Selenium in Waters 1984
Selenium and Arsenic in Sludges, Soils and Related Materials 1985
A Note on the Use of Hydride Generator Kits 1987

Methods for the Examination of Waters at Associated Materials

Her Majesty's Stationery Office

Selenium in Waters 1984
Selenium and Arsenic in Sludges, Soils and Related Materials 1985
A Note on the Use of Hydride Generator Kits 1987

LIBRARY
N.R.A.
SOUTH WEST REGION
MANLEY HOUSE
KESTREL WAY
EXETER
EX2 7LQ

LONDON: Her Majesty's Stationery Office

© *Crown copyright 1987*
First published 1987

ISBN 0 11 751933 2

This booklet contains the following 3 methods, all tentative, and a note

A Selenium in Raw, Potable and Saline Waters, (Low Level) Gas Chromatographic Method

B Selenium in Raw and Potable Waters, (High Level) Fluorimetric Method

C Arsenic and Selenium in Sludges, Soils and Related Materials by Hydride Generation and Atomic Absorption Spectrophotometry

D A Note on Commercial Hydride Generation — AAS Methods

Chromatographic methods are very sensitive to minor physical and chemical variations in the quality of the materials and apparatus used. Hence this method mentions the actual materials used for the evaluation tests. This in no way endorses these materials as superior to other similar materials. Equivalent materials are acceptable, though it must be understood that the performance characteristics may be different, and can vary with batch. It is left to the senior supervising analyst to evaluate and choose from the appropriate brands available.

Contents

About this series 4

Warning to Users 5

Note on the determination of Selenium 6

A Selenium in Raw, Potable and Saline Waters (Low Level) Gas Chromatographic Method 7
- A1 Performance Characteristics of the Method 7
- A2 Principle 8
- A3 Interferences 8
- A4 Hazards 8
- A5 Reagents 8
- A6 Apparatus 11
- A7 Sample Collection and Preservation 11
- A8 Analytical Procedure 13
- A9 Checking the Linearity of the Calibration Curve 15
- A10 Changing the Concentration Range of the Method 15
- A11 Sources of Error 15

B Selenium in Raw and Potable Waters (High Level) Fluorimetric Method 16
- B1 Performance Characteristics of the Method 16
- B2 Principle 16
- B3 Interferences 17
- B4 Hazards 17
- B5 Reagents 17
- B6 Apparatus 19
- B7 Sample Collection and Preservation 20
- B8 Analytical Procedure 20
- B9 Measurement of Fluorescence 22
- B10 Checking the Linearity of the Calibration Curve 22
- B11 Changing the Concentration Range of the Method 22
- B12 Sources of Error 22

C Arsenic and Selenium in Sludges, Soils and Related Materials by Hydride Generation and Atomic Absorption Spectrophotometry 23
- C1 Performance Characteristics of the Method 23
- C2 Principle 24
- C3 Interferences 24
- C4 Hazards 26
- C5 Reagents 27
- C6 Apparatus 29
- C7 Sample Collection and Preservation 33
- C8 Preliminary Procedures 33
- C9 Analytical Procedure 33
- C10 Checking the Linearity of the Calibration Curve and Efficiency of the Reduction Stage 36
- C11 Changing the Concentration Range of the Method 36
- C12 Sources of Error 37

D A Note on Commercial Hydride Generation — AAS Methods 38

Checking the Accuracy of Analytical Results 40

References 41

Address for Correspondence 42

Membership Participating in Preparing these Methods 43

About this Series

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

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

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

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

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

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

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

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

L R PITTWELL
Secretary

1 July 1986

Warning to Users

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

Local Safety Regulations must be observed.

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

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

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

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

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

It cannot be too strongly emphasised that prompt first aid, decontamination, or administration of the correct antidote can save life; but that incorrect treatment can make matters worse. It is suggested that both supervisors and operators be familiar with emergency procedures before starting even a slightly hazardous operation, and that doctors consulted after any accident involving chemical contamination, ingestion, or inhalation, be made familiar with the chemical nature of the injury, as some chemical injuries required specialist treatment not normally encountered by most doctors. Similar warning should be given if a biological or radio-chemical injury is suspected. Some very unusual parasites, viruses and other micro-organisms are occasionally encountered in samples and when sampling in the field. In the latter case, all equipment including footwear should be disinfected by appropriate methods if contamination is suspected. If an ambulance is called or a hospital notified of an incoming patient give information on the type of injury, especially if poisoning is suspected, as the patient may be taken directly to a specialized hospital.

Note on the determination of Selenium

Selenium is an essential trace element for animal life, but at marginally higher levels is very toxic. The element occurs in unpolluted natural waters at concentrations ranging between 10 and c.300 ng/1. In oxygenated waters both selenite and selenate are usually present together in non-equilibrium proportions, however, under reducing conditions the colloidal elemental form along with the selenide ion may predominate. This booklet describes 3 different techniques for the determination of selenium.

A A gas chromatographic technique with a detection limit of 1 ng/1 capable of determining the element in unpolluted natural waters.

B A simpler fluorimetric procedure having a detection limit of 1 μg/1, ie 1/10 of the EEC Directive.

By variation of the pretreatment process it is possible with both methods to determine selenite alone, and total selenium viz, selenite + selenate + elemental selenium + selenide + organoselenium compounds.

C A hydride evolution Atomic Absorption Spectrophotometric technique suitable for sewage sludges, soils and similar materials. Organic matter is first oxidized, then the selenium is converted to selenite and finally to hydride for determination by atomic absorption spectrophotometry. Arsenic may also be determined by the same method.

A

Selenium in Raw, Potable and Saline Waters (Low Level) Gas-Liquid Chromatographic Method

A1 Performance characteristics of the Method

(For further information on the determination and definition of the characteristics see General Principles of Sampling and Accuracy of Results 1980 also published in this series).
Note: Throughout this method selenium is expressed as the element (Se).

A1.1	Substance determined	All forms of selenium (see Section A2)
A1.2	Types of sample	Raw, potable and saline waters
A1.3	Basis of method	Pre-treatment to convert to selenite which is reacted with diamino-dibromobenzene hydrochloride to give a piazselenol which is extracted with toluene and determinated by electron capture gas-chromatography.
A1.4	Range of application (a)	Up to 400 ng/1 (See Section A11)
A1.5	Calibration curve (a) (b)	linear to 400 ng/1

A1.6 Within batch standard deviation (a)

Type of sample		Standard deviation (ng/1)	Degrees of Freedom
Distilled water spiked with 20 $ngSe^{4+}/1$		0.4	(n = 6)
Distilled water spiked with 40 $ngSe^{4+}/1$		0.4	(n = 6)
Distilled water spiked with 120 $ngSe^{4+}/1$		1.2	(n = 6)
Distilled water spiked with 180 $ngSe^{4+}/1$		1.5	(n = 6)
Distilled water spiked with 20 $ngSe^{6+}/1$		1.2	(n = 5)
Distilled water spiked with 120 $ngSe^{6+}/1$		3.0	(n = 5)
Distilled water spiked with 20 $ngSe^{0}/1$		1.0	(n = 5)
Distilled water spiked with 180 $ngSe^{0}/1$		5.0	(n = 5)
Liverpool tap water (c)		1.0	(n = 5)
Irish Sea Water (a) (d)	selenate	1.0	(n = 5)
	selenite	0.4	(n = 5)

A1.7	Limit of detection (a) (e) (f)	1.0 ng/1 with 5 degrees of freedom
A1.8	Bias (a)	Not known, but Liverpool tap water spiked with 80 $ngSe^{4+}/1$ gave a recovery (n = 6) of 99 ± 3%. Similarly, Irish Sea water spiked with 40, 120 and 200 $ngSe^{4+}/1$ gave recoveries of 102, 98 and 97% respectively (all relative to standards prepared using distilled water)
A1.9	Interference (a)	See Section A3

A1.10	Time required for analysis. (a)	Total and operator times for determination of selenite in 10 samples are 8 and 6 hours respectively.

(a) These data were obtained in the Oceanography Department, University of Liverpool using a Pye 104 gas chromatograph fitted with an electron capture detector. (1)
(b) Linear range very dependent on make of gas chromatograph and detector used.
(c) Found 5 $ngSe^{4+}/1$
(d) Found 5 $ngSe^{4+}$ and 45 $ngSe^{6+}/1$
(e) The limit of detection will depend on the instrument used.
(f) For distilled water.

A2 Principle

A2.1 The method described, which is a modification of that proposed by Shimoishi (2,3), is based on experimental work carried out at the Department of Oceanography, University of Liverpool. (1)

A.2.2 After a preliminary extraction of the sample with toluene to remove possible organic interferants, selenite is reacted under acidic conditions with 1, 2-diamino-3,5-dibromobenzene hydrochloride. The resulting piazselenol is extracted into toluene which, after washing twice with perchloric acid, is injected into the gas chromatograph. Separation is carried out on a gas chromatographic column (2m column of 3% OV 330 on Chromosorb W at 195°C), and the piazselenol peak is detected using an electron capture detector and identified by retention time. Total selenium (ie Se^{4+} + Se^{6+} + Se^{0} + Se^{2-}) is determined in the same way after boiling with hydrochloride and hydrobromic acids in the presence of bromine to convert all forms of the element to selenite. Organo-selenium compounds may not be broken down by this pretreatment. See table below.

organo selenium compound	concentration (ng/1)	recovery of selenium (%)
seleno-DL-methionine	131.6	100.6
seleno-cystamine dihydrochloride	131.6	28.4
seleno urea	580.0	0.0

A3 Interferences

The effects of a number of other substances on the determination of selenium were investigated at selenium (IV) levels of 40 ng/1 and 200 ng/1 (Table 1). The concentrations of most of these substances were set at, or above, the levels recommended by the Standing Committee of Analysts. (4) However, the effects of the major anions of sea water have been omitted from Table A1 since the response with sea water is identical to that with distilled water. None of the substances tested showed significant interference at the 95% confidence level.

A3.1 If organically bound selenium is sought, see Ref 14 for a pretreatment of solids. See method B for a pretreatment for waters.

A4 Hazards

Bromine, toluene and diamino-dibromobenzene are toxic and all operations involving them should be carried out in a fume cupboard. Selenium compounds are toxic and care should be taken in handling them and their solutions. If any are ingested carry out gastric aspiration and lavage and obtain medical attention.

A5 Reagents

All reagents and standard solutions should be stored in polyethylene or glass bottles which have been cleaned as described in Section A6.3. Analytical reagent grade chemicals are suitable unless otherwise specified.

Table 1 Effect of other substances on the determination of selenium by gas chromatography (g)

Other substance		Substance added as	Concentration of other substances (ng/1)	Effect (h) of other substances in ng Se/1 at a selenium (iv) concentration of 40ngSe/1	200ngSe/l
Silver	(as Ag^+)	Nitrate	50	−0.4	−2
Aluminium	(as Al^{3+})	Nitrate	1000	0.0	−6
Arsenic	(as As^{5+})	Sodium arsenate	50	+1.5	+2
Boron	(as B)	Boric Acid	1000	+1.6	+4
Barium	(as Ba^{2+})	Chloride	3000	0.0	+4
Bismuth	(as Bi^{3+})	Nitrate	200	+1.0	−6
Bromide	(as Br^-)	Potassium	1000	−1.2	+4
Calcium	(as Ca^{2+})	Chloride	3×10^6	−1.0	+2
Cadmium	(ss Cd^{2+})	Chloride	20	−1.2	−6
Cobalt	(as Co^{2+})	Chloride	20	0.8	+4
Chromium	(as Cr^{3+})	Chloride	50	+0.4	−8
Copper	(as Cu^{2+})	Chloride	5000	0.0	−4
Cyanide	(as CN^-)	Potassium	100	−0.8	−12
Fluoride	(as F^-)	Sodium	1000	−0.8	0
Iron	(as Fe^{3+})	Chloride	5000	+0.8	−6
Mercury	(as Hg^{2+})	Chloride	1	0.0	−4
Lithium	(as Li^+)	Chloride	100	+1.5	−6
Magnesium	(as Mg^{2+})	Chloride	10^6	+1.6	+4
Manganese	(as Mn^{2+})	Chloride	1000	+2.0	+5
Sodium	(as Na^+)	Chloride	3×10^5	−1.2	+4
Nickel	(as Ni^{2+})	Chloride	2000	0.0	−4
Phosphates	(as P)	Disodium hydrogen	5000	−1.5	+6
Lead	(as Pb^{2+})	Nitrate	5000	+0.8	−4
Antimony	(as Sb^{3+})	Potassium Antimonyl Tartrate	10	+1.0	+6
Thiocyanate	(as SCN^-)	Potassium	1000	+0.3	−8
Tin	(as Sn^{2+})	Chloride	1000	−0.8	+4
Strontium	(as Sr^{2+})	Chloride	3000	−1.4	+2
Zinc	(as Zn^{2+})	Chloride	100	+1.0	−4
Phenol		Substance	1000	+1.2	+3
Nitrilo triacetic acid		Substance	1000	−0.8	0
Ethylene diamine tetra acetic acid		Di-Sodium salt	1000	+1.3	−6

(g) These determinations were carried out in distilled water spiked with the stated concentrations of other substances using the procedure described in Sections A8.4–A8.11.

