Arsenic in Potable Waters by Atomic Absorption Spectrophotometry (semi-automatic method) 1982

Methods for the Examination of Waters and Associated Materials

London Her Majesty's Stationery Office £2.80 net

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Methods for the Examination of Waters and Associated Materials

This method is an alternative to the 1978 booklet but does not replace it.

Contents

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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. Lone working, whether in the laboratory or field, should be discouraged. Reagents of adequate purity must be used, along with properly maintained apparatus and equipment of correct 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.

There are numerous handbooks on first aid and laboratory safety. Among such publications are: 'Code of Practice for 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.

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

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.

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. 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.

First published 1983

ISBN 0 11 751679 1

About this series

This booklet is part of a series intended to provide recommended methods for the determination of water quality. In addition, the series contains 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 individual methods, thus allowing for the replacement or addition of methods as quickly as possible without need of waiting for the next edition. The rate of publication will also be related to the urgency of requirement for that particular method, tentative methods being issued when necessary. The aim is to provide as complete and up to date a collection of methods and reviews as is practicable, which will, as far as possible, take into account the analytical facilities available in different parts of the Kingdom, and the quality criteria of interest to those responsible for the various aspects of the water cycle. Because both needs and equipment vary widely, where necessary, a selection of methods may be recommended for a single determinand. It will be the responsibility of the users — the senior analytical chemist, biologist, bacteriologist etc, to decide which of these methods to use for the determination in hand. Whilst the attention of the user is drawn to any special known hazards which may occur with the use of any particular method, responsibility for proper supervision and the provision of safe working conditions must remain with the user.

The preparation of this series and its continuous revision is the responsibility of the Standing Committee of Analysts (to review Standard Methods for Quality Control of the Water Cycle). The Standing Committee of Analysts is one of the joint technical committees of the Department of the Environment and the National Water Council. It has 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, and the current status of publication and revision will be given in the biennial reports of the Standing Committee of Analysts.

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 for booklets 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 the booklet.

T A DICK
Chairman

L R PITTWELL
Secretary

3 February 1983

Arsenic in Potable Waters by Atomic Absorption Spectrophotometry (Semi-Automatic Method) Tentative Method (1982) Version

Note: Throughout this method arsenic is expressed as the element (As).

1 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, also published in this series.)

1.1	Substance determined	All forms of arsenic likely to occur in potable waters (see Section 2.3).
1.2	Type of sample	Potable waters.
1.3	Basis of the method	Conversion of arsenic to arsine followed by atomic absorption spectrophotometry.
1.4	Range of application (a)	Up to 5 μg/l.
1.5	Calibration curve (a)	Linear to 2 μg/l.

1.6 Standard deviation (a)

Arsenic Concentration (μg/l)	Within batch (μg/l)	Between batch (μg/l)	Total (μg/l)	Degrees of Freedom
0.1 (b)(c)	0.0097			5
0.5 (c)	0.0302	0.0228	0.0379	5,4,9
4.0 (c)	0.0434	0.1211	0.1286	5,4,9
Tap water	0.0311	0.0661	0.0731	5,4,9
Tap water + 0.5 μgAs/l	0.0392	0.0892	0.0974	5,4,9

1.7	Limit of detection (a)	0.055 μg/l (5 degrees of freedom).
1.8	Sensitivity (a)	2.0 μg/l gives an absorbance of approximately 0.10.
1.9	Bias (a)	London tap water spiked with 0.5 μg/l of arsenic gave a recovery of 0.501 ± 0.061 μg/l (95% confidence limits). Certain volatile arsenic compounds, if present, may not be recovered if pretreatment is applied (see Sections 2.3 and 8.1).
1.10	Interferences (a)	see Section 3.
1.11	Time required for analysis (a)	After the initial equilibration period (approximately 30 min) the total analysis and operator times for 40 samples and associated standards are 3.5 and 2.0 hours respectively.

(a) These data were obtained at the Laboratory of the Government Chemist [1] using an atomic absorption spectrophotometer with an electrodeless discharge lamp but without pretreatment of the sample.
(b) The limit of detection was based on this value.
(c) Doubly distilled water spiked with the stated arsenic concentrations.

2 Principle

2.1 The method described is based on that of Goulden and Brooksbank(2), with modifications made to the design of the apparatus at the Laboratory of the Government Chemist(1).

