed with steps I8.5 to I8.11.	
I8.4	**Calibration Standards** Calibration standards must be run with each batch of determinations using the same batch of reagents as for samples. In a series of 100 ml calibrated flasks dilute appropriate amounts of standard nickel Solution C to cover the calibration range for the instrument (See Section I9). It is preferable to use at least five calibration standards, including the blank.	(b) If the instrument can automatically prepare calibration standards, then this facility may be utilized. (c) It is advisable to analyse an AQC standard of a suitable concentration.
I8.5	**Electrothermal Atomization Atomic Absorption Stage** Set up the instrument according to the manufacturer's instructions for the determination of nickel by electrothermal atomization. (Note d). Each new tube should be conditioned as described in Section A6.2.	(d) Operating conditions are given for the two instruments used for this work, however, it is essential that each operator obtains optimum conditions for the particular instrument.
I8.6	Inject an appropriate volume of a calibration standard and ensure that the instrument gives a satisfactory response (Note e).	(e) An appropriate volume or nebulization time is usually in the range 5–30 μl or 2–10 s respectively, depending on the particular instrument employed. The same volume or nebulization time should be used for all subsequent samples, standards and blanks.
I8.7	Inject the blank and calibration standards (Note f).	(f) All injections must be carried out in duplicate. Repeat the determination if satisfactory agreement is not achieved.
I8.8	Inject a standard, a spiked sample and an unspiked sample (See Section A12.4) and note the responses (Note g).	(g) The recovery of the spike addition should meet the criteria given in Section A12. Any failure to do so should be investigated and overcome before proceeding with analysis of samples.
I8.9	Inject the samples and note the response (Note h).	(h) The preferred method of sample injection is by automatic sampler. Manual techniques can be used but are considered less precise.

Step	Procedure	Notes
I8.10	Instrument drift should be checked for at the end of each batch of samples (eg up to 10 samples). Inject both the blank and a suitable calibration standard.	
I8.11	**Calculation of Results**	
	The preferred method of calculation is by use of data processing facilities in conjunction with a 5 point calibration graph and check standards. (Note i)	(i) A suitable recorder can be used for manual calculation of results with appropriate adjustments for variations in sensitivity and blank value.

I9 Checking the Linearity of the Calibration Curve

The procedure given in this section must be carried out on at least two independent occasions before application of this method to any samples and regularly thereafter.

I9.1 Into a series of 100 ml calibrated flasks, pipette 4.0, 8.0, 12.0, 16.0 and 20.0 ml all ± 0.05 ml of standard nickel solution C. Dilute to 100 ml with water and add 2.0 ± 0.05 ml of 50% V/V nitric acid and mix well. These solutions correspond to nickel concentrations of 4, 8, 12, 16 and 20 μg^{-1} respectively in the stabilized sample.

I9.2 The calibration curve is normally linear to 16 or 20 μgl^{-1} nickel (see Section 1.5) however, the linearity of the curve may depend on the type of instrumentation used and therefore linearity must be checked. If the calibration curve significantly departs from linearity, the top calibration standard chosen for step I8.4 should be the highest concentration on the linear portion of the calibration curve and the concentration range of the method should be adjusted accordingly.

I10 Change of Concentration Range of the Method

See the Antimony method, Section A10; but use Procedure I8.

I11 Sources of Error

See the Antimony Method, Section A11.

I12 Checking the accuracy of Analytical Results

See the Antimony Method, Section A12

J Silver in Raw and Potable Waters

J1 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, (4) also published in this series).

J1.1	Substances determined	All forms of silver likely to occur in raw and potable waters.
J1.2	Type of sample	Raw and potable waters.
J1.3	Basis of the method	Direct analysis by electrothermal atomization atomic absorption spectrophotometry of samples pre-treated with acid. Use of Phosphoric Acid as a matrix modifier is necessary with some but not all makes of instrument.
J1.4	Range of application	Up to 20 μgl^{-1} Ag.
J1.5	Calibration curve	Perkin Elmer:— typically linear to 15 μgl^{-1} Ag. †Instrumentation Laboratory:— typically linear to 15 μgl^{-1} Ag.
J1.6	Standard deviation	Instrument / Silver Concentration μgl^{-1} / Standard Deviation μgl^{-1} PE 1.5 0.12 (n = 9)* 13.5 0.20 (n = 9) IL 1.5 0.08 (n = 9) 13.5 0.24 (n = 9)
J1.7	Limit of detection	Perkin Elmer:— 0.41 μgl^{-1} Ag (n = 10). Instrumentation Laboratory:— 0.37 μgl^{-1} Ag (n = 9).
J1.8	Sensitivity	Perkin Elmer:— 2.90 pg for 1% absorption. Instrumentation Laboratory:— 5.08 g for 1% absorption.
J1.9	Bias	Not known.
J1.10	Interferences	See Section J3 at Table J1.
J1.11	Spiking recoveries	See Table J2.
J1.12	Time required for analysis	The total analytical time for 20 pre-treated samples is approximately 2 hours for both instruments. The corresponding operator time is approximately 45 minutes, assuming automatic data calculation.

Note See the General Comment on Instrument Performance

*n = number of degrees of freedom.
† = now Thermo Electron Ltd.

Data obtained by Yorkshire WA, Sheffield Laboratory.