(h) If the other substances had no effect, results would be expected (95% confidence) to lie within the range 0±1 ng/1 for 40 ngSe/1 and 0±6 ng/1 for 200 ngSe/1.

A5.1 Water

The water used for blank determinations and for preparing standard and reagent solutions should have a selenium content which is negligible compared with the lowest concentration to be determined in the samples. Water doubly distilled from an all glass apparatus has been found to be satisfactory.

A5.2 3% m/V bromine water

Dissolve 1.0 ± 0.1 ml of ultra-pure bromine in 100 ml water. Store in a glass-stoppered bottle.

A5.3 7% m/V hydrazine hydrochloride solution.

Dissolve 7.0 ± 0.5 g of hydrazine hydrochloride solution in 50 ml of water and dilute to 100 ml with water.

A5.4 50% m/m Hydrobromic acid.

Ultra-pure hydrobromic acid (d_{20} 1.50) must be used. Purify by extracting 500 ml with three 10 ml aliquots of toluene.

A5.5 m/m Hydrochloric acid.

Ultra-pure hydrochloric acid (d_{20} 1.18) must be used. Purify by extracting 500 ml with three 10 ml aliquots of toluene.
Note: although some batches of analytical grade hydrochloric acid may prove satisfactory others may contain unacceptably high levels of selenium (greater than 10 μSe/1;.

A5.6 45% m/m Perchloric acid

Carefully mix 400 ml of 60% m/m perchloric acid (d_{20} 1.54) with 200 ml of water.

A5.7 Toluene

Fractionally distil toluene and collect the fraction boiling at 111–112°C.

A5.8 1, 2-Diamino-3, 5-dibromobenzene hydrochloride reagent.

This compound is not, at present, available commercially, but may be readily prepared from 2-nitro-aniline in the following way.

A5.8.1 Preparation of diamino compound

Dissolve 13.8 ± 0.1 g of 2-nitro-aniline in 120 ml of glacial acetic acid and, while stirring, add a solution of 10.0 ± 0.1 ml of bromine in 10.0 ± 0.1 ml of glacial acetic acid. After the colour of the bromine has been discharged pour the mixture into 800 ml of water. Filter the precipitated dibromo-compound and wash it with water. Recrystallize it from aqueous methanol and air-dry it. (yield approximately 27 g). Moisten 6.0 ± 0.1 g of it with ethanol and heat it under reflux with 15.0 ± 0.2 g of granulated tin and 50 ± 1 ml of hydrochloric acid (d_{20} 1.18) until both the solution and the solid are colourless. Filter the solution after cooling and dissolve the solid in the minimum volume of boiling 1M hydrochloric acid and add 0.2 g of decolourizing charcoal. Filter the solution into a similar volume of hydrochloric acid (d_{20} 1.18). After cooling, filter the crystals off and recrystallize them in the same way. Suck the product dry on the filter and store *in vacuo* in a desiccator over sodium hydroxide pellets (yield 60–70% of theoretical).

A5.8.2 Preparation of reagent (0.12% m/V)

Dissolve 0.12 ± 0.01 g of diamino-dibromo-benzene hydrochloride in 100 ± 5 ml of hydrochloric acid. (d_{20} 1.18). Purify the solution by extracting with three 10 ml aliquots of toluene. The extracted reagent can be stored for up to one week in a well-stoppered bottle at 4°C.

A5.9 Standard selenium solutions

A5.9.1 Solution A 1 ml contains 100 μg Se

Weigh out 100 ± 0.5 mg of greater than 99.9% selenium shot into a 25 ml conical flask and add 3.0 ± 0.2 ml of nitric acid (d_{20} 1.42). Cover the flask with a loosely fitting bulb stopper and reflux its contents on a hot plate at a low setting. When all the selenium has dissolved transfer the contents of the flask quantitatively to 1-litre calibrated flask and dilute to volume with water. This solution is stable indefinitely if stored in a glass bottle in the dark. Commercially available standard selenium solutions may also be used.

A5.9.2 Solution B 1 ml contains 1 μg Se

Dilute 10.00 ± 0.02 ml of Solution A to 600 ml with water in a 1 1 calibrated flask, add 1.0 ± 0.1 ml of hydrochloric acid (d_{20} 1.18) and dilute to the mark with water. This solution should be prepared freshly before use.

A5.9.3 **Solution C** 1 ml contains 10 ngSe

Pipette 5.00 ± 0.02 ml of Solution B into a 500 ml calibrated flask and dilute to volume with water. This solution should be prepared freshly before use.

A5.10 Argon

Argon is used as the carrier gas and is purified by passage through a column of molecular sieve and an oxygen trap at an appropriate flow rate (approximately 65 ml/min has been found satisfactory).

A6 Apparatus

A6.1 A gas chromotagraph equipped with:

a ^{63}Ni election capture detector operated in accordance with the manufacturers instructions;
a 2 m × 4 mm glass column packed with acid washed — dimethylchlorosilane treated — (60–80 mesh) high performance grade Chromosorb W coated with a 3% m/m 0 V330;
Operating conditions which have been found satisfactory are:
column temperature 195°C, carrier gas flow 65 ml/min, detector oven 265°C;
a typical chromatogram is shown in Figure 1.

A6.2 Glassware

If possible, apparatus should be reserved solely for selenium determinations. Clean all glass and plastic ware by filling with, or soaking in, 10% V/V hydrochloric acid overnight. Rinse thoroughly with water. Thereafter, a thorough rinse with 10% V/V hydrochloric acid followed by a careful rinse with water after each determination should suffice.

A6.3 Special Glassware

500 ml separatory funnels fitted with polytetrafluoroethylene stopcocks.
5 ml mircolitre syringe for injection of the sample into the gas chromatograph.

A7 Sample collection and preservation

After collection, samples should be transferred to polyethylene bottles and treated with 1.0 ± 0.1 ml of hydrochloric acid (d_{20} 1.18) per litre. Samples preserved in this way are stable with respect to total selenium for at least one week. However, there is a possibility that changes may occur in the Se^{4+} : Se^{6+} ratio.

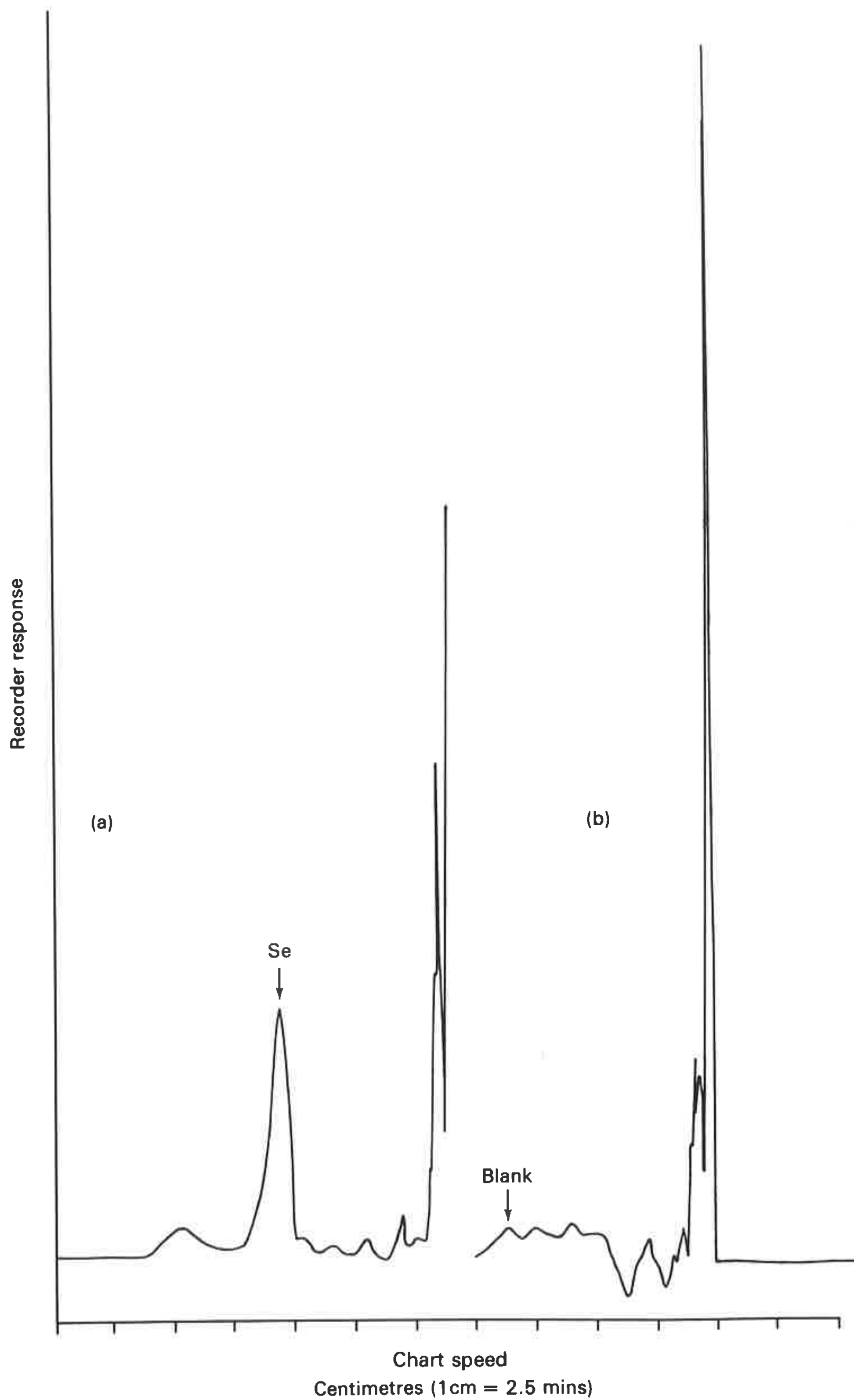


Figure 1 GC record for chromotography of (a) 40ngSe1^{-1} (b) a blank using OV330 column (chart speed 1 cm/2.5 minutes)

A8 Analytical Procedure

READ SECTION 4 ON HAZARDS BEFORE STARTING THIS PROCEDURE

A pre-treatment procedure is described for conversion of selenate, selenide and colloidal selenium to selenite followed by the determination of the latter. This must be used when **total** selenium is to be determined, when this pre-treatment stage is omitted only selenite is determined.