2.2 Inorganic arsenic V is reduced to arsenic III using stannous chloride/ hydrochloric acid solution and then the arsenic III is reduced to arsine using aluminium slurry (for the latter step an alternative reducing agent based on sodium borohydride has been described by the Water Research Centre(3)). The arsine is decomposed in a heated silica tube to elemental arsenic which is determined by atomic absorption spectrophotometry.

2.3 Some samples may need pretreatment to convert organoarsenic compounds to inorganic arsenic. The total arsenic content can be determined after preliminary oxidation (see Section 8.1) and application of this technique to representative samples will indicate whether pretreatment is necessary. The following recoveries were obtained from the digestion of organoarsenic compounds at concentrations equivalent to 5μg/1 arsenic; cacodylic acid — 95%; arsanilic acid — 103%; triphenylarsine — 90%. The recoveries would be expected (95% confidence) to be within 100 ± 8%.

3 Interferences

Table 1 gives details of the effect of potential interfering substances on the determination of arsenic. These results were obtained at the Laboratory of the Government Chemist(1). Of the substances tested only copper greater than 2.0 mg/1, antimony greater than 0.2 mg/1, selenium greater than 0.05 mg/1 and nitrate greater than 100 mg/1 interfere at 1.0 μg/1 arsenic.

4 Hazards

4.1 Arsenic compounds are toxic and care is required when preparing and handling solutions (see Sections 5.11 and 5.12) containing them.

4.2 Hot hydrochloric acid (see Section 5.2.2 and Figure 1) and concentrated sulphuric acid (see Section 5.3 and Figure 1) are continuously pumped during the use of the apparatus and suitable protection must be provided for the operator by enclosing the apparatus. The toxic and corrosive exhaust gases must be vented to a fume extractor.

5 Reagents

It is recommended that, wherever possible, reagents and standards are stored in polyethylene vessels as some glassware is known to contain arsenic, which may be leached out. All glass and polyethylene vessels should be cleaned by the procedure given in Section 6.3 unless otherwise stated. Analytical grade reagents have generally been found to be suitable.

5.1 Water

The water used for preparing standard and reagent solutions and for dilutions should have an arsenic content that 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.

5.2 Hydrochloric acid (d_{20} 1.18)

5.2.1 6M Hydrochloric acid (approximately)

Dilute 550 ± 10 ml of hydrochloric acid (d_{20} 1.18) with water to 1 litre in a measuring cylinder.

5.2.2 Hydrochloric acid/stannous chloride solution

See Section 4 on hazards. Dissolve 3.6 ± 0.1 g of stannous chloride dihydrate, in a Winchester bottle containing about 2.5 litres of hydrochloric acid (d_{20} 1.18). Any opalescence should disappear within a short period. The solution is stable for at least one week.

5.3 Sulphuric acid (d_{20} 1.84)

See section 4 on hazards.

5.3.1 20% V/V Sulphuric acid

Add slowly and cautiously with stirring 50 ± 2 ml of sulphuric acid (d_{20} 1.84) to 150 ml of water in a 400 ml beaker which is standing in cold water. When thoroughly mixed and cooled, dilute with water to 250 ml in a measuring cylinder.