Table J1 Effect of Other Substances on the Determination of Silver

Other Substance	Concentration of other Substance (mgl^{-1})	Other Substance added as	Effect in μgl^{-1} Silver of other substance at a Silver concentration of (μgl^{-1})			
			PE		IL	
			0.0	13.5	0.0	13.5
Calcium	300	nitrate	0.01	−0.48	−0.04	−0.53
Magnesium	100	nitrate	−0.02	−0.18	0.00	−0.06
Sodium	300	nitrate	−0.09	−1.63	−0.01	−0.23
Potassium	20	nitrate	−0.05	0.07	0.10	−0.53
Calcium / Magnesium	300 / 100	nitrate	−0.05	0.09	−0.00	0.48
Chloride	500	acid	−0.05	−1.03	0.05	−0.17
Sulphate	300	acid	−0.02	0.12	0.03	−0.02
Silicon	30	ammonium fluorosilicate	−0.08	−0.29	−0.16	−1.81
Iron / Aluminium / Manganese	5 / 5 / 5	nitrate	0.02	−0.52	0.03	0.17
Copper / Zinc	20 / 20	nitrate	−0.04	0.00	−0.28	−0.06
Flouride	0	sodium fluoride	−0.07	−0.11	−0.01	−0.34
Phosphate	10	acid	−0.01	0.26	0.01	−0.13
Calcium / Magnesium / Sodium / Chloride / Sulphate	100 / 20 / 100 / 200 / 300	nitrate / acid	0.05	−2.11	−0.01	−0.44

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

Perkin Elmer:—
0.0 ± 0.10 at 0 μgl^{-1} Ag and
0.0 ± 0.54 at 13.5 μ gl^{-1} Ag.

Instrumentation Laboratory:—
0.0 ± 0.34 at 0 μgl^{-1} Ag and
0.0 ± 0.54 at 13.5 μgl^{-1} Ag.

Table J2 Spiking Recoveries on Potable Water Samples (13.5 μgl^{-1} spike for both PE and IL Instrument)

Sample	Ca mgl^{-1}	Mg mgl^{-1}	Na mgl^{-1}	Conductivity $uScm^{-1}$	Perkin Elmer Unspiked ugl^{-1}	Spiked ugl^{-1}	% Recovery
1	55.0	19.0	12.9	488	0.05	13.0	95.9
2	57.0	22.4	10.8	476	−0.04	12.9	95.9
3	56.3	22.4	10.7	485	−0.03	13.3	98.7
4	11.8	3.18	8.30	145	−0.08	13.1	97.6
5	12.1	3.38	8.37	146	−0.04	13.3	98.8
6	13.8	3.04	8.64	153	−0.06	13.3	99.0

Sample	Ca mgl^{-1}	Mg mgl^{-1}	Na mgl^{-1}	Conductivity $uScm^{-1}$	Instrumentation Laboratory Unspiked ugl^{-1}	Spiked ugl^{-1}	% Recovery
1	55.0	19.0	12.9	488	0.14	13.1	96.0
2	57.0	22.4	10.8	476	0.04	13.3	98.2
3	56.3	22.4	10.7	485	0.14	12.9	94.5
4	11.8	3.18	8.30	145	−0.01	13.5	100.1
5	12.1	3.38	8.37	146	0.12	13.7	100.6
6	13.8	3.04	8.64	153	−0.04	13.5	100.3

Table J3 Instrument Conditions

Perkin Elmer [1]

Step	1	2	3	4
Temp °C	140	825	1900	2500
Ramp (s)	15	10	0	1
Hold (s)	25	20	5	5
Read			/	

Internal flow (ml min^{-1}) = 10

Integration Time (s) = 4
Sample volume (μl) = 20
Tube Type = Pyro-coated L'vov platform
Mode = Peak Area
Matrix Modification (inject with sample) = 5 μl of 0.5% Phosphoric Acid
Injection = Auto:— AS40
Wavelengh (nm) = 328.1
Band Width (nm) = 0.7 Alt
Lamp Current (mA) = 4
Deuterium Arc
Background Correction = Yes

Instrumentation Laboratories [2]

Step	1	2	3	4	5	6
Temp °C	0	130	350	600	2000	2400
Time (s)	0	5	10	10	0	5
Read					/	

Internal flow (l min^{-1}) = 1.3

Integration Time (s) = 4
Delay (s) = 7
Deposit (s) = 2
Tube Type = DAC pyro-coated
Mode = Peak Area
Matrix Modification = None
Injection = Auto:— IL254
Wavelength (nm) = 328.1
Band Width (nm) = 1.0
Lamp Current (mA) = 1.5
High Voltage (V) = 460
Deuterium Arc
Background Correction = Yes

[1] Atomic Absorption Spectrophotometer : PE 272 (single beam)
Electrothermal Atomizer : HGA 500

[2] Atomic Absorption Spectrophotometer : IL 451 (double beam)
Electrothermal Atomizer : IL 655

J2 Principle

Silver in raw and potable waters is determined directly in acidified aqueous samples by electrothermal atomization atomic absorption spectrophotometry. Phosphoric acid is used as a matrix modifier with one instrument. No matrix modifier is needed with another model of different manufacture.

The conditions used are given for both instruments in Table J3. It is essential that these conditions are used only as a guideline to determining optimum conditions for other instruments.

J3 Interference

The effects of other substances vary considerably between electrothermal atomization atomic adsorption spectrophotometers. It is essential that each analyst using this technique should check the interference effects of other substances for his particular instrument and decide whether any effects are important enough to consider means of overcoming the interference. For the two instruments used to obtain the test data (See Table J3), matrix modification was considered necessary for the Perkin Elmer only (See Tables J1 and J2). The use of phosphate as a matrix modifier did not overcome the two significant interferences observed on the Instrumentation Laboratory instrument. Thus, no matrix modification was thought necessary for this instrument.

The effects of other substances on the determination of silver is shown in Table J1.

J4 Hazards

See the Antimony method, Section A4.

J5 Reagents

All reagents and standard solutions should be stored in polyethylene bottles (See Section A6.3). Analytical reagent grade chemicals are suitable unless otherwise stated.

J5.1 Water

See the Antimony method, Section A5.1.

J5.2 Nitric Acid (d_{20} 1.42), atomic spectroscopy grade.

J5.3 10% V/V Nitric Acid

See the Antimony method, Section A5.3.

J5.4 50% V/V Nitric Acid

See the Antimony method, Section A5.4.

J5.5 Solution A: 1 ml contains 1 mg silver

Weigh 1.575 ± 0.005 g of anhydrous solution nitrate and dissolve it in a mixture of 65 ± 2 ml of nitric acid (d_{20} 1.42) and 65 ml of water, carrying out the operation in a fume cupboard. Quantitatively transfer the solution to a 1 litre calibrated flask, dilute with water to the mark and mix well. The solution is stable for at least several months. Alternatively use a commercially available standard silver solution.