Step	Procedure	Notes
	Pretreatment for conversion of selenate, selenide and colloidal selenium to selenite (Notes a and b)	(a) this stage is essential in the determination of total selenium.
A8.1	Place 250 ± 1 ml of the sample in a 500 ml conical flask and add 15 ± 1 ml of hydrochloric acid (d_{20} 1.18) 12.5 ± 0.5 ml of hydrobromic acid (d_{20} 1.50) and 0.25 ± 0.02 ml of 3% m/V bromine water. Boil gently on a hot plate for 15 mins.	(b) It is possible that some volatile selenium compounds may be lost by this procedure.
A8.2	Cool, and add 1.0 ± 0.1 ml of 7% m/V hydrazine hydrochloride solution to reduce residual bromine.	
A8.3	Transfer the sample to a 500 ml separatory funnel. Add 25 ± 1 ml of toluene and shake vigorously for 60 ± 10 secs. After the phases have separated transfer the aqueous layer to a 500 ml separatory funnel and discard the organic phase. Proceed to Step A8.5	
	Determination of selenite	
A8.4	If only selenite is to be determined, place 250 ± 2 ml of the sample in a separatory funnel, add 25 ± 1 ml of toluene and shake for 60 ± 10 sec. Allow the phases to separate, run the aqueous phase into a 500 ml separatory funnel and reject the organic layer. Add 15 ± 1 ml of hydrochloric acid (d_{20} 1.18).	
	Determination of selenium	
A8.5	To the sample from Steps A8.3 or A8.4 add 10 ± 0.5 ml of 0.12% m/V diamino-dibromo-benzene reagent. Mix well and allow to stand for 120 ± 10 ml.	
A8.6	Add 1.00 ± 0.01 ml of toluene and shake the funnel vigorously for 2.0 ± 0.1 ml. Allow to stand until the two phases have completely separated. Run off and discard the aqueous phase.	
A8.7	Wash the toluene phase by shaking it with two 3.0 ± 0.1 ml aliquots of 45% m/m perchloric acid. Discard the acid.	
	Gas chromatography of piazselenol	
A8.8	With a syringe inject 2 l of the toluene extract onto the gas chromatographic column (see Section A6.1 for details). Measure the area of the piazselenol peak, eg with an integrator or with a planimeter. Let the reading be S.	

Step	Procedure	Notes

Blank determination

A8.9 A blank must be run with each batch of determinations in an identical way to that used with the samples.

A8.10 When total selenium is being determined carry out Steps A8.1 to A8.3 and A8.5 to A8.8 inclusive using 250 ± 5 ml of water. Let the area of the piazselenol peak be B_1.

A8.11 When selenite is being determined carry out Steps A8.4 to A8.8 using 250 ± 2 ml of water. Let the area of the piazselenol peak be B_2.

Calibration standards

A8.12 A duplicate calibration standard must be run with each batch of determinations in an identical manner to the samples.
When total selenium is being determined add 1.00 ± 0.01 ml of standard selenium Solution C to 250 ± 5 ml of water and carry out Steps A8.1 to A8.3 and A8.5 to A8.8 inclusive. Let the areas of the piazselenol peaks be C_1 and C_2; these correspond with a selenium concentration of 40 ng/1. When selenite is being determined add 1.00 ± 0.01 ml of standard selenium solution C to 250 ± 5 ml of water and carry out Steps A8.4 to A8.8. Let the areas of the piazselenol peaks be C_3 and C_4; these correspond with a selenium concentration of 40 ng/1.

Calculation of results

A8.13 Calculate the concentration of total selenium A from

$$A_T = \frac{S - B_1}{\bar{C}_T - B_1} \times 40 \text{ ng/1}$$

where

$$\bar{C}_T = \frac{C_1 + C_2}{2}$$

Calculate the concentration of selenite A_s from

$$A_S = \frac{S - B_2}{\bar{C}_S - B_2}$$

where

$$\bar{C}_S = \frac{C_3 - C_4}{2}$$

These calculations assume a linear calibration curve and linearity must be checked. (See Section A9).

A9 Checking the Linearity of the Calibration Curve

The procedure in this Section must be carried out on at least 2 independent occasions before the method is applied to any samples and regularly thereafter. It should be noted that the range of linear response very much depends on the design of the detector itself, although the slope of the linear portion of the curve is constant.

In each of a series of 500 ml separatory funnels place 250 ± 5 ml of water, 15 ± 1 ml of hydrochloric acid (d_{20} 1.18) and by pipette add 0.0, 1.0, 2.5, 5.0, 10.0 and 15.0 ml of standard selenium solution C. These volumes correspond with 0.0, 10.0, 25.0, 50.0 and 100 and 150 ng of selenium. Carry out steps A8.5 to A8.8 inclusive. Plot the area of the piazselenol chromatographic peak against the ng of selenium added.

The calibration curve is normally linear between 0.0 ngSe/1 and at least 400 ngSe/1.

A10 Changing Concentration Range of the Method

The procedure given can be used without modification to determine selenium in potable and saline waters in the concentration range 0–400 ng/1. When the selenium concentration of the sample exceeds this level, the sample should be diluted accordingly and an appropriate factor applied in the calculations given in Section A8.13.

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 main sources of error are summarized in the following subsections.

A11.1 Contamination

Because of the very low concentration at which selenium is present in uncontaminated natural waters, accurate results can only be achieved if the working conditions are critically examined so as to minimize any possibility of contamination. Sulphuric acid and sulphates contain significant amounts of selenium and it is advisable to carry out the analysis in a laboratory in which these compounds are not used.

A11.2 Presence of selenium in the water used for blanks

If selenium is present in the water used for the blank the results will be falsely low. A method for the determination of selenium in water used for the blanks has not yet been evaluated. However, it is thought that the following approach should prove satisfactory.

Carry out selenium determinations using exactly the procedures prescribed in Steps A8.1 to A8.8 inclusive with both 250 ± 1 ml and 125 ± 1 ml of the water.

The selenium content 125 ml of the blank water is equivalent to an integrated area of Y, where

$$Y = B_{250} - B_{125}$$

where B_{250} and B_{125} are the integrated areas of the piazselenol peaks obtained with 250 ml and 125 ml of the water respectively. The concentration of selenium (A_W) in the blank water is then given by

$$A_W = \frac{Y}{\bar{C}_T - B_1} \times 320 \text{ g/1 Se}$$

This concentration must then be added to the selenium concentration as determined in Step A8.13.

A11.3 Interfering substances

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

B Selenium in Raw and Potable Waters Fluorimetric Method (High Level)

B1 Performance Characteristics of the Method

(For further information on the determination and definition of the characteristics see General Principles of Sampling and Accuracy of Results 1980 also published in this series).
Note: Throughout this method selenium is expressed as the element (Se)

B1.1	Substance determined	Selenate and selenite
B1.2	Types of samples	Raw and potable waters.
B1.3	Basis of method	Pre-treatment to convert to selenite, followed by reaction with diamino naphthalene to give a piazselenol which is extracted with cyclo-hexane and determined fluorimetrically.
B1.4	Range of application (a) (b)	Up to 40 g/1 (See Section B11)
B1.5	Calibration curve (a) (b)	Linear up to at least 40 μ/1

B1.6 Standard deviation (a) (within batch)

Type of sample	standard deviation μg/1	Degrees of Freedom
Distilled water spiked with 0.4 μg/1Se^{6+}	0.02	(n = 5)
Distilled water spiked with 2.0 μ/1Se^{6+}	0.08	(n = 5)
Distilled water spiked with 10 μg/1Se^{6+}	0.25	(n = 6)

B1.7	Limited of detection (a) (b)	1.1 μg/1
B1.8	Bias (a)	Not known
B1.9	Interferences (a)	See Section 3
B1.10	Time required for analysis	For analysis of 10 samples including pre-treatment operator time 10 hours total 14 hours.

(a) These data were obtained at the Department of Oceanography University of Liverpool (1) using a Turner fluorimeter.
(b) The range of application, linear range, detection limit and sensitivity depends markedly on the instrument used.

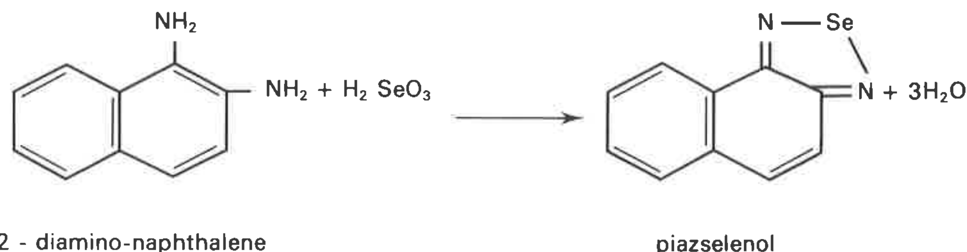
B2 Principle

B2.1

The method, which is a modification of earlier procedures (5–9), is based on work carried out in the Department of Oceanography, University of Liverpool. (1)

B2.2

The sample is buffered to pH 8.0 ± 0.1, hydrogen peroxide added and irradiated with ultra-violet radiation[b], to inter-convert selenate and selenite to an equilibrium mixture containing approximately 86% Se^{4+} and approximately 14% Se^{6+}. After irradiation the sample is extracted with cyclo-hexane to remove flourescent material. EDTA is added as a masking agent, and following adjustment of the pH to 2.00 ± 0.05, a solution of 1,2-diamino-naphthalene is added to form a fluorescent piazselenol which is extract with cyclo-hexane.



1,2 - diamino-naphthalene piazselenol

The extract is excited with radiation of wavelength 382 nm and the fluorescence is measured at 528 nm. Selenite alone can be determined if the irradiation step is omitted.

B2.3

The UV oxidation procedure was found to breakdown piazselenol, seleno-D-L-methionine, seleno-cystamine hydrochloride and seleno-urea quantitatively.

B3 Interferences

The effects of a number of potential interfering substances at the levels recommended by the Standing Committee of Analysts (10) are shown in Table 2. No significant interferences were encountered with any of these at a selenium level of 10 μg/1.

B4 Hazards

B4.1

Particular care must be taken to avoid exposure to the intense ultra-violet radiation produced by the mercury lamp as this can cause permanent eye and skin damage. Copious quantities of ozone are produced by the lamp; this is toxic and it is essential that the cooling air from the irradiation apparatus is vented to a fume hood.

B4.2

Both toluene and diamino-naphthalene are toxic and perhaps carcinogenic and all work with them must be carried out in a fume hood.

B4.3

Care is required when preparing and handling solutions containing selenium (see Section A5.9) as these are toxic. If any are ingested, immediately carry out gastric aspiration and lavage and obtain medical attention.

B5 Reagents

All reagents and standard solutions should be kept in polyethylene or glass bottles which have been cleaned by the procedure described in Section A6.3. Except where otherwise stated analytical grade chemicals are suitable.

B5.1 Water

See section A5.1

Table 2 Effect of other substances on the fluorimetric determination of Selenium (iv)

Other Substance		Other Substance added as	Concentration of other substance (mg/1)	Effect of other substance in µg Se/1 at selenium concentrations of (µg/1) (c)			
				0.00	0.10	1.00	10.00
Cadmium	(as Cd^{2+})	Chloride	2	+0.02	+0.06	+0.01	−0.20
Calcium	(as Ca^{2+})	Chloride	500	+0.02	+0.01	−0.03	−0.20
Cobalt	(as Co^{2+})	Chloride	5	+0.02	0.00	+0.04	+0.30
Copper	(as Cu^{2+})	Chloride	5	−0.03	0.00	0.00	+0.30
Iron	(as Fe^{3+})	Chloride	1	0.00	−0.03	0.00	0.00
Magnesium	(as Mg^{2+})	Chloride	100	+0.02	0.00	+0.02	+0.20
Potassium	(as K^{+})	Chloride	20	+0.02	0.00	−0.03	−0.10
Sodium	(as Na^{+})	Chloride	300	−0.02	+0.01	+0.03	−0.30
Strontium	(as Sr^{2+})	Chloride	3	+0.03	0.00	+0.02	−0.40
Fluoride	(as F^{-})	Sodium	10	+0.02	+0.01	0.00	+0.40
Nitrate	(as NO_3^{-})	Sodium	50	+0.01	+0.03	0.00	0.00
Nitrite	(as NO_2^{-})	Sodium	0.5	+0.02	−0.03	0.00	−0.20
Fulvic acid		Substance	50		0.00	+0.01	

(c) If the other substances did not interfere the effect would be expected to lie (95% confidence) within the following ranges:–

0.00 ± 0.04 µg Se/1 at 0.00 µg/1 selenium
0.00 ± 0.04 µg Se/1 at 0.10 µg/1 selenium
0.00 ± 0.05 µg Se/1 at 1.00 µg/1 selenium
0.00 ± 0.50 µg Se/1 at 10.00 µg/1 selenium

It should be noted that measurements at low levels of selenium were carried out at a considerably higher instrumental sensitivity setting than those at the higher levels of selenium.