Table 1 Effect of other substances on the determination of arsenic

Other substance		Other substance added as	Concentration of other substance (mg/l)	Effect of other substances in µg/l at an arsenic concentration of (d)	
				0.0 µg/l	1.0 µg/l
Silver	(as Ag^{+})	Perchlorate	10.0	+ 0.06	+ 0.02
Aluminium	(as Al^{3+})	Perchlorate	10.0	0.00	- 0.03
Cadmium	(as Cd^{2+})	Perchlorate	10.0	+ 0.12	+ 0.03
Chromium	(as Cr^{3+})	Perchlorate	10.0	0.00	- 0.01
Copper	(as Cu^{2+})	Perchlorate	0.5		- 0.04
Copper	(as Cu^{2+})	Perchlorate	1.0		- 0.06
Copper	(as Cu^{2+})	Perchlorate	2.0		- 0.06
Copper	(as Cu^{2+})	Perchlorate	5.0		- 0.15
Copper	(as Cu^{2+})	Perchlorate	10.0		- 0.19
Copper	(as Cu^{2+})	Perchlorate	20.0	0.00	- 0.30
Iron	(as Fe^{3+})	Perchlorate	10.0	0.00	0.00
Mercury	(as Hg^{2+})	Perchlorate	10.0	+ 0.13	- 0.04
Manganese	(as Mn^{2+})	Perchlorate	10.0	+ 0.09	+ 0.04
Nickel	(as Ni^{2+})	Perchlorate	0.5		- 0.02
Nickel	(as Ni^{2+})	Perchlorate	1.0		- 0.03
Nickel	(as Ni^{2+})	Perchlorate	2.0		- 0.03
Nickel	(as Ni^{2+})	Perchlorate	10.0	0.00	- 0.10
Lead	(as Pb^{2+})	Perchlorate	10.0	0.00	- 0.05
Antimony	(as Sb^{5+})	Chloride	0.2	0.00	- 0.04
Antimony	(as Sb^{5+})	Chloride	0.5		- 0.12
Antimony	(as Sb^{5+})	Chloride	1.0		- 0.23
Antimony	(as Sb^{5+})	Chloride	2.0		- 0.26
Antimony	(as Sb^{5+})	Chloride	5.0		- 0.28
Antimony	(as Sb^{5+})	Chloride	10.0	+ 0.24	- 0.57
Selenium	(as Se^{4+})	Nitrate	0.01		+ 0.03
Selenium	(as Se^{4+})	Nitrate	0.02		+ 0.01
Selenium	(as Se^{4+})	Nitrate	0.05		- 0.07
Selenium	(as Se^{4+})	Nitrate	0.1		- 0.28
Selenium	(as Se^{4+})	Nitrate	0.2		- 0.42
Selenium	(as Se^{4+})	Nitrate	0.5	0.00	- 0.81
Tin	(as Sn^{4+})	Chloride	0.5		0.00
Tin	(as Sn^{4+})	Chloride	1.0		- 0.05
Tin	(as Sn^{4+})	Chloride	2.0		- 0.04
Tin	(as Sn^{4+})	Chloride	5.0		- 0.05
Tin	(as Sn^{4+})	Chloride	10.0	+ 0.09	- 0.08
Zinc	(as Zn^{2+})	Chloride	10.0	+ 0.04	+ 0.01
Nitrate	(as NO_3^{-})	Nitric acid	10.0		- 0.04
Nitrate	(as NO_3^{-})	Nitric acid	50.0		0.00
Nitrate	(as NO_3^{-})	Nitric acid	100.0		- 0.09
Nitrate	(as NO_3^{-})	Nitric acid	250.0	0.00	- 0.21
Perchlorate	(as ClO_4^{-})	Perchloric acid	10.0	+ 0.09	- 0.07
Phosphate	(as PO_4^{3-})	Potassium dihydrogen	10.0	0.00	+ 0.02
Sulphate	(as SO_4^{2-})	Sulphuric acid	250.0	+ 0.04	+ 0.01

(d) If the other substances did not interfere the effect would be expected to be within 0.00 ± 0.02 and 0.00 ± 0.08 µg/l at arsenic concentrations of 0.0 and 1.0 µg/l respectively.

5.4 Nitric acid (d_{20} 1.42)

5.4.1 10% V/V Nitric acid

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

5.5 2% m/V Potassium iodide solution

Dissolve 20.0 ± 0.1 g of potassium iodide in 1 litre of water in a measuring cylinder. This solution is stable for at least one week.

5.6 Aluminium slurry

Aluminium powder, particle size $< 50\,\mu m$, has been shown to be satisfactory. This powder should be free from grease. Add 5.0 ± 0.1 g of aluminium powder to a vessel containing 1 litre of water which is being agitated with a magnetic or paddle stirrer to keep the aluminium in suspension (see Figure 4). This slurry must not be prepared until required, see Section 8.2.10.

5.7 Argon 99.9% (V/V)

5.8 Air

Compressed air from a cylinder is suitable. An air line with a suitable trap should also be satisfactory.

5.9 2% m/V Potassium persulphate solution

Dissolve 20.0 ± 0.1 g of potassium persulphate in 1 litre of water in a measuring cylinder. This solution should be freshly prepared before use.

5.10 4% m/V Sodium hydroxide solution

Dissolve 4.0 ± 0.1 g of sodium hydroxide in water in a polyethylene beaker, cool, and dilute with water to 100 ml in a polyethylene measuring cylinder.

5.11 Standard arsenic solutions

See Section 4 on hazards.