J5.6 Solution B: 1 ml is equivalent to 10 μg Ag

Dilute 5 ± 0.01 ml of Solution A with water to 500 ml in a calibrated flask containing 10 ± 0.1 ml of 50% V/V nitric acid. This solution is stable for at least one month. Store in the dark in a polyethylene bottle.

J5.7 Solution C: 1 ml is equivalent to 0.1 μg Ag

Dilute 10 ± 0.01 ml of Solution B with water to 1 litre in a calibrated-flask containing 20 ± 0.2 of 50% V/V nitric acid. Prepare immediately before use.

J5.8 0.5% Phosphoric Acid Solution Matrix Modifier

(required with some instruments eg the Perkin Elmer used to obtain the test data).

Using a preweighed weighing bottle, weigh out 3.46 ± 0.01 g of orthophosphoric acid d_{20} 1.75 (85%), dissolve in about 500 ml of water and make up to 1 litre in a volumetric flask with water.

J6 Apparatus

See the Antimony method, Section A6.

J7 Sample Collection and Preservation

See the Antimony Method, Section A7.

To minimize the loss of silver, samples must be stored in the dark and analysed within 24 hours. The use of polyethylene bottles for the storage of samples and standards is recommended (Ref. 6).

J8 Analytical Procedure

Read Section A4 on hazards before starting this procedure:

Step	Procedure	Notes
J8.1	**Pre-treatment Stage** Allow the acidified sample to stand for at least 12 hours (Note a). See also J7.	(a) If the sample contains a significant amount of suspended matter, the bottle should be placed in an oven at 70°C for at least 12 hours. The bottle cap should be loosened slightly.
J8.2	**Blank Determination** A blank must be run with each batch (eg up to 10 samples) of determinations using the same batch of reagents as for the samples.	
J8.3	Add 2.0 ml ± 0.05 ml of 50% V/V nitric acid to 100 ml of water in a calibrated flask. Proceed with steps J8.5 to J8.11.	
J8.4	**Calibration Standards** Calibration standards must be run with each batch of determinations using the same batch of reagents as for samples. In a series of 100 ml calibrated flasks dilute appropriate amounts of standard silver Solution C to cover the calibration range for the instrument (See Section J9). It is preferable to use at least five calibration standards, including the blank (Notes b and c).	(b) If the instrument can automatically prepare calibration standards, then this facility may be utilized. (c) It is advisable to analyse an ACQ standard of a suitable concentration.
J8.5	**Electrothermal Atomization Atomic Adsorption Stage** Set up the instrument according to the manufacturer's instructions for the determination of silver by electrothermal atomization. (Note d). Each new tube should be conditioned as described in Section A6.2.	(d) Operating conditions are given for the two instruments used for this work, however, it is essential that each operator obtains optimum conditions for the particular instrument.
J8.6	Inject an appropriate volume of a calibration standard with an appropriate volume of matrix modifier (if required by that particular instrument). Ensure that the instrument gives a satisfactory response (Note e).	(e) An appropriate volume or nebulization time is usually in the range 5–30 µl or 2–10 s respectively, depending on the particular instrument employed. The same volume or nebulization time should be used for all subsequent samples, standards and blanks.
J8.7	Inject the blank and calibration standards (Note f).	(f) All injections must be carried out in duplicate. Repeat the determination if satisfactory agreement is not achieved.

Step	Procedure	Notes
J8.8	Inject a standard, a spiked sample and an unspiked sample (See Section A12.4) and note the responses (Note g).	(g) The recovery of the spike addition should meet the criteria given in Section A12. Any failure to do so should be investigated and overcome before proceeding with analysis of samples.
J8.9	Inject the samples and note the response (Note h).	(h) The preferred method of sample injection is by automatic sampler. Manual techniques can be used but are considered less precise.
J8.10	Instrument drift should be checked for at the end of each batch of samples (eg up to 10 samples). Inject both the blank and a suitable calibration standard.	
J8.11	**Calculation of Results**	
	The preferred method of calculation is by use of data processing facilities in conjunction with a 5 point calibration graph and check standards. (Note i).	(i) A suitable recorder can be used for manual calculation of results with appropriate adjustments for variations in sensitivity and blank value.

J9 Checking the Linearity of the Calibration Curve

The procedure given in this section must be carried out on at least two independent occasions before application of this method to any samples and regularly thereafter.

J9.1 Into a series of 100 ml calibrated flasks, pipette 3.0, 6.0, 9.0, 12.0 and 15.0 ml all ± 0.05 ml of standard silver solution C. Dilute to 100 ml with water and add 2.0 ± 0.05 ml of 50% V/V nitric acid and mix well. These solutions correspond to silver concentrations of 3, 6, 9 and 12 and 15μgl^{-1} respectively in the stabilized sample. Mix well.

J9.2 The calibration curve is normally linear to 15μgl^{-1} silver however, the linearity of the curve may depend on the type of instrumentation used and therefore linearity must be checked. If the calibration curve significantly departs from linearity, the top calibration standard chosen for step J8.4 should be the highest concentration on the acceptable portion of the calibration curve and the concentration range of the method should be adjusted accordingly.

J10 Change of Concentration Range of the Method

See the Antimony method, Section A10; but use procedure J8.

J11 Sources of Error

See the Antimony method, Section A11.

J12 Checking the accuracy of Analytical Results

See the Antimony Method Section A12.

K Thallium in Raw and Potable Waters

K1 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, (4) also published in this series).