B5.2 1M borate buffer

Dissolve 3.81 ± 0.03 g of sodium tetraborate deca-hydrate in water and dilute to 100 ml with water. This solution is stable indefinitely.

B5.3 30% m/m hydrogen peroxide

B5.4 Cyclo-hexane

Fractionally distil cyclo-hexane and collect the fraction boiling in the range 80.5°C–81.5°C.

B5.5 0.1M Hydrochloric acid (approximately)

Dilute 8.9 ± 0.2 ml of hydrochloric acid (d_{20} 1.18) to 1 litre with water in a calibrated flask. Extract 500 ml of the solution twice with 10 ml aliquots of cyclo-hexane to purify it.

B5.6 2M Ammonium hydroxide (approximately)

Dilute 14.1 ± 0.2 ml of ammonia solution (d_{20} 0.90) to 100 ml with water.

B5.7 0.1M Ethylene diamine tetra-acetic acid solution (EDTA) approximately

Dissolve 1.45 ± 0.02 g of ethylene diamine tetra-acetic acid (di-sodium salt) in 15 ml of 2M ammonia solution and dilute to 50 ± 1 ml with water. Purify this solution by extracting it with 10 ml of cyclo-hexane.

B5.8 0.1% m/V Diamino-naphthalene solution (DAN)

If the commercial 2,3-diamino-naphthalene is discoloured recrystallize it from water and allow the crystals to stand at 0°C overnight with the mother liquor. Filter off the

crystals, dry overnight *in vacuo*, and store in a tightly stoppered container under refrigeration. Prepare the reagent by dissolving 100 ± 2 mg of the DAN in 100 ± 2 ml of 0.1M of hydrochloric acid, if necessary, warming briefly to complete the dissolution. Cool, and extract the solution twice with 15 ml portions of cyclohexane. The solution can be stored at 4°C in a dark glass bottle for up to 2 days.

B5.9 Standard selenium solutions

B5.9.1 **Solution A**

1 ml contains 100 μgSe
Prepare and store as described in Section A5.9.1.

B5.9.2 **Solution B**

1 ml contains 1 μSe
Prepare freshly when required as described in Section A5.9.2

B6 Apparatus

B6.1 Spectrofluorimeter or fluorimeter fitted with optical filters having their maximum transmission at 382 nm (excitation) and 528 nm (emission).

B6.2 Ultra violet irradiation apparatus

The apparatus which is used for pretreatment of samples (Section B8.3) is shown diagrammatically in figure 2. It consists basically of a cylindrical aluminium box containing an axially mounted 1 Kw medium pressure mercury lamp around which are arranged ten 25 cm by 4 cm diameter fused silica tubes each at a distance of approximately 10 cm from the lamp. Cooling, to the optimum temperature of 60 ± 3°C, is provided by an externally mounted fan.

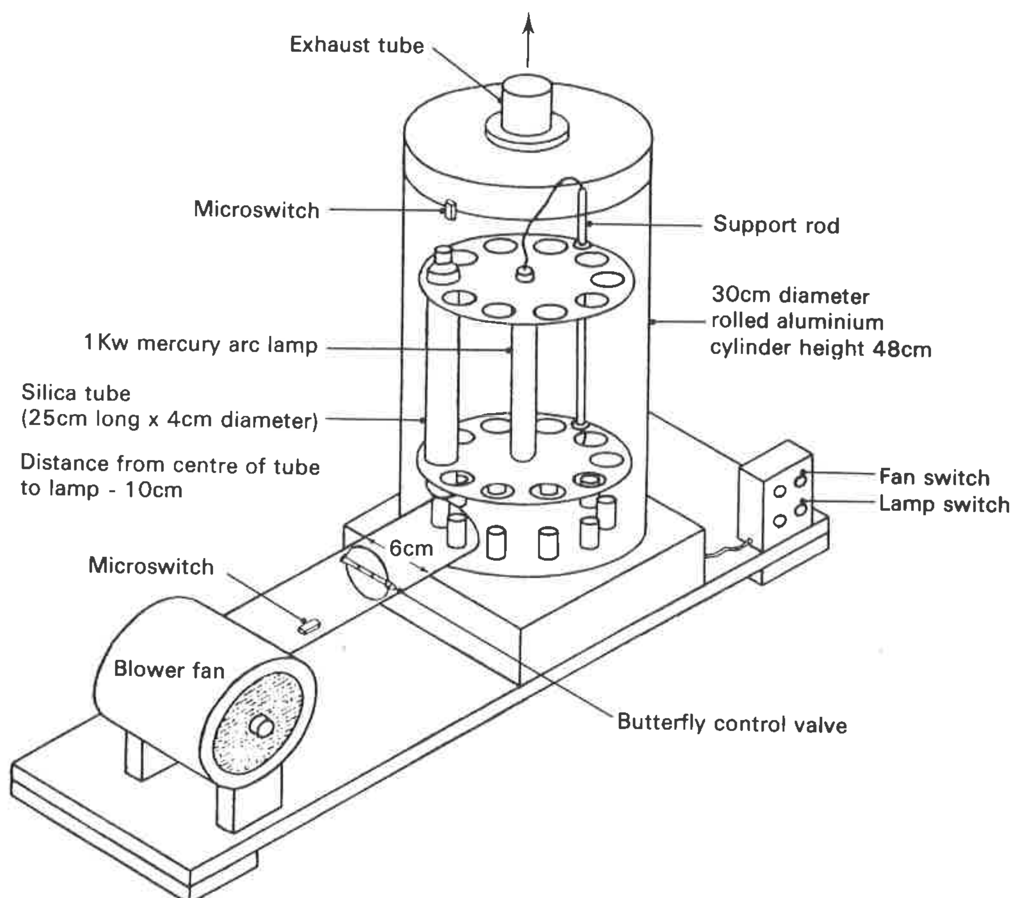


Figure 2 Ultraviolet Photolysis Apparatus

The expelled air is vented to a fume cupboard to remove ozone which is toxic. The lid of the irradiation chamber is fitted with an interlocked micro-switch so that the mercury lamp cannot be operated when the lid is open. A pressure sensitive switch in the air duct from the fan ensures that the lamp is extinguished if the fan fails.

B6.3 Separatory funnels

(500 ml) fitted with PTFE stopcocks.
Note: on no account must greased glass stopcocks be used.

B6.4 Glassware

(see Section A6.4)

B7 Sample Collection and Preservation

See Section A7.

B8 Analytical Procedure

READ SECTION B4 BEFORE STARTING THIS PROCEDURE
If the pre-treatment is omitted only selenite is determined.

Step	Procedure	Notes
	Pretreatment	
B8.1	Place 250 ± 2 ml of the samples in a beaker and adjust to pH 8.1 ± 0.1 by cautious addition of 1M borate buffer (note a).	(a) use a pH meter.
B8.2	Transfer the solution quantitatively to a silica irradiation tube and add 0.05 ± 0.02 ml of 30% m/m hydrogen peroxide.	
B8.3	Close the tube with a bulb stopper and place it in the irradiation apparatus. Illuminate with ultra-violet light for 5.0 ± 0.5 hours at a temperature 60 ± 3°C and then allow to cool to room temperature.	
	Determination of selenium (note b)	(b) if only selenite is to be determined commence at Step 8.4 using 250 ± 2 ml of sample.
B8.4	Transfer to a 500 ml separatory funnel and extract twice with 10 ± 1 ml of **cyclo**-hexane. Reject the organic phase.	
B8.5	Run the aqueous phase into a 300 ml conical flask and add 0.5 ± 0.1 ml of 0.1 M EDTA solution.	
B8.6	Adjust the pH of the solution to 2.00 ± 0.05 by cautious addition of 0.1M hydrochloric acid (note c) and then add 5.0 ± 0.1 ml of 0.1% m/V diamino-naphthalene solution.	(c) a pH meter should be used.
B8.7	After mixing, heat the flask in a waterbath at 50 ± 3°C for 120 ± 10 min. and then cool to room temperature.	

Step	Experimental procedure	Notes
B8.8	Quantitatively transfer the solution to a 500 ml separatory funnel and extract it with 10.0 ± 0.05 ml of cyclo-hexane for 60 ± 5 sec.	
B8.9	Allow the two phases to separate and then run off and discard the lower, aqueous, phase. Wash the organic layer with two 25 ± 1 ml aliquots of 0.1M hydrochloric acid.	
B8.10	Set up the spectrofluorimeter or fluorimeter according to the manufacturer's instructions. Select the suitable sensitivity range and set the instrument to zero with cyclo-hexane in the cuvette.	
B8.11	Transfer the piazselenol extract to the cuvette and measure the intensity of its fluorescence (I_s). (Note d).	(d) the piazselenol extracts can be stored for at least 3–4 days at 4°C without significant loss of fluorescence.

Blank determination

Step	Experimental procedure	Notes
B8.12	A blank must be run with each batch of determinations. If pre-treatment was used carry out Steps B8.1 to 8.11 inclusive using 250 ± 5 ml of water. If no pre-treatment stage was used (ie if only selenite is being determined), use the same volume of water and carry out Steps B8.4 to B8.11 inclusive. Let the intensity of the fluorescence be I_S.	

Calibration standards

Step	Experimental procedure	Notes
B8.13	A duplicate calibration standard must be run with each batch of samples in an identical manner to that used for the samples. Add 5.00 ± 0.02 ml of standard selenium **solution B** to 245 ± 5 ml of water and carry out Steps B8.1 to B8.11 if pretreatment is being employed or Steps B8.4 to B8.11 if only selenite is being determined (note 3). Let the intensities of the fluorescence of these calibration standards be I_{C_1} and I_{C_2}. These correspond with the fluorescence from 20 μg/1Se.	(e) it is essential that separate standards be used for calibration of the total selenium and selenite procedures.

Calculation of results

B8.14 Calculate the concentration A of selenium from

$$A = \frac{(I_S - I_B)}{(I_{\bar{C}} - I_B)} \times 20\ \mu g/1$$

$$\text{where } I_{\bar{C}} = \frac{I_{C_1} + I_{C_2}}{2}$$

This calculation assumes that the calibration curve is linear which must be checked (see Section B10).

B9 Measurement of Fluorescence

The procedure used for measuring the intensity of fluorescence should be rigorously controlled to ensure satisfactory precision of measurement. The same cuvette must be used for measurement of the sample, blank and calibration standards. Before insertion in the instrument it must be carefully wiped to ensure cleanliness. It should always be placed in the same position in the cell-holder and if it is rectangular the same side should face the light source.

B10 Checking the Linearity of the Calibration Curve

The procedure given in this Section must be carried out on at least two independent occasions before the method is used for any samples and regularly thereafter.

To each of a series of 250 ± 5 ml aliquots of water by pipette add 0.0, 2.5, 5.0, 7.5 and 10.0 ml of standard selenium **solution C** and carry out the procedures described in Steps B8.1 to B8.11 inclusive, or if only selenite is being determined Steps B8.4 to B8.11 inclusive. These volumes correspond with selenium concentrations of 0, 10, 20, 30 and 40 μg selenium. Plot the fluorescence intensity against μg/l selenium for each solution. The calibration curve is normally linear up to at least 40 μg/l selenium.

B11 Changing Concentration Range of the Method

The procedure described can be used without modification to determine selenium in raw and potable waters in the concentration range 0–40 μg/l selenium. When the selenium level exceeds this, a proportionately smaller volume (V) of the sample should be taken and diluted to 250 ± 5 ml with water before proceeding to Steps B8.1 or B8.4 as appropriate.

In these cases the calculation (B8.14) must be modified to

$$A = \frac{(I_S - I_B)\ 5000}{(I_C - I_B)\quad V} \mu g/l \text{ Se}$$

B12 Sources of Error

The attention which must be paid to sources of error depends on the accuracy which is required. The following sub-sections summarize the main sources of error.