5.11.1 Solution A. 1 ml contains 1 mg As

Dissolve 1.321 ± 0.001 g of arsenic (III) oxide (dried in an oven for about 2 hours at 110 ± 5°C) in 100 ± 1 ml of 4% m/V sodium hydroxide solution in a polyethylene beaker. When dissolved dilute with water, transfer quantitatively to a 1-litre calibrated flask and dilute with water to the mark. Mix well and transfer to a polyethylene container. This solution is stable for at least one month. Commercially available standards for atomic absorption spectrophotometry have also been found to be suitable.

5.11.2 Solution B. 1 ml contains 10 µg As

Dilute 10.00 ± 0.02 ml of solution A with water to 600 ml in a 1-litre calibrated flask, add 2.0 ± 0.1 ml of 6 M hydrochloric acid, dilute with water to the mark and mix well. This solution should be freshly prepared before use.

5.11.3 Solution C. 1 ml contains 0.1 µg As

Dilute 10.00 ± 0.02 ml of solution B with water to 600 ml in a 1-litre calibrated flask, add 2.0 ± 0.1 ml of 6M hydrochloric acid, dilute with water to the mark and mix well. This solution should be freshly prepared before use.

5.12 Calibration solutions

Into each of seven 500-ml calibrated flasks add 1.0 ± 0.1 ml of 6M hydrochloric acid. Pipette into the flasks 0.00, 2.50, 5.00, 10.00, 15.00, 20.00 and 25.00 ml of solution C, dilute with water to the mark and mix well. These solutions contain respectively 0.0, 0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 µg As per litre. Label them D, E, F, G, H, I and J respectively. These solutions should be freshly prepared before use.

6 Apparatus

6.1 An atomic absorption spectrophotometer

Fitted with an arsenic electrodeless discharge lamp (or arsenic hollow cathode lamp). A chart recorder has been shown to be a satisfactory form of readout.

6.2 Special Apparatus

A schematic diagram of the apparatus is given in Figure 1. The sample is mixed with hydrochloric acid/stannous chloride and then potassium iodide in coiled tube A, and then passed through the coiled tube B in the heating bath. The aluminium slurry is introduced and the mixture passed through the second heated coil C. A stream of argon is

introduced and the arsine is separated into the gas phase in the stripping column. The gas is cooled, dried with sulphuric acid in the wash column, then mixed with air and passed into the furnace tube of the atomic absorption spectrophotometer.

6.2.1 Proportioning 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.

6.2.1.1 Argon 3 ml/min (the device for splitting the argon supply is shown in Figure 3).

6.2.1.2 Argon 1.5 ml/min.

6.2.1.3 Sample/wash 12 ml/min.

6.2.1.4 Stannous chloride/hydrochloric acid 6 ml/min.

6.2.1.5 Potassium iodide 0.9 ml/min.

6.2.1.6 Aluminium slurry about 2 ml/min. The slurry is pumped with argon (6.2.1.1.) to give a combined rate of 5 ml/min. 0.1 mm Internal diameter polyethylene tube is used to carry the slurry to the pump tube and from the pump tube to the heated coil, (see Figures 1 and 4).

6.2.1.7 Sulphuric acid 4 ml/min.

6.2.1.8 Water 12 ml/min.

6.2.2 Other reagent lines

6.2.2.1 Argon about 150 ml/min. The gas is passed through a constant flow controller and flowmeter and the flow rate is optimised to obtain an appropriate compromise between the noise level and sensitivity.

6.2.2.2 Air about 12 ml/min. The gas is passed through a constant flow controller and flowmeter and the flow rate is optimised to obtain an appropriate compromise between the noise level and sensitivity.

6.2.3 Magnetic or paddle stirrer.

This is used to agitate the aluminium slurry.

6.2.4 Oil bath

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

6.2.4.1 Glass tubing, coiled to fit the 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 shown to be satisfactory. The minimum length of acid resistant tubing should be used to connect the two coils.

6.2.5 Stripping column

The design and dimensions are given in Figure 2. The column is packed with glass helices, 4 mm diameter by 4 mm long, wound with resistance wire (25 ohms) and thermally insulated. A potential of about 50 volts is applied to the wire through a variable transformer to give an indicated temperature of 150 ± 10°C measured by a thermocouple placed on the column under the heating wire, when the gas/liquid mixture is passing through the column. The stripping column is connected to the condenser and drain with heat shrink polytetrafluoroethylene (PTFE) sleeve (see Figure 2).