K1.1	Substances determined	All forms of thallium likely to occur in raw and potable waters.
K1.2	Type of sample	Raw and potable waters.
K1.3	Basis of the method	Direct analysis by electrothermal atomization atomic absorption spectrophotometry of samples pre-treated with acid. Sulphuric acid is used as a matrix modifier.
J1.4	Range of application	Perkin Elmer:— Up to 20 μgl^{-1} Tl. Instrumentation laboratory:— Up to 25 μgl^{1} Tl.
K1.5	Calibration curve	Perkin Elmer:— typically linear to 25 μgl^{-1} Tl. †Instrumentation Laboratory:— typically linear to 15 μgl^{-1} Tl.
K1.6	Standard deviation	See table below.
J1.7	Limit of detection	Perkin Elmer:— 0.92 μgl^{-1} Tl (V = 9)*. Instrumentation Laboratory:— (a) 0.33 μgl^{-1} Tl (V = 14). (b) 0.58 μgl^{-1} Tl (V = 11).
J1.8	Sensitivity	Perkin Elmer:— 18.3 pg for 1% absorption. Instrumentation Laboratory:— (a) 25.4 pg for 1% absorption. (b) 15.7 pg for 1% absorption.
K1.9	Bias	Not known.
K1.10	Interferences	See Section K3 and Table K1.

Instrument	Thallium Concentration μgl^{-1}	Standard Deviation μgl^{-1}	
PE	2.5	0.18	(n = 9)*
	22.5	0.25	(n = 9)
IL (a)	2.5	0.15	(n = 9)
	22.5	0.47	(n = 14)
IL (b)	2.5	0.12	(n = 11)
	22.5	0.47	(n = 9)

K1.11	Spiking recoveries	See Table K2.
K1.12	Time required for analysis	The total analytical time for 20 pre-treated samples is approximately 2 hours for both instruments. The corresponding operator time is approximately 45 minutes, assuming automatic data calculation.

Note See the General Comment on Instrument Performance

*n = number of degrees of freedom.
† = now Thermo Electron Ltd.
IL (a) = with matrix modification.
IL (b) = without matrix modification.

Data obtained by Yorkshire WA Sheffield Laboratory

Table K1 Effect of Other Substances on the Determination of Thallium

Other Substance	Concentration of other Substance (mgl^{-1})	Other Substance added as	Effect in μl^{-1} Thallium of other substances at a Thallium concentration of (μgl^{-1})					
			PE		IL (a)		IL (b)	
			0.0	10.0	0.0	10.0	0.0	10.0
Calcium	300	nitrate	−0.34	−0.75	−2.13	−5.10	0.16	−1.43
Magnesium	100	nitrate	−0.67	−0.90	−0.88	−2.33	0.00	0.21
Sodium	300	nitrate	−2.04	−2.12	0.67	−2.43	0.54	−2.80
Potassium	20	nitrate	−0.22	−0.14	0.02	−1.53	−0.04	−3.85
Calcium Magnesium	300 100	nitrate	−0.93	−1.09	−0.15	−6.61	−0.24	−1.20
Chloride	500	acid	−0.44	−0.44	−0.47	−1.62	0.04	−2.24
Sulphate	300	acid	0.15	−0.56	−0.09	0.26	0.12	−0.01
Silicon	30	ammonium fluorosilicate	−0.65	−0.52	−0.27	−2.42	0.08	−1.99
Iron Aluminium Manganese	5 5 5	nitrate	0.33	0.11	0.17	0.28	0.04	−0.54
Copper Zinc	20 20	nitrate	0.47	0.18	0.32	−0.10	−0.21	−0.75
Fluoride	10	sodium fluoride	0.39	0.75	−0.15	−0.91	0.38	−2.29
Phosphate	10	acid	0.39	−0.17	−0.02	−1.90	0.35	3.37
Calcium Magnesium Sodium Chloride Sulphate	100 20 100 200 300	nitrate acid	0.00	0.19	−0.94	−4.59	0.33	−2.62

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

Perkin Elmer:—
0.0 ± 0.34 at 0 μgl^{-1} Tl and
0.0 ± 0.61 at 10 μ gl^{-1} Tl.

(a) Instrumentation Laboratory:—
0.0 ± 0.24 at 0 μgl^{-1} Tl and
0.0 ± 0.47 at 10 μgl^{-1} Tl.

(b) 0.0 ± 0.48 at 0 μgl^{-1} Tl and
0.0 ± 0.72 at 10 μgl^{-1} Tl

(a) and (b) as in Section K1 above.

Table K2 Spiking Recoveries on Potable Water Samples (10 μgl^{-1} spike for both PE and IL Instrument)

Sample	Ca mgl^{-1}	Mg mgl^{-1}	Na mgl^{-1}	Conductivity $uScm^{-1}$	Perkin Elmer		
					Unspiked ugl^{-1}	Spiked ugl^{-1}	% Recovery
1	9.16	5	5.95	110	−0.38	9.58	99.6
2	8.56	5	5.17	109	−0.18	10.3	104.8
3	9.35	5	3.90	100	0.38	10.3	99.2
4	59.8	21.6	12.60	461	−0.19	9.35	95.4
5	53.2	17.7	8.92	411	0.00	10.1	101.0
6	59.3	22.1	12.80	499	−0.21	9.40	96.1

Sample	C mgl^{-1}	Mg mgl^{-1}	Na mgl^{-1}	Conduc-tivity $uScm^{-1}$	Instrumentation Laboratory					
					IL (a)			IL (b)		
					Unspiked ugl^{-1}	Spiked ugl^{-1}	Recovery %	Unspiked ugl^{-1}	Spiked ugl^{-1}	Recovery %
1	9.16	5	5.95	110	−0.58	9.52	101.0	0.04	9.36	93.2
2	8.56	5	5.17	109	−0.52	9.15	96.7	0.08	9.72	96.4
3	9.35	5	3.90	100	−0.19	9.50	96.9	0.20	9.72	95.2
4	59.8	21.6	12.60	461	−1.00	6.44	74.4	0.04	8.77	87.3
5	53.2	17.7	8.92	411	−0.17	7.09	72.6	0.28	8.26	79.8
6	59.3	22.1	12.80	499	−0.51	6.25	67.5	0.16	8.41	82.5

IL (a) = with matrix modifier.
IL (b) = without matrix modifier.