B12.1 Contamination

Because the sensitivity of the fluorimetric method is much lower than that of the gas chromatographic method contamination causes much less difficulty with it than does the latter.

Nevertheless cleanliness in working is of great importance and care should be taken to minimize any possibility of contamination.

B12.2

If selenium is present in the water used for the blank, the results will be erroneously low. No difficulties have been experienced in this way, but if the presence of significant concentrations of selenium in the water is suspected it can be evaluated using the procedure described in Section A11.2.

B12.3 Interfering substances

See Sections B3 and A11.3

Arsenic and Selenium in Sludges, Soils and Related Materials by Hydride Generation and Atomic Absorption Spectrophotometry

Performance Characteristics of the Method

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

Note: Throughout this method arsenic and selenium are expressed as their elements (As and Se) respectively.

C1.1 Substances determined: All forms of arsenic and selenium

C1.2 Types of sample: Liquid and solid sludges, soils, sediments, plant material and animal tissue.

C1.3 Basis of the method: Manual treatment whereby the sample is ashed under oxidizing conditions, and inorganic arsenic and selenium are extracted into an acid solution. This is followed by automated hydride generation, thermal atomization, and measurement by atomic absorption spectrophotometry.

C1.4 Range of application: 0–1 mg/kg for liquid sludges; 0–20 mg/kg for solid samples (for both As and Se). These ranges may be extended (see Section C11).

C1.5 Calibration curve: Linear to at least 8 μg/1 for both As and Se at the measurement of pretreated extracts stage.

C1.6 Total standard

Type of sample	Arsenic Conc (mg/kg)	Arsenic SD (mg/kg)	Selenium Conc (mg/kg)	Selenium SD (mg/kg)
Grass	0.3	0.1	0.3	0.03
Liquid sludge (c)	0.6	0.03	0.06	0.03
Dried sludge	11	0.5	4	0.6
Soil	14	0.6	0.2	0.03
Fish tissue	14	0.6	1.6	0.1

C1.7 Limit of detection (a) (b): Approximately 0.05 mg/kg As and 0.05 mg/kg Se for liquid sludge; 0.5 mg/kg As and 0.2 mg/kg Se for solid samples.

C1.8 Sensitivity (b): 5 μg/1 As and Se in the pretreated extract gives an absorbance of approximately 0.25.

C1.9	Bias	Negative bias may be observed, particularly if samples contain volatile arsenic and selenium compounds, or if arsenic and selenium are bound inside mineral grains. The extent of bias will vary from sample to sample, but in most cases will not be significant.
C1.10	Interferences	Copper and Silver also Iron III. Antimony, Bismuth, Cobalt, Mercury, Nickel, Fluoride and oxidizing agents can interfere. The extent of interference will vary from sample to sample too, but in most cases will not be significant. See Tables 3, 4 and 5.
C1.11	Time required for analysis (b)	Excluding time for ashing (conveniently carried out overnight) the time required to pretreat 1 to 30 samples is typically 2 to 7 h. The time required to measure the arsenic (or selenium) concentration in 1 to 90 pretreated extracts is typically 2 to 7 h.

(a) Guide values only. Analysis of variance was used to estimate the standard deviation for a multi-stage evaluation. Estimation of degrees of freedom involves complex calculations and has not been determined.
(b) This data was obtained at the Water Research Centre, Stevenage Laboratory. (11)
(c) Sample spiked with sodium arsenate and sodium selenate.

C2 Principle

C2.1

This method is based on the technique described by Goulden and Brooksbank (12) and the Department of the Environment (13) for waters and has been modified and developed by the Water Research Centre (11) so that it is applicable to sludges, soils and related materials.

C2.2

The sample is digested with nitric acid and ashed with magnesium nitrate to destroy organic matter under oxidizing conditions. The inorganic arsenic and selenium resulting from this procedure are extracted into hydrochloric acid and diluted to a suitable concentration. The extracted solution is treated automatically with a series of reagents. Firstly hydrochloric acid, stannous chloride and potassium iodide are added to reduce any As (+5) to As (+3) and Se (+6) to Se (+4). Secondly aluminium is added to convert the arsenite and selenite produced to their respective hydrides As (−3), Se (−2). The volatile hydrides are entrained together with hydrogen in a stream of argon, dried by passing through sulphuric acid, mixed with air and passed into a quartz furnace where the presence of arsenic and selenium is detected by atomic absorption spectrophotometry. The concentrations of arsenic and selenium in the sample are calculated from the concentrations of arsenic and selenium in the extracts which are determined by reference to standard solutions treated in the same way.

C3 Interferences

C3.1

Tables 3 and 4 below give details of potential interfering substances which have been taken through part of the analytical procedure. The solutions for interference testing were prepared from either solid reagents or concentrated solutions of the reagents in such a way that 500 ml of the solution contained the stated mass of other substance and the stated mass of arsenic or selenium. The solutions were then run through the measurement stage (Steps C9.7 to C9.13) of the method and the results expressed as the effect on the stated mass of arsenic or selenium.

C3.2

Assuming samples containing 250 mg of dried solids are ashed, extracted and diluted to the equivalent of 500 ml then 100 mg and 250 mg of the other substance used would correspond to the solid samples containing 40% and 100% of the other substance, respectively; and 3.75 μg of As or Se would correspond to the solid samples containing 15 mg/kg of As or Se.

Table 3 Effect of other substances on the determination of arsenic and selenium

Other substances	Mass of other substance (mg)	Effect in μg As of other substance on 3.75 μg As (c)	Effect in μg Se of the other substance on 3.75 μg Se (c)
Sodium as chloride	250	0.0	0.0
Potassium as chloride	250	0.2	−0.1
Calcium as chloride	250	0.0	0.0
Magnesium as chloride	250	−0.2	0.2
Aluminium as sulphate	250	0.4	0.2
Lanthanum as chloride	250	0.1	−0.3
Borate as sodium salt	250	0.0	−0.1
Carbonate as sodium salt	250	−0.1	−0.2
Nitrate as sodium salt	250	−0.6	−0.5
Ammonium salt as hydroxide	250	0.0	0.0
Phosphate as potassium salt	250	0.2	0.2
Sulphate as sodium salt	250	0.2	0.0
Fluoride as sodium salt	250	1.2	−0.7
Bromide as sodium salt	100	0.0	0.2
Iodide as sodium salt	100	−0.2	0.1
Chromium III as chloride	100	0.1	−0.2
Manganese II as sulphate	100	0.1	0.3
Iron III as chloride	250	−0.7	0.5
Cobalt II as chloride	100	−0.9	−1.7
Nickel as sulphate	100	−1.1	−3.4
Copper II as chloride	250	−3.4	−1.8
Zinc as oxide	250	0.0	0.2
Cadmium as chloride	100	0.1	0.3
Mercury II as chloride	100	−1.9	−2.9
Tin II as chloride	100	−0.4	−0.4
Lead II as acetate	100	−0.7	0.5
Antimony as sodium tartrate	250	−2.5	−3.7
Bismuth as nitrate	100	−0.3	−3.0

(c) If the other substances did not interfere the effect would be expected (95% confidence) to lie within the range 0.0 ± 0.2 μg As or Se.

C3.3

These results indicate that the method should be suitable for most normal samples. Large quantities of some substances eg copper and nickel will interfere if not removed. Other experimental work indicates that the procedure may be affected by substances present in the original sample but not present in the extracts, for example selenium in the form of mercuric selenide may well be volatilized with mercury at the ashing stage.

Table 4 Effect of other substances on the determination of arsenic and selenium

Other substances (salt as in Table 3)	Mass of other substance (mg)	Effect in µg As of other substance on 3.75 µg As (c)	Effect in µg Se of the other substance on 3.75 µg Se (c)
Cobalt	0.5	0.0	0.0
	2.5	0.1	−0.7
	5	−0.4	−1.0
	10	−0.8	−1.1
Nickel	0.5	−0.3	−0.3
	2.5	−0.2	−1.2
	5	−0.6	−2.1
	10	−1.0	−3.1
Copper	0.5	0.0	−0.1
	2.5	−0.2	−1.3
	5	−0.3	−2.6
	10	−0.6	−3.3
Antimony	0.5	0.0	−2.0
	2.5	−0.3	−2.4
	5	−0.7	−2.9
	10	−1.6	−3.5
Mercury	0.5	0.2	−1.5
	2.5	−0.1	−2.5
	5	−0.3	−2.6
	10	−0.2	−2.8

(c) If the other substances did not interfere the effect would be expected (95% confidence) to lie within the range 0.0 ± 0.2 µg As or Se.

In tests with arsenic standards alone and selenium standards alone no evidence of cross interference was noted.

C4 Hazards

C4.1

Care is required when handling arsenic and selenium compounds and solutions as these are toxic.

C4.2

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

C4.3

Particular care is required when disposing of unused and used reagents since large volumes of flammable hydrogen and highly toxic arsenic and selenium hydrides could be produced. It is essential that aluminium slurries, acid solutions and solutions containing arsenic and selenium should be disposed of individually and separately.

C4.4

When pumping sulphuric acid ensure that adequate safety screens and safety trays are in place to prevent any harm from a burst tube. Pump switches should be well clear of the pumping area for safe access.

Table 5 Interference data for arsenic and selenium but using 0.15M hydrochloric acid and sodium borohydride solution (3% for Se, 2.5% for As), at optimum conditions in absence of interferent in a commercial generator kit.

Other substance (as chloride or sodium salt)	Other substance concentration mg/l	% Recovery relative to no interference	
		Se Iv at 2 µg/l	As III at 6 µg/l
			†
Na^+	200	100.7	100
K^+	200	102.0	100
Mg^{2+}	200	97.5	100
Ca^{2+}	200	98.0	100
Sr^{2+}	100		85
Ba^{2+}	20		c100
	1	100.0	
Mn^{2+}	200	157[1]	
Fe^{3+}	200	73.9	
	100		85
	20		higher than 85
Cd^{2+}	1	99.0	
Co^{2+}	1	100.6	
	2		86
	5		65
Cu^{2+}*	1	15.6	95
	2		c100
Pb^{2+}	1	96.4	
Zn^{2+}	1	98.7	
Hg^{2+}	1	98.0	
Ag^{+}*	0.1	50.7	30
Ni^{2+}	1	97.8	
V as VO_{3-}	1	97.0	
In^{3+}	1	98.0	
Si as SiO_3^{2-}	1	99.0	
Mo as Mo O_4^{2-}	1	99.0	
P as PO_4^{3-}	1	100.8	
NO_3^-	20	100	100
$S0_4^=$	20	100	100
Cr as CrO_4^{2-}	1	97.0	
Al^{3+}	1	100.0	100
Ti^{4+}	20		100
Se as SeO_3^-	2		60‡

* EDTA and citric acid both failed to repress these interferences
† As V gives lower values than as III (c 80%)
‡ But see Table 4
[1] Checked in multiplicate; at nil Se there was no effect.

C5 Reagents

C5.0.1 Unacceptable baseline and blank values can be caused by minute amounts of contaminants, particularly arsenic, in the reagents. Very highly purified chemicals claimed to have been manufactured and tested to specifications which are orders of magnitude higher than those of the equivalent analytical reagent grade are not necessarily better than the analytical grade, and may be unacceptable even though they comply with the maximum limit claimed. At the time when the work leading to the development of this method was undertaken, analytical grade hydrochloric acid contained much less arsenic than the highly purified grade from the same supplier.

When a satisfactory batch has been found it should be reserved for arsenic and selenium use only.

C5.0.2 If for any reason metal sulphates are used for checking a suspected interference, these should be proved free from selenium by X-ray fluorescence spectrometry (see other booklets in this series Refs 15 and 16).

The following reagents are required for the pretreatment-ashing stage of the analytical procedure.

C5.1 Nitric Acid (d_{20} 1.42)

C5.2 Magnesium Nitrate Hexahydrate.

C5.3 Anti-Bumping Granules.

The following reagents are required for the pretreatment-extraction stage the measurement stage, and for checking linearity and reduction efficiency. Laboratories not using the measurement stage described should consider which of these reagents are required for their particular system.