6.2.6 Wash column

The design and dimensions are given in Figure 2. The column is packed with 4 mm diameter by 4 mm long glass helices.

6.2.7 Tube furnace

The furnace is made from silica tubing, 1 cm internal diameter by 10 cm long, with a 0.2 cm internal diameter silica tubing inlet, 3 cm long, fused to the middle of the tube. The

Figure 2 STRIPPING AND WASH COLUMNS

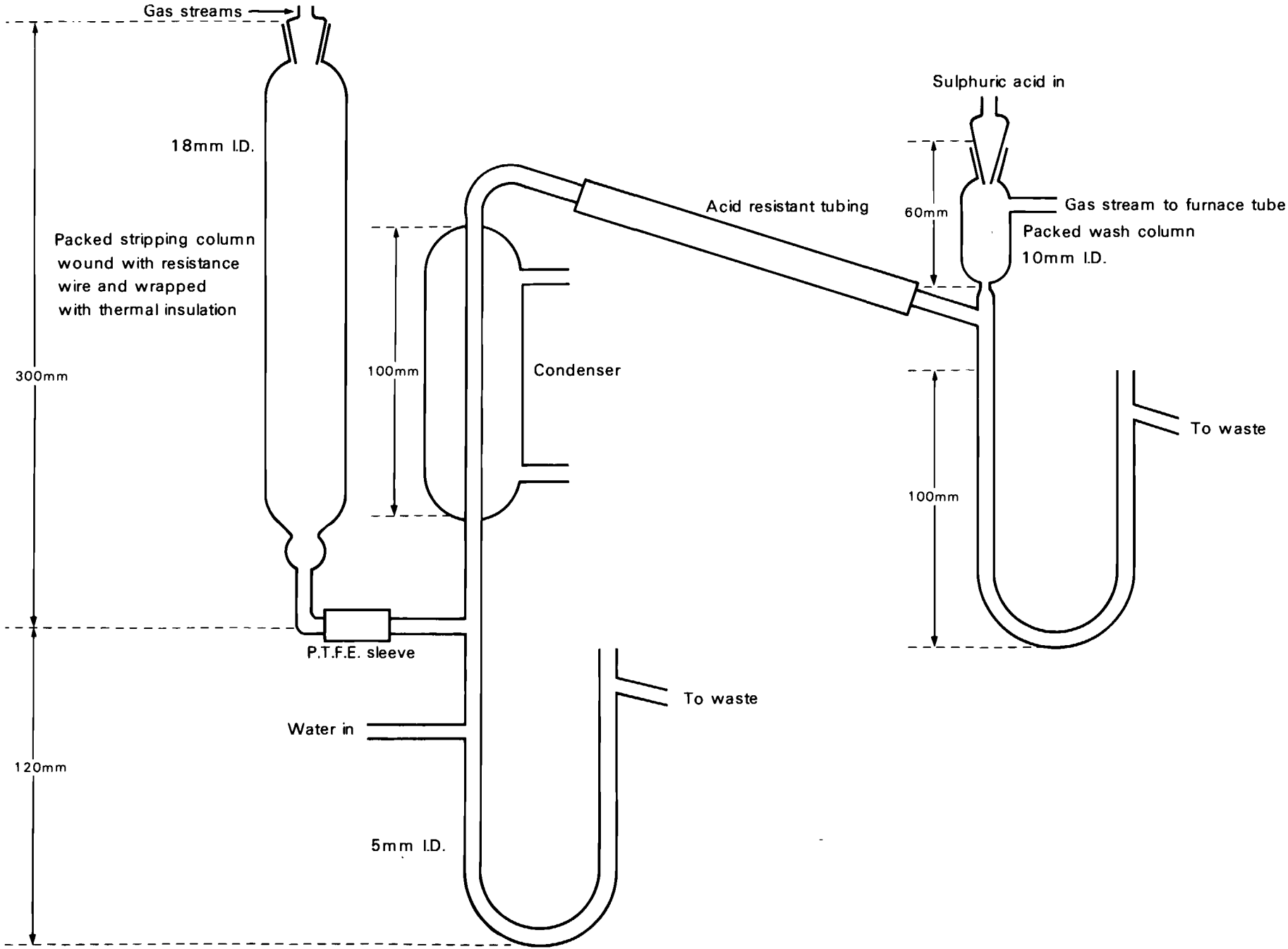


Figure 3 ARGON SPLITTER