Table K3 Instrument Conditions

Perkin Elmer [1]					Instrumentation Laboratories [2]						
Step	1	2	3	4	Step	1	2	3	4	5	6
Temp °C	130	600	1500	2500	Temp °C	0	190	450	500	2200	2200
Ramp (s)	15	10	0	1	Time (s)	0	5	15	15	0	10
Hold (s)	25	20	7	2	Read					/	
Read			/								
Internal flow (ml min^{-1}) = 10					Internal flow (l min^{-1}) = 1.3						
Integration Time (s) = 6					Integration Time (s) = 3						
Sample volume (µl) = 25					Delay (s) = 7						
Tube Type = Pyro-coated					Deposit (s) = (a) 15. (b) 5						
Mode = Peak Area					Tube Type = DAC						
Matrix Modification (inject with sample) = 5 µl of 6% H_2SO_4					Mode = Peak Area						
					Matrix Modification (inject with sample) = (a) 1% H_2SO_4 (B) None.						
Injection = Auto:— AS40					Injection = Auto:— IL254 (Fastac 2)						
Wavelengh (nm) = 276.8					Wavelength (nm) = 276.8						
Band Width (nm) = 0.7 Alt					Band Width (nm) = 1.0						
Lamp Current (mA) = 6					Lamp Current (mA) = 8						
Deuterium Arc					High Voltage (V) = 530						
Background Correction = Yes					Deuterium Arc						
					Background Correction = Yes						

[1] Atomic Absorption Spectrophotometer : PE 272 (single beam)
Electrothermal Atomizer : HGA 500

[2] Atomic Absorption Spectrophotometer : IL 451 (double beam)
Electrothermal Atomizer : IL 655

IL (a) = with matrix modifier.
IL (b) = without matrix modifier.

K2 Principle

Thallium in raw and potable waters is determined directly in acidified aqueous samples by electrothermal atomization atomic absorption spectrophotometry. Sulphuric acid is added as a matrix modifier.

The conditions used are given for both instruments in Table 3. It is essential that these conditions are used only as a guideline to determining optimum conditions for other instruments. (Refs 7 and 11)

K3 Interferences

The effects of other substances vary considerably between electrothermal atomization atomic absorption spectrophotometers. It is essential that each analyst using this technique should check the interference effects of other substances for his particular instrument and decide whether any effects are important enough to consider means of overcoming the interference.

For the two instruments used to obtain the test data (See Table K3), matrix modification was used for both instruments and the study was also completed on the IL without the use of matrix modification (See Tables K1 and K2). Significant interferences were observed on both instruments. Other means of overcoming the interferences were tried without success, these included the use of Lanthanum, Lithium, Ascorbic acid, Phosphoric acid and Palladium as matrix modifiers. A recent paper (Ref. 11) reported the successful use of Palladium/Magnesium Nitrate matrix modification for the determination of thallium by electrothermal atomization. The paper was not published in time for use of this matrix modifier to be treated. (See also Note N)

The effects of other substances on the determination of thallium is shown in Table K1.

K4 Hazards

See the Antimony method, Section A4.

K5 Reagents

All reagents and standard solutions may be kept in glass or polyethylene bottles (See Section A6.3). Analytical reagent grade chemicals are suitable unless otherwise stated.

K5.1 Water

See the Antimony method, Section A5.1

K5.2 Nitric Acid (d_{20}1.42), atomic spectroscopy grade.

K5.3 10% V/V Nitric Acid

See the Antimony method, Section A5.3

K5.4 50% V/V Nitric Acid

See the Antimony method, Section A5.4

K5.5 Solution A: 1 ml contains 1 mg thallium

Dissolve 1.304 g of thallium (I) nitrate in approximately 500 ml of water. Quantitatively transfer the solution to a 1 litre calibrated flask, add 15 ml of nitric acid (d_{20} 1.42), dilute to the mark with water and mix well. The solution is stable for at least several months. Alternatively, use a commercially available standard thallium solution.

K5.6 Solution B: 1 ml is equivalent to 10 μg Tl

Dilute 5 ± 0.01 ml of Solution A with water to 500 ml in a calibrated flask containing 10 ± 0.1 ml of 50% V/V nitric acid. This solution is stable for at least one month.

K5.7 Solution C: 1 ml is equivalent to 0.1 μg Tl

Dilute 10 ± 0.1 ml of Solution B with water to 1 litre in a calibrated flask containing 20 ± 0.2 of 50% V/V nitric acid. Prepare immediately before use.

K5.8 Sulphuric acid (d_{20} 1.84), atomic spectroscopy grade.

K5.9 Matrix Modifier

Perkin Elmer:— 5 μl of 6% V/V H_2SO_4 added to 25 μl of sample. Add 6 ml ± 0.05 ml of sulphuric acid (d_{20} 1.84) to approximately 80 ml of water, dilute to 100 ml with water and mix well. Instrumentation Laboratory:— 2 ml of 50% V/V H_2SO_4 added to 100 ml of sample. Add 50 ml ± 1 ml of sulphuric acid (d_{20} 1.84) to approximately 40 ml of water with constant stirring and cooling. Dilute to 100 ml with water and mix well.

K6 Apparatus

See the Antimony Method, Section A6.

K7 Sample Collection and Preservation

See the Antimony method, Section A7.

K8 Analytical Procedure

Read Section A4 on hazards before starting this procedure:

Step	Procedure	Notes
K8.1	**Pre-treatment Stage** Allow the acidified sample to stand for at least 24 hours (Note a).	(a) If the sample contains a significant amount of suspended matter, the bottle should be placed in an oven at 70°C for 24 hours. The bottle cap should be loosened slightly.
K8.2	**Blank Determination** A blank must be run with each batch (eg up to 10 samples) of determinations using the same batch of reagents as for the samples.	