C5.4 Water

The water used for preparing standard solutions, reagent solutions and for washing purposes should have arsenic and selenium contents that are less than 0.1 μg/1. Distilled or deionized water is usually suitable.

C5.5 Hydrochloric Acid (d_{20} 1.18)

The importance of using hydrochloric acid which is free from arsenic and selenium must be stressed. Hydrochloric acid containing 10 μg/1 As (ie 0.01 mg/1 or 0.01 ppm or 0.000001%) is not suitable. It should contain less than 1 μg/1 and preferably less than 0.1 μg/1.

C5.6 6M Hydrochloric Acid (Approximately)

Dilute 530 ± 10 ml of hydrochloric acid (d_{20} 1.18) with water to 1 litre in a measuring cylinder.

C5.7 0.6M Hydrochloric Acid (Approximately)

Dilute 53 ± 1 ml of hydrochloric acid (d_{20} 1.18) with water to 1 litre in a measuring cylinder. This solution is also used as the zero calibration standard for both arsenic and selenium.

C5.8 Stannous Chloride Reagent

Dissolve 3.6 ± 0.1 g of stannous chloride dihydrate in 2.5 litres of hydrochloric acid (d_{20} 1.18)

C5.9 Potassium Iodide Reagent

Dissolve 10.0 ± 0.1 g of potassium iodide in water and dilute with water to 500 ml in a measuring cylinder. Store in a polyethylene bottle and discard when discoloured.

C5.10 Aluminium Slurry

Add 2.50 ± 0.05 g aluminium powder (< 50 μm particle size) to 500 ml water. The aluminium should be kept in suspension by stirring continuously with the aid of a plastic coated magnetic stirrer. Prepare fresh each day — dispose with care (see section 4.3 on hazards).

C5.11 Sulphuric Acid (d_{20} 1.84)

(Selenium free, see C5.0.2)
(Acid containing arsenic is not unknown)

C5.12 Argon

C5.13 Standard Arsenic Solutions

The solutions are hazardous — see section C4.1

Standard solutions are required, and may be prepared in many suitable ways. The following are suggested as being useful.

C5.13.1 Stock arsenic solution A:

1 ml = 1000 μg As
This is commercially available as an arsenic standard for AAS.

C5.13.2 Stock arsenic solution B:

1 ml = 25 μg As
Dilute 25.00 ± 0.1 ml of solution A to 1 litre with 0.6M hydrochloric acid in a calibrated flask.

C5.13.3 Stock arsenic solution C:

1 ml = 10 μg As
Dilute 10.00 ± 0.02 ml of solution A to 1 litre with 0.6M hydrochloric acid in a calibrated flask.

C5.13.4 Stock arsenic solution D:

1 ml = 0.1 μg As
Dilute 10.00 ± 0.02 ml of solution C to 1 litre with 0.6M hydrochloric acid in a calibrated flask.

C5.13.5 Calibration standard arsenic solution E:

1 ml = 0.005 μg As
Dilute 50.0 ± 0.1 ml of solution D to 1 litre with 0.6M hydrochloric acid in a calibrated flask.

C5.13.6 Other calibration standards

Other calibration standards may be required for checking linearity. These may be prepared from appropriate volumes of solution D and 0.6M hydrochloric acid.

C5.13.7 Standard arsenite, arsenate, and organo-arsenic solutions

Standard solutions of As (+3) and As (+5) will be required to check the efficiency of the reduction step. Standard solutions of organo-arsenic compounds may be required to check the efficiency of the ashing stage. It is recommended that 1000 mg/l As standards are prepared from appropriate quantities of sodium arsenite, sodium arsenate and sodium cacodylate in 0.6M hydrochloric acid. From these 25 mg/l As solutions in 0.6M hydrochloric acid may be prepared and assayed for As content using conventional flame AAS and the stock arsenic solution B. These assayed solutions can then be used to prepared solutions for efficiency checking.

C5.14 Standard Selenium Solutions

These solutions are hazardous — see Section C4.1

These may be prepared in exactly the same way as standard arsenic solutions, except that commercially available selenium standard for AAS, sodium selenite (Se +4) and sodium selenate (Se +6) and an organoselenium compound, such as seleno-methionine are used in place of the arsenic compounds or solutions.

C6 Apparatus

C6.1

An atomic absorption spectrophotometer fitted with arsenic and selenium electrodeless discharge lamps. A chart recorder is a satisfactory form of read out for the signal from the atomic absorption spectrophotometer.

C6.2 Special apparatus

A schematic diagram of the automated hydride generation apparatus is given in figure 3. The sample is mixed with stannous chloride in hydrochloric acid and then potassium iodide in coiled tube A and then passed through coiled tube B in the heating bath. The aluminium slurry is introduced and the mixture passed through coiled tube C in the heating bath. A stream of argon is introduced and the hydride is separated into the gasphase in the stripping column in which it is also cooled and dried with sulphuric acid. Finally the gas stream is mixed with air and passed into the furnace tube of the atomic absorption spectrophotometer. Figure 4 shows a diagram of the furnace.

C6.2.1 Proportionating pump

Eight channels are required. More may be necessary if the required flow rates cannot be achieved using a single channel. Connections are made using silicone rubber or acid resistant tubing as appropriate. The flow rates are given for guidance and need to be optimized for a particular apparatus.

C6.2.1.1 Argon 2.0 ml/min.

C6.2.1.2 Argon 0.5 ml/min.

C6.2.1.3 Sample 6.7 ml/min.

C6.2.1.4 Stannous chloride in hydrochloric acid 6.1 ml/min.

C6.2.1.5 Potassium iodide 0.3 ml/min.

C6.2.1.6 Aluminium slurry 1.7 ml/min. The slurry is pumped with argon (C6.2.1.1) to give a combined rate of 3.7 ml/min. (See fig 6 for dispenser)

C6.2.1.7 Sulphuric acid 3.3 ml/min.

C6.2.1.8 Water 13.9 ml/min.

C6.2.2 Other reagent lines.

C6.2.2.1 Argon about 75 ml/min.

C6.2.2.2. Air about 8 ml/min.

C6.2.3 Magnetic Stirrer

This is used to agitate the aluminium slurry.

C6.2.4 Oil bath

The bath must be stirred and capable of thermostatic control (±1°C) at a temperature of about 95°C.

C6.2.4.1 Glass tubing, coiled to fit oil bath. 0.24 cm internal diameter, 250 cm long tubing for coil B and 0.24 cm internal diameter, 500 cm long for coil C have been found to be satisfactory. The minimum length of acid resistant tubing should be used to connect the two coils.

C6.2.5 Stripping column

The design and dimensions are given in Figure 5. The column is packed with glass helices, 4 mm diameter by 4 mm long, wound with resistance wire (5 ohms) and thermally insulated. A potential is applied to the wire through a variable transformer so that a temperature of 110 ± 5°C is registered by the thermocouple placed on the column under the heating wire, when the gas/liquid is passing through the column. The stripping column is connected to the condenser drain with a heat shrink polytetrafluoroethylene (PTFE) sleeve. The sulphuric acid wash column is also packed with 4 mm diameter, 4 mm long glass helices.

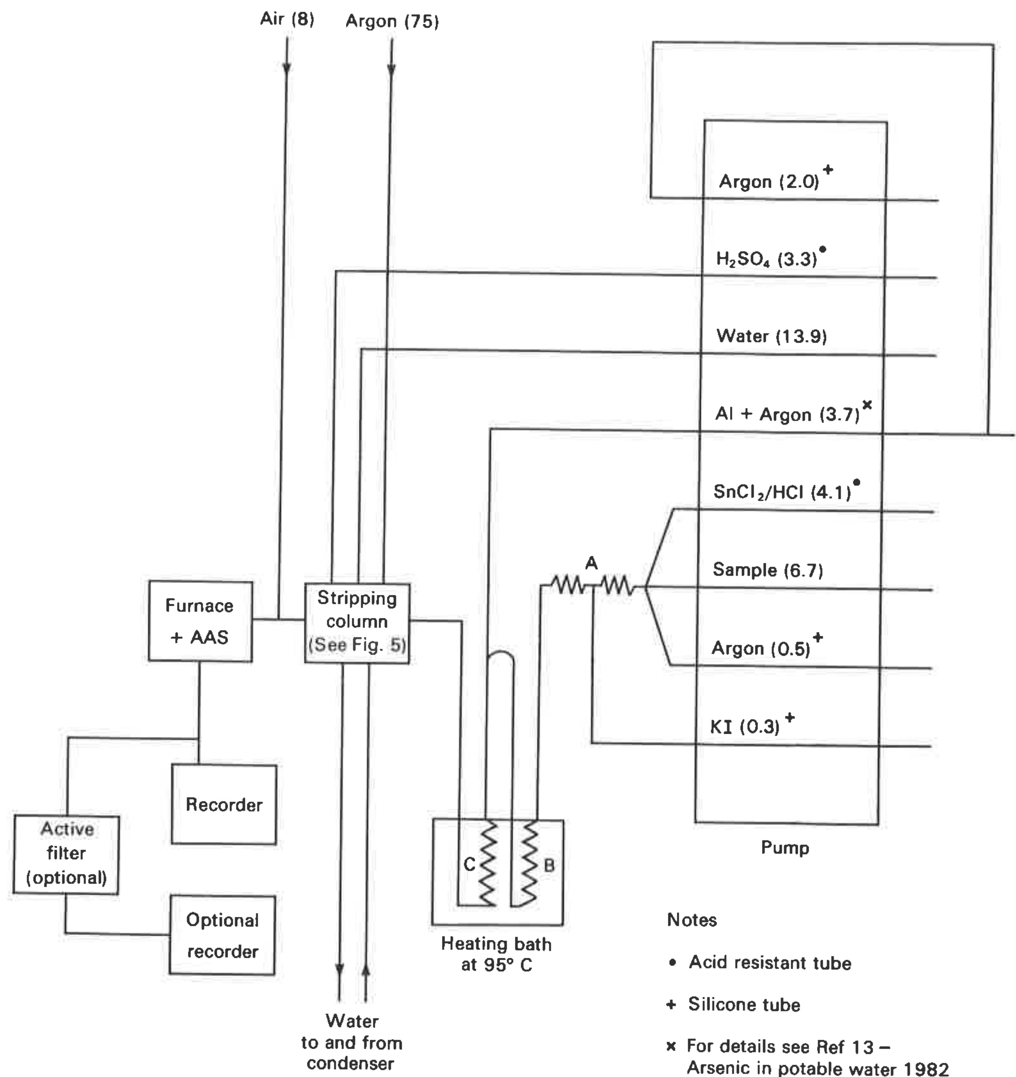
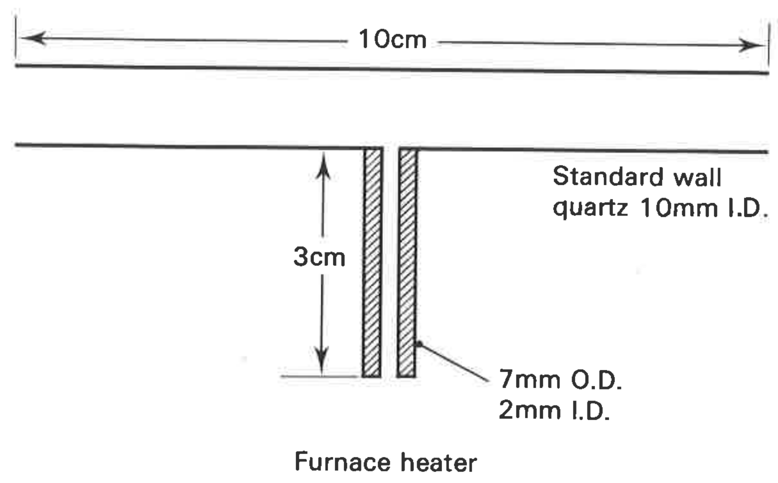


Figure 3 Manifold for Determination of As & Se (figures in parentheses are volumes (ml) per min.)