Step	Procedure	Notes
K8.3	Add 2.0 ml ± 0.05 ml of 50% V/V nitric acid to 100 ml of water in a calibrated flask. Proceed with steps K8.5 to K8.11.	
K8.4	**Calibration Standards** Calibration standards must be run with each batch of determinations using the same batch of reagents as for samples. In a series of 100 ml calibrated flasks dilute appropriate amounts of standard thallium Solution C to cover the calibration range for the instrument (See Section K9). It is preferable to use at least five calibration standards, including the blank. (Notes b and c).	(b) If the instrument can automatically prepare calibration standards, then this facility may be utilized. (c) It is advisable to analyse an AQC standard of a suitable concentration.
K8.5	**Electrothermal Atomization Atomic Absorption Stage** Set up the instrument according to the manufacturer's instructions for the determination of thallium by electrothermal atomization. (Note d). Each new tube should be conditioned as described in Section A6.2.	(d) Operating conditions are given for the two instruments used for this work, however, it is essential that each operator obtains optimum conditions for the particular instrument.
K8.6	Add 2.0 ± 0.05 ml of 50% V/V sulphuric acid matrix modifier and mix well if experience shows that it is required for the instrument used. Inject an appropriate volume of a calibration standard and ensure that the instrument gives a satisfactory response (Note e).	(e) An appropriate volume or nebulization time is usually in the range 5–30 μl or 2–10 s respectively, depending on the particular instrument employed. The same volume or nebulization time should be used for all subsequent samples, standards and blanks.
K8.7	Inject the blank and calibration standards (Note f).	(f) All injections must be carried out in duplicate. Repeat the determination if satisfactory agreement is not achieved.
K8.8	Inject a standard, a spiked sample and an unspiked sample (See Section A12.4) and note the responses (Note g).	(g) The recovery of the spike addition should meet the criteria given in Section A12. Any failure to do so should be investigated and overcome before proceeding with analysis of samples.
K8.9	Inject the samples and note the response (Note h).	(h) The preferred method of sample injection is by automatic sampler. Manual techniques can be used but are considered less precise.
K8.10	Instrument drift should be checked for at the end of each batch of samples (eg up to 10 samples). Inject both the blank and a suitable calibration standard.	
K8.11	Calculation of Results The preferred method of calculation is by use of data processing facilities in conjunction with a 5 point calibration graph and check standards. (Note i)	(i) A suitable recorder can be used for manual calculation of results with appropriate adjustments for variations in sensitivity and blank value.

K9 Checking the Linearity of the Calibration Curve

The procedure given in this section must be carried out on at least two independent occasions before application of this method to any samples and regularly thereafter.

K9.1 Into a series of 100 ml calibrated flasks, pipette 5.0, 10.0, 15.0, 20.0 and 25.0 ml all ± 0.05 ml of standard thallium solution C. Dilute to 100 ml with water and add 2.0 ± 0.05 ml of 50% V/V nitric acid and mix well. These solutions correspond to thallium concentrations of 5, 10, 15, 20 and 25 $\mu g l^{-1}$ respectively in the stabilized sample. Mix well.

K9.2 The calibration curve is normally linear to 15 or 25 $\mu g l^{-1}$ thallium (see Section A1.5) however, the linearity of the curve may depend on the type of instrumentation used and therefore linearity must be checked. If the calibration curve significantly departs from linearity, the top calibration standard chosen for step K8.4 should be the highest concentration on the acceptable portion of the calibration curve and the concentration range of the method should be adjusted accordingly.

K10 Change of Concentration Range of the Method

See the Antimony method, Section A10; but see Procedure K8.

K11 Sources of Error

See the Antimony method, Section A11.

K12 Checking the accuracy of Analytical Results

See the Antimony Method, Section A12.

L. Vanadium in Raw and Potable Waters by Electrothermal Atomization Atomic Absorption Spectrophotometry

L1 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, (4) also published in this series).

L1.1	Substances determined	All forms of vanadium likely to occur in raw and potable waters.
L1.2	Type of sample	Raw and potable waters.
L1.3	Basis of the method	Direct analysis by electrothermal atomization atomic absorption spectrophotometry of sample pre-treated with acid.
L1.4	Range of applications	Up to 50 $\mu g l^{-1}$ V
L1.5	Calibration curve	Linear to 50 $\mu g l^{-1}$
L1.6	Standard deviation	Vanadium Concentration $\mu g l^{-1}$ / Standard Deviation $\mu g l^{-1}$: 5 / 0.59 (n = 9)*; 45 / 1.29 (n = 9)
L1.7	Limit of detection	3.14 $\mu g l^{-1}$ (n = 9).
L1.8	Sensitivity	39.3 pg for 1% absorption.
L1.9	Bias	Not Known.
L1.10	Interferences	See Section L3 and Table L1.
L1.11	Spiking recoveries	See Table L2.
L1.12	Time required for analysis	The total analytical time for 20 pre-treated samples is approximately 2 hours. The corresponding operator time is approximately 45 minutes, assuming automatic data calculations.

*n = number of degrees of freedom.

Note: See the General Comments on Instrument Performance.

Data obtained by Yorkshire WA, Sheffield Laboratory.

Table L1 Effect of Other Substances on the Determination of Vanadium

Other Substances	Concentration of other substances (mgl^{-1})	Other Substance added as	Effect in μgl^{-1} Vanadium of other substances at a Vanadium concentration of (μgl^{-1})	
			0.0	20.0
Calcium	300	nitrate	0.00	0.66
Magnesium	100	nitrate	0.80	0.72
Sodium	300	nitrate	0.11	0.18
Potassium	20	nitrate	0.30	−0.45
Calcium + Magnesium	300 + 100	nitrate	0.11	0.82
Chloride	500	acid	0.66	−0.10
Sulphate	300	acid	−0.22	0.11
Silicon	30	ammonia fluorosilicate	−0.55	0.16
Iron + Aluminium + Manganese	5 + 5 + 5	nitrate	−0.33	−0.14
Copper + Zinc	20 + 20	nitrate	0.11	−0.17
Fluoride	10	sodium fluoride	0.66	−0.24
Phosphate	10	acid	−0.44	−0.24
Calcium + Magnesium + Sodium + Chloride + Sulphate	50 + 10 + 50 + 100 + 150	nitrate + sulphate acid	0.55	1.11

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

0.0 ± 1.20 at 0 μgl^{-1} V and
0.0 ± 1.28 at 20 μgl^{-1} V

Table L2 Spiking Recoveries on Potable Water Samples (20 µg/l spike)

Sample	Ca mgl^{-1}	Mg mgl^{-1}	Na mgl^{-1}	Conductivity μScm^{-1}	Unspiked μgl^{-1}	Spiked μgl^{-1}	%Recovery
1	9.95	2.04	4.28	109	0.096	19.93	99.1
2	10.20	1.98	4.29	110	−0.86	19.84	103.5
3	10.10	2.02	4.52	109	−0.19	19.55	98.7
4	49.5	20.7	13.8	487	−0.48	21.04	107.6
5	51.0	20.6	14.5	491	−0.48	20.07	102.8
6	52.6	20.89	13.3	488	0.29	21.04	103.8

Table L3 Instrument Conditions

Instrumentation Laboratories [1]

Step	1	2	3	4	5	6
Temp °C	0	120	950	1400	3000	3000
Time (s)	0	5	10	10	0	15
Read					/	

Internal flow (1 min^{-1}) = 1.3

Integration Time (s)	= 8
Delay (s)	= 6
Deposit (s)	= 10
Tube Type	= DAC
Mode	= Peak Area
Matrix Modification	= None
Injection	= Auto:—IL254
Wavelength (nm)	= 318.5
Band Width (nm)	= 0.3
Lamp Current (mA)	= 12
High Voltage	= 620
Deuterium Arc	
Background Correction	= Yes

[1] Atomic Absorption Spectrophotometer: I.L. 451 (double beam)
Electrothermal Atomizer: I.L. 655

L2 Principle

Vanadium in raw and potable waters is determined directly in acidified aqueous samples by electrothermal atomization atomic absorption spectrophotometry. Matrix modification has not been found to be necessary.

The conditions used are given in Table L3. It is essential that these conditions are used only as a guideline to determining optimum conditions for other instruments.

L3 Interferences

The effects of other substances vary considerably between electrothermal atomization atomic absorption spectrophotometers. It is essential that each analyst using this technique should check the interference effects of other substances for his particular instrument and decide whether any interference effects are important enough to consider means of overcoming the interference. For the instrument used in obtaining these performance characteristics (See Table L3), no matrix modification was considered necessary (See Tables L1 and L2).

The effects of other substances on the determination of vanadium is shown in Table L1.

L4 Hazards

See the Antimony method, Section A4.

L5 Reagents

All reagents and standard solutions may be kept in glass or polyethylene bottles (see Section A6.3). Analytical reagent grade chemicals are suitable unless otherwise stated.

L5.1 Water

See the Antimony method, Section A5.1.

L5.2 Nitric Acid (d_{20} 1.42), atomic spectroscopy grade.

L5.3 10% V/V Nitric Acid

See the Antimony method, Section A5.3.

L5.4 50% V/V Nitric Acid

See the Antimony method, Section A5.4.

L5.5 Solution A: 1 ml contains 1 mg Vanadium

Dissolve 2.296 ± 0.005 g of ammonium metavanadate in 65 ml nitric acid d_{20} 1.42 and 65 ml of water. Quantitatively transfer the solution to a 1 litre calibrated flask, dilute with water to the mark and mix well. The solution is stable for several months. Alternatively use a commercially available standard vanadium solution.

L5.6 Solution B: 1 ml is equivalent to 10 μg V

Dilute 5 ± 0.01 ml of Solution A with water to 500 ml in a calibrated flask containing 10 ± 0.1 ml of 50% V/V nitric acid. This solution is stable for one month.

L5.7 Solution C: 1 ml is equivalent to 1 μg V

Dilute 10 ± 0.01 ml of Solution B with water to 100 ml in a calibrated flask containing 2.0 ± 0.2 ml of 50% V/V nitric acid. This solution should be prepared immediately before use.

L6 Apparatus

See the Antimony method, Section A6.

L7 Sample Collection and Preservation

See the Antimony method, Section A7.

L8 Analytical Procedure

Read Section A4 on hazards before starting this procedure:

L8 Analytical Procedure

Read Section A4 on hazards before starting this procedure:

Step	Procedure	Notes
L8.1	**Pre-treatment Stage** Allow the acidified sample to stand for at least 24 hours (Note a).	(a) If the sample contains a signifant amount of suspended matter, the bottle should be placed in an oven at 70°C for 24 hours. The bottle cap should be loosened slightly.
L8.2	**Blank Determination** A blank must be run with each batch (eg up to 10 samples) of determinations using the same batch of reagents as for the samples.	
L8.3	Add 2.0 ml ± 0.05 ml of 50% V/V nitric acid to 100 ml of water in a calibrated flask. Proceed with steps L8.5 to L8.11.	
L8.4	**Calibration Standards** Calibration standards must be run with each batch of determinations using the same batch of reagents as for the samples. In a series of 100 ml calibrated flasks dilute appropriate amounts of standard vanadium Solution C to cover the calibration range for the instrument (See Section L9). It is preferable to use at least five calibration standards, including the blank (Notes b and c).	(b) If the instrument can automatically prepare calibration standards, then this facility may be utilized. (c) It is advisable to analyse an AQC standard of a suitable concentration with each batch of samples.

Step	Procedure	Notes
L8.5	**Electrothermal atomization Atomic Absorption Stage** Set up the instrument according to the manufacturer's instructions for the determination of vanadium by electrothermal atomization. (Note d). Each new tube should be conditioned as described in Section A6.2.	(d) Operating conditions are given for the instrument used for this work, however, it is essential that each operator obtains optimum conditions for the particular instrument.
L8.6	Inject an appropriate volume of a calibration standard and ensure that the instrument gives a satisfactory response (Note e).	(e) An appropriate volume or nebulization time is usually in the range 5–30 μl or 2–10 s respectively, depending on the particular instrument employed. The same volume or nebulization time should be used for all subsequent samples, standards and blanks.
L8.7	Inject the blank and calibration standards (Note f).	(f) All injections must be carried out in duplicate. Repeat the determination if satisfactory agreement is not achieved.
L8.8	Inject a standard, a spiked sample and an unspiked sample (See Section A12.4) and note the responses (Note g).	(g) The recovery of the spiked addition should meet the criteria given in Section A12. Any failure to do so should be investigated and overcome before proceeding with analysis of samples.
L8.9	Inject the samples and note the response (Note h).	(h) The preferred method of sample injection is by automatic sampler. Manual techniques can be used but are less precise.
L8.10	Instrument drift should be checked for at the end of each batch of samples (eg up to 10 samples). Inject both the blank and a suitable calibration standard.	
L8.11	**Calculation of Results** The preferred method of calculation is by use of data processing facilities in conjunction with a 5 point calibration graph and check standards (Note i).	(i) A suitable recorder can be used for manual calculation of results with appropriate adjustments for variations in sensitivity and blank value.