20 ohm heater, 10 ohms each side of T-piece, with thermocouple embedded in the cement covering

Figure 4 Quartz Furnance

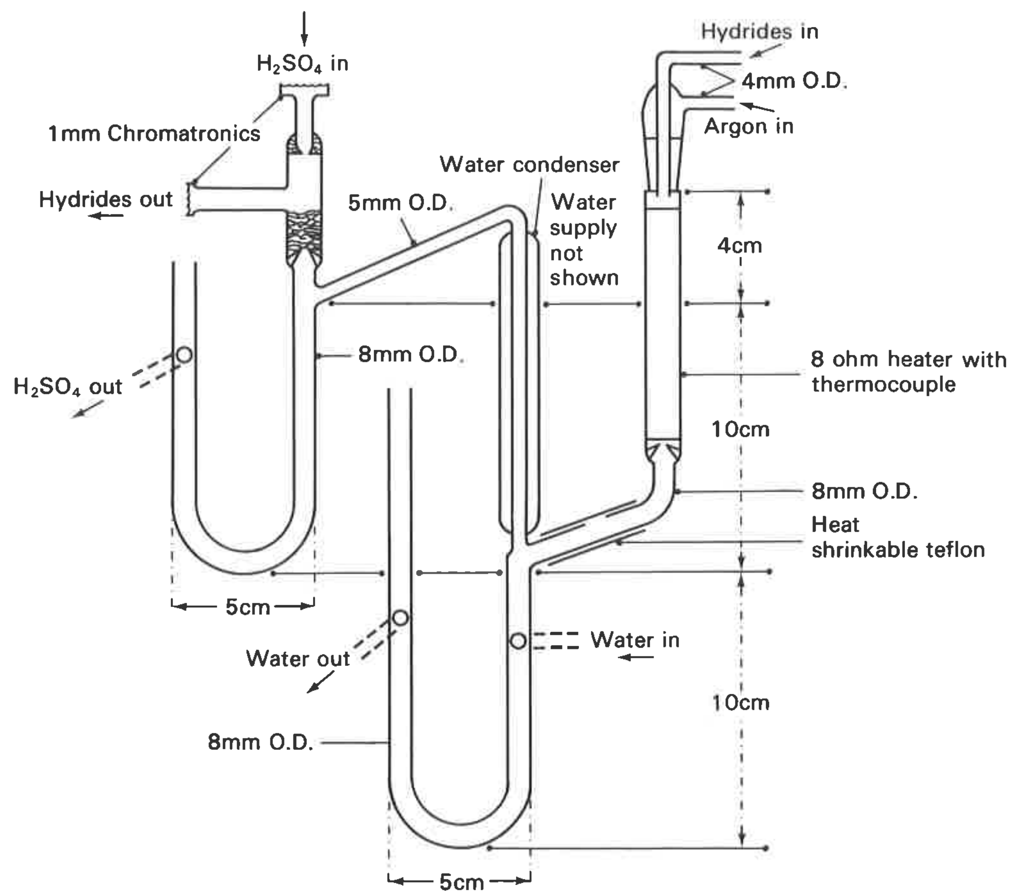


Figure 5 Stripping Column

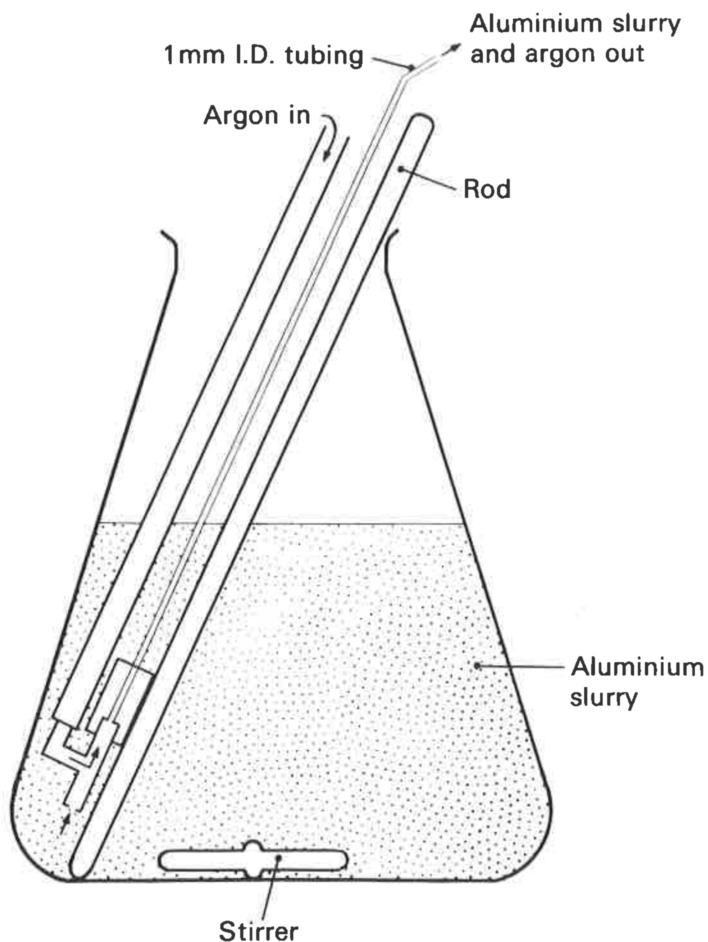


Figure 6 Aluminium slurry dispenser

C6.2.6 Tube furnace

The design and dimensions are shown in Figure 4. The furnace is made from silica tubing 1 cm internal diameter and 10 cm long, with a 0.2 cm internal diameter silica tubing inlet, 3 cm long, fused to the middle of the tube. The tube is wound with resistance wire (20 ohms) and thermally insulated. A potential is applied to this wire through a variable transformer to give a temperature of 650 ± 50°C (approximately 550°C at the centre of the tube), and registered by a thermocouple placed on the tube under the heating wire. Connection is made to the silica tube by a heat shrink PTFE sleeve.

C6.3 Cleanliness

Cleanliness is essential for this determination. All glassware should be made of good quality low arsenic borosilicate glass. All glass and plastic ware should be reserved, if possible, for arsenic and selenium determinations. Clean all glass and plastic ware by filling with or soaking in 10% V/V nitric acid for 2 days. Rinse thoroughly with water. Thereafter a thorough rinse with 10% V/V nitric acid followed by rinsing with water after each determination should suffice.

C6.4 Muffle furnace for operation up to 500°C for ashing stage

C7 Sample Collection, Preservation and Preparation

The choice of sample collection, preservation and preparation procedure depends on the requirements of the analyst and the facilities available. Ideally, when requirements are not stringent and analytical facilities are readily available, the sample can be collected in a clean glass bottle (see section C6.3) and analysis to the pretreatment-ashing stage carried out as soon as possible. The ash may then be reserved until sufficient samples are available to make extraction and determination worthwhile. If required, the dry solids should be determined on a separate sample.

For more accurate work where a homogeneous sample is required, freeze-drying and grinding is recommended. In this case the dried ground sample can be kept for considerably longer before analysis is commenced.

C8 Preliminary Procedures

Before analysing any samples, ensure that the hazards section (Section C4) has been read and understood, that the apparatus is in good operating condition and that the reagents to be used are of a suitable quality. It is recommended that, whatever measurement system is used, checks are carried out to ensure that the system is fully capable of reliably determining arsenic and selenium in standard solutions. When satisfactory operation is achieved, the purity of the reagents at the ashing stage should be checked by making blank determinations.

C9 Analytical Procedure

READ SECTION C4 ON HAZARDS BEFORE STARTING THIS PROCEDURE

Step	Procedure	Notes
	Pretreatment stage — ashing	
C9.1	Transfer an appropriate quantity, W g (weighed accurately to three significant figures) to a 50 ml borosilicate glass beaker (note a). Add 4.00 ± 0.05 ml of nitric acid (d_{20} 1.42), 2.00 ± 0.02 g of magnesium nitrate hexahydrate and 4–6 antibumping granules and cover the beaker with a watch glass.	(a) For liquid sludges take about 5 g and for solid samples about 0.25 g of dry solids.

Step	Procedure	Notes
C9.2	Place the beaker on a hot plate and heat gently, ensuring that any vigorous reaction is allowed to subside. Continue heating for 30 ± 15 min in such a way that acid vapours condense on the watch glass and return to the beaker. Then heat more strongly to evaporate to dryness (note b).	(b) Occasionally it may be necessary to add more nitric acid because charring (indicating reducing conditions) occurs. It may be necessary to wash spattered material down from the sides of the beaker. If it is judged that significant material has been lost, the procedure must be started again using a larger beaker.
C9.3	Allow to cool, add 1.00 ± 0.02 ml of nitric acid (d_{20} 1.42) and evaporate to dryness. Remove watch glass and place the beaker in a muffle furnace, gradually raise the temperature stepwise to 500 ± 10°C and leave until a clean ash is obtained (note c). Allow to cool.	(c) The furnace may be preheated to 200°C. Steps of 100°C are suitable. A clean ash is usually obtained after 2–3 hours. Or if convenient leave overnight.

Pre-treatment stage — dissolution

Step	Procedure	Notes
C9.4	Add 10.0 ± 0.1 ml of 6M hydrochloric acid and simmer gently on a hot plate for 10 ± 1 min; cool and dilute to 100 ± 1 ml with water. The solution is the primary extract P and should be reserved for future use.	
C9.5	Transfer 20.00 ± 0.02 ml of primary extract P to a 100 ml calibrated flask, add 8.0 ± 0.6 ml of 6M hydrochloric acid and dilute with water to the mark. This solution is the secondary extract S and should be reserved for future use (note d)	(d) If the arsenic or selenium content is unknown or expected to be outside the range of the method it is advisable to make further serial dilutions in 0.6M hydrochloric acid before proceeding to step C9.7.

Blank determination

Step	Procedure	Notes
C9.6	A blank should be prepared at the same time and in the same way by carrying out steps C9.1 to C9.5 but omitting the sample.	

Measurement stage

Step	Procedure	Notes
C9.7	Connect the special apparatus (section C6.2) as shown in Figures 3 and 5 to the atomic absorption spectrophotometer ensuring that all the required services are connected. Switch on the oil heating bath.	
C9.8	Switch on the atomic absorption spectrophotometer and set up the instrument and associated apparatus according to the instructions. The wavelengths required are 193.7 nm for arsenic and 196.0 nm for selenium.	

Step	Procedure	Notes
C9.9	Adjust the position of the tube furnace so that the radiation from the lamp passes through the tube and gives minimum absorbance. Switch on the tube furnace heater. Start the flow of water to the condenser and turn on the argon and air. Switch on the stripping column heater.	
C9.10	Place the sulphuric acid line in its reservoir (note e). Place all other lines pumping liquid into water and start the proportionating pump.	(e) Never pump water through the sulphuric acid line.
C9.11	When the temperatures of the tube furnace heater, stripping column and oil bath have equilibrated place the reagent lines in their respective solutions and leave for at least five minutes.	
C9.12	Switch on the recorder and adjust the atomic absorption spectrophotometer to give a zero response. Put the sample line into an appropriate calibration standard and optimize the flow rates of argon and air. Put the sample line into water and, if necessary, readjust the zero response and flow rates of argon and air.	
C9.13	The following order of presentation of samples and standards has been found satisfactory: two 5.0 g/1 standard solutions, followed by the secondary extracts S of each sample and then a blank with zero and 5.0 g/1 standards after each four sample extracts. Then present any repeat extracts, primary extracts P including the blank and serially diluted extracts with a zero and 5.0 g/1 standard solution after each four extracts (note f). The system is flushed with water between each solution. Present the solution until a plateau is reached and wash until the baseline returns (35s sample/35s wash for arsenic and 60s sample/60s wash for selenium have been found to be suitable).	(f) When the peak from a secondary extract is off scale run a suitable serial dilution. When a peak corresponds to less than 2 μg/1 it is desirable to run the primary extract. When a small peak follows a much larger peak there may be a carry over effect and that sample should be re-presented.

Shut down procedure

Step	Procedure	Notes
C9.14	Turn off the lamps, tube furnace and stripping column heaters, atomic absorption spectrophotometer and recorder. Put all reagent lines (except the sulphuric acid) into water and flush for at least 5 minutes. Turn off the pump, argon and air supply, water and the oil bath.	

Step	Procedure	Notes
	Calculation of results	
C9.15	From the response of each sample extract (note g) ie peak height, calculate the arsenic or selenium concentration in the extract by reference to the response of the 0.0 and 5.0 μg/1 standards. Let the concentrations (μg/1) in the sample secondary extracts be S_s blank secondary extracts be S_b sample primary extracts be P_s blank primary extracts be P_b	(g) Take into account any serial dilutions of the secondary extracts.
C9.16	Then calculate the concentration C of arsenic or selenium in the original sample from $$C = \frac{(S_s - S_b)}{2W} \text{ or } \frac{(P_s - P_b)}{10W}$$	

C10 Checking the Linearity of the Calibration Curve and the Efficiency of the Reduction Stage

C10.1

The entire procedure given in this Section must be carried out on at least one occasion before application of the measurement stage steps 9.7 to 9.12 to any sample extracts. Thereafter it is recommended that checks of linearity of the calibration curve and efficiency of reduction are made regularly. Any significant departure from linearity indicates that the technique is suspect at some stage. Any significant departure from 100% in the efficiency of reduction indicates that this stage of the measurement is suspect. The analyst must decide what departure is acceptable and what action, if any, is required.

C10.2

Using standard arsenic and selenium stock solutions and 0.6M hydrochloric acid prepare six series of standard solutions (commercially available standards of As and Se together with standards containing As^{3+}, As^{5+}, Se^{4+} and Se^{6+}) to contain 0, 2, 4, 6, 8, 10 μg/1 of the element. Subject the three series of solutions containing arsenic and the three series of solutions containing selenium to the measurement procedure given in Section C9, Steps C9.7 to C9.12. Plot the response (eg peak height above baseline) against μg/1 for each series. The curves for the three arsenic series should coincide and be linear to at least 8 μg/1 and the curves for the three selenium series should coincide and be linear to at least 8 μg/1.

C11 Changing the concentration range of the method

C11.1

The method is designed to determine arsenic and selenium in the range 0.0 to 1.0 μg/g for liquid sludges and 0.0 to 20.0 μg/g for solid samples. For many samples whose concentrations are at the lower part of these ranges there is some evidence that by using the primary extracts (range 0.0 to 0.2 μg/g for liquid sludges and 0.0 to 4.0 μg/g for solid samples) more accurate results can be obtained, although with some heavily contaminated samples this may not be possible because interference results.

C11.2

For samples containing arsenic and selenium above the range given, it will normally be sufficient to dilute the secondary extract further with 0.6M HCl; but it will often be advantageous to use a smaller initial sample weight, particularly for samples where the composition is uncertain and low limits of detection are not usually required.

C12 Sources of Error

C12.1 Arsenic and Selenium Content of the Water used

Distilled or deionized water should not normally contain sufficient arsenic or selenium to introduce a significant error. However occasional checks on the water, by evaporating a large volume of water acidified with nitric acid and then treating as a sample, might reveal whether sufficient contamination has occurred to cause a significant error.

C12.1 Arsenic Content of the Reagents

Hydrochloric acid may contain sufficient arsenic to make the determination step impossible — see Section C5.5. It is also necessary to use other reagents which are substantially free from arsenic and selenium to ensure that low blank values are obtained. The error due to contaminated reagents can be substantially reduced when a blank correction is made.

C12.3 Contamination

The technique and working conditions should be critically examined and any sources of contamination eliminated or minimized. High variations in replicate blanks are indicative of contamination. It is particularly desirable to reserve the glass apparatus used solely for arsenic and selenium determinations, and to carry out a preliminary series of blank determinations before analysing any samples.

C12.4 Arsenic in Glassware

Some glass products contain relatively high concentrations of arsenic compounds, deliberately added during the glassmaking procedure. Some samples may contain compounds which attack glass during the pretreatment stage. Loss of arsenic and selenium by absorption appear to be negligible but gains of arsenic could be significant. It is advisable to use only glassware which is known to be low in arsenic (borosilicate glass normally contains less than 5 ppm).

C12.5 Interfering Substances

The effect of possible interfering substances on the measurement stage may be determined by spiking standards and sample extracts with various concentrations of the potential interfering substance.

D A Note on Commercial Hydride Generation AAS Methods

D.1

The information in this note is based on enquiries of Committee members using these methods.

D.2 Substances determined

(in descending order of frequency) in Waters
Arsenic
Selenium
Mercury (as element not hydride)
Antimony
Tin
Tellurium
Germanium

D.3 Limits of Detection

Instrument dependent also maintenance dependent, c0.5 µg/1 to 2 µg/1, except Ge and Te. Lower values are reported in the literature.

D.4 Relative Standard Deviations

Close to the Limit of Detection results are very variable indeed.

Arsenic	at 0.5 µg/1	10%
	at 3 µg/1	3%
Selenium	at 3 µg/1	3%
Mercury	at 0.5 µg/1	3%
Tin	at 1 µg/1	5–10%

Antimony similar to arsenic
Germanium both elements relatively insensitive unless high
Tellurium furnace temperatures are used

D4.1

Very thorough testing by three laboratories has shown that these methods are exceedingly sensitive to almost undetectable variations in technique with relative standard deviations varying from c1% to over 20% for no apparent reason. See Section D7.

D5 Principle

Acidified samples are reduced by sodium borohydride or other similar suitable reagents, to form their hydrides or free mercury which are swept into a heated silica or graphite tube furnace and examined, preferably by flameless AAS, similar to Ref 13.

D6 Interferences

Table 5 in method C gives typical data for arsenic and selenium. Similar interferences occur for antimony, germanium and tellurium. Iron III is definitely a problem. With tin the hydrochloric acid concentration is critical.

D7 General

Use of burner AAS can lead to problems with films of oxide forming on the optics. Use of electrothermal furnaces can lead to metal films forming. Even with cold vapour systems, for best results it is vital to ensure cleanliness of the absorption tube, and, if it is open ended, of any adjacent optics. With open ended tubes, care is needed as excess hydrogen may ignite and the resultant flames may distort the optical path producing erratic results. For the hydrides, electrically wound open tube furnaces gave better results than flame heated tubes. As mentioned in Sections D4 and D4.1, it is exceedingly easy unexpectedly to lose both precision and accuracy even with scrupulous cleanliness and attention to detail. All possible interferences should be checked, several standards, spiked samples and duplicate samples should be included in each batch of analyses (as in Method C) if acceptably reliable results are to be achieved. With these provisos, all commercial models were satisfactory.

For mercury, procedures as detailed for flameless AAS in the Mercury booklets in this series suffice.

Checking the accuracy of analytical results

(For further information see General Principles of Sampling and Accuracy of Results 1980, also published in this series.) Once the methods have 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 test are possible (10) and they should be used as appropriate. For Methods A and B, it is recommended that standard solution of selenium in the valence states to be expected in samples be analysed in the same way and at the same time as normal samples. For Method C, since a reasonable quantity of homogenized dry sludge, plant material, soil or sediment can be stored it is recommended that, as a minimum, an aliquot of the stored material, a duplicate blank and a duplicate of one of the samples in the batch be analysed with each batch. The results should be plotted on a quality control chart which, although it will not necessarily expose all errors, will provide a useful check on the day to day performance of the method. A control standard solution might also be used to check the final stages of the procedure.

References

(1) Final Report to the Department of the Environment for Grant DOE 480/476, March 1982.

(2) Shimoishi, Y *J. Chromatorgr* 1977, **136**, 85.

(3) Shimoishi, Y and Toei K, *Analyt Chim Acta* 1978, **100**, 65.

(4) Department of the Environment, File WS/646/4, Paper SCA 226.

(5) Sugimura Y and Suzuki Y *J, Oceanogr Soc Japan*, 1977, **33**, 22.

(6) Parker C A and Harvey L G, *Analyst*, 1962, **87**, 558.

(7) Lott P F, Cukor P, Moriber G and Solga J, *Analyt Chem*, 1963, **35**, 1159.

(8) Cukor P, Walzcyk J and Lott P F, *Analyt Chim Acta* 1964, **30**, 473.

(9) Measures C I and Burton J D, *Analyt Chim Acta* 1980, **120**, 177.

(10) Wilson A L and Cheeseman R V, Water Research Centre, *Technical Report TR66*, 1978.

(11) Frost J A and Musselwhite C, Water Research Centre. Contract Report 132–5, 1982.

(12) Goulden P D and Brooksbank P, *Anal Chem* 1974, **46**, 1432.

(13) *Arsenic in Potable Waters by Atomic Absorption Spectrophotometry 1982*, HMSO, in this series.

(14) *Metals in Soils, Sediments and Sewage Sludge, by Hydrochloric-Nitric acid Digestion etc, 1985*, HMSO, in this series.

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

(16) *Measurement of Alpha and Beta Activity of Water Samples and Sludges, The Determination of Radon-222 and Radium-226, The Determination of Uranium (including General X-ray Fluorescent Spectrometric Analysis 1985*, HMSO in this series).

Address for Correspondence

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

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

Standing Committee of Analysts

Members assisting in the preparation of these methods

Name	
G Ashley	2
S Bailey	2
H T Barnhoorn	1
Dr G I Barrow	1
F B Basketter	1
Dr M L Berrow	2
Dr G A Best	1
M P Burtenshaw	2
Dr J D Burton	2
P A Chave	1
Dr G W Clayfield	1
Mr B E P Clement	1
M Cornber	2
E C Conchie	2
Dr B T Croll	1
Dr J V Dadswell	1
T A Dick	1
J W Dutton	1.2
B J Farey	2
M C Finniear	1
Dr J Gardiner	1.2
G I Goodfellow	1
T R Graham	1
Dr A M Gunn	2
L Hancock	2
D J Harper	2
Dr J Heslop	2
E Hodges	1
Dr D T E Hunt	1.2
M R Hurcombe	1
O D Hydes	2
Dr J G Jones	1.2
J J Kay	2
J S Leahy	1
P J Long	1
R Mackinson	2
J C McCullins	1
Dr D McIntyre	2
D L Miles	2
C C Musselwhite	2
D Myles (deceased)	1
Dr E J Newman	
A H Nield	1
Dr D J Packham	1
J F Palframan	2
I Penburthy	2
J Perkins	2
G J Pickford	2
L R Pittwell	1.2
A Poole	2
Dr R S Porter	2
Dr J E Portmann	1
H Pugh	
L D Purdie	1
B D Ravenscroft	1
B R Rhodes	1
L A Richards	1
Prof J P Riley	1.2
M G Rolph	2
M I R Scholes	2
Dr B L Sharp	2
Dr R Snook	2
D Stickley	2
Dr D Taylor	1.2
A Tetlow	1
Dr K C Thompson	1.2
Dr M Thompson	2
R Toff	2
G Topping	2
Dr A M Ure	1
R J Vincent	1
J G Welsh	2
B T Whitham	1
Dr D A Williams	1
S A Wilson	2
S C Wilson	2
Dr R Wood	1
G Yates	2

1. Working Group/Panel member
2. Main Committee member

HMSO publications are available from:

HMSO Publications Centre
(Mail and telephone orders only)
PO Box 276, London, SW8 5DT
Telephone orders 01–622 3316
General enquiries 01–211 5656
(queuing system in operation for both numbers)

HMSO Bookshops
49 High Holborn, London, WC1V 6HB 01–211 5656 (Counter service only)
258 Broad Street, Birmingham, B1 2HE 021–643 3740
Southey House, 33 Wine Street, Bristol, BS1 2BQ (0272) 264306
9–21 Princess Street, Manchester, M60 8AS 061–834 7201
80 Chichester Street, Belfast, BT1 4JY (0232) 238451
13a Castle Street, Edinburgh, EH2 3AR 031 225 6333

HMSO's Accredited Agents
(see Yellow Pages)

and through good booksellers

£5.50 net
ISBN 0 11 7519332

Selenium in Waters; Selenium and Arsenic in Sludges, Soils etc; Hydride Kits

HMSO