L9 Checking the linearity of the Calibration Curve

The procedure given in this section must be carried out on at least two independent occasions before application of this method to any samples and regularly thereafter.

L9.1 Into a series of 100 ml calibrated flasks, pipette 1.0, 2.0, 3.0, 4.0 and 5.0 ml all ± 0.05 ml of standard vanadium solution C. Dilute to 100 ml with water. Add 2.0 ± 0.05 ml of nitric acid. Mix well. These solutions correspond to vanadium concentrations of 10, 20, 30, 40 and 50 μgl^{-1} respectively in the stabilized sample.

L9.2 The calibration curve is normally linear to 50 μgl^{-1} vanadium for the Varian Spectra AA-40 + GTA-96 instrument, however, the linearity of the curve may depend on the type of instrumentation used and therefore linearity must be checked. If the calibration curve significantly departs from linearity, the top calibration standard chosen for step L8.4 should be the highest concentration on the acceptable portion of the calibration curve and the concentration range of the method should be adjusted accordingly.

L10 Change of Concentrations Range of the Method

See the Antimony method, Section A10; but use Procedure L8.

L11 Sources of Error

See the Antimony method, Section A11.

L12 Checking the accuracy of Analytical Results

See the Antimony method, Section A12.

M. Zinc in Raw and Potable Waters by Electrothermal Atomization Atomic Absorption Spectrophotometry—A Note

M1 The Flame Atomic Absorption Spectrophotometric method for Zinc in Potable Waters (Ref 8) is usually sensitive enough for water analysis. If however, it becomes necessary to lower the limit of detection for zinc, substitution of a graphite furnace instrument with the spectrometer set on the 213.8 nm ground state line of zinc will give a limit of detection of less than 0.03 μgl^{-1} provided that satisfactory blanks can be obtained. The practical upper limit of the method (10 μgl^{-1}), without quantitative dilution precludes its use for many samples. For sampling see also Ref 6.

M2 For raw waters, if they are sufficiently free from suspended solids, after collection with the 2.00 ± 0.05 ml of 50% V/V nitric acid (as recommended in this booklet for metals which are to be analysed directly) treat as potable water.

M3 If there is an appreciable amount of suspended matter present, see the Marine, Estuarine and other Water methods. (Ref 3).

N

Note on the Determination of Arsenic and Selenium using the Palladium/Magnesium Nitrate Matrix Modification Method

N1 Introduction

Welz, Schlemmer and Mudakavi (14) have developed a method for arsenic, and selenium using a palladium and magnesium nitrate matrix modifier. The technique is also applicable to antimony, cadmium, copper, lead, manganese and thallium (15). The method was developed on a Perkin Elmer HGA-500 graphite furnace. Pyrolytic graphite coated tubes, pyrolytic graphite L'vov platforms and peak area measurements are used.

N2 Performance Characteristics

Table N1 gives some basic performance characteristics.

Table N1 Basic Performance Characteristics for Arsenic and Selenium (Reproduced with permission from ref. N1)

Element	Calibration Range $\mu g l^{-1}$	Sensitivity	Limit of Detection $\mu g l^{-1}$ (20 μl sample volume)	RSD (%)*	Concn $\mu g l^{-1}$
As	0–50	14	2.4	2.8	30
Se	0–70	20	1.2	1.3	30

*4 degrees of freedom

N3 Reagents

Palladium nitrate solution is prepared by dissolving palladium metal powder in the minimum amount of nitric acid (d_{20} 1.42) and further dilution with deionized water. Solubility of palladium depends on grain size. In case of incomplete solution 10 μl of hydrochloric acid (d_{20} 1.18) is added to the cold nitric acid and carefully heated until the solution clears.

Alternatively a nominal 10% m/V solution of palladium nitrate is available from Johnson and Matthey. Use the analysis provided by the supplier when making the subsequent dilution.

The Palladium nitrate-magnesium nitrate matrix modifier is prepared by mixing equal volumes of a solution containing 3000 mg l^{-1} Pd and 2000 mg l^{-1} $Mg(NO_3)_2$. Ten μl of this solution is added to the furnace together with 20 μl of sample for each determination, corresponding to masses of 15 μg of Pd (32.5 μg$Pd(NO_3)_2$) and 10 μg of $Mg(NO_3)_2$.

N4 Operating Conditions

Tables N2 and N3 give details of the operating conditions for a Perkin Elmer 500 graphite furnace.

Table N2 Graphite Furnace Temperature Program for the Determination of As and Se in Water using the Palladium Nitrate-Magnesium Nitrate Modifier. (Reproduced with permission from ref. 14).

Step	1	2	3	4	5	6
Temperature/°C	90	120	1000	2200	2650	20
Ramp time/s	1	10	10	0	1	1
Hold time/s	10	20	20	6	5	5
Read				ON		
Internal Ar flow/ml.min^{-1}	300	300	300	0	300	300

Note

The above conditions were also found to be suitable for Antimony, Copper, Lead, and Manganese.

Table N3 Instrumental Parameters. (Reproduced with permission from ref. 14)

Element	Wavelength (nm)	Spectral bandpass (nm)	Light Source	Power (W)	Sample Vol (μl)	Palladium-Magnesium Modifier Reagent Volume (μl)
As	193.7	0.7	EDL	6	20	10
Se	196.0	2.0	EDL	6	20	10

N5 Interferences

A wide range of substances likely to be encountered in potable water were tested and recoveries between 95 and 105% were found for both arsenic and selenium.

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Address for Correspondence

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

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

Department of the Environment

Standing Committee of Analysts

Membership responsible for these methods

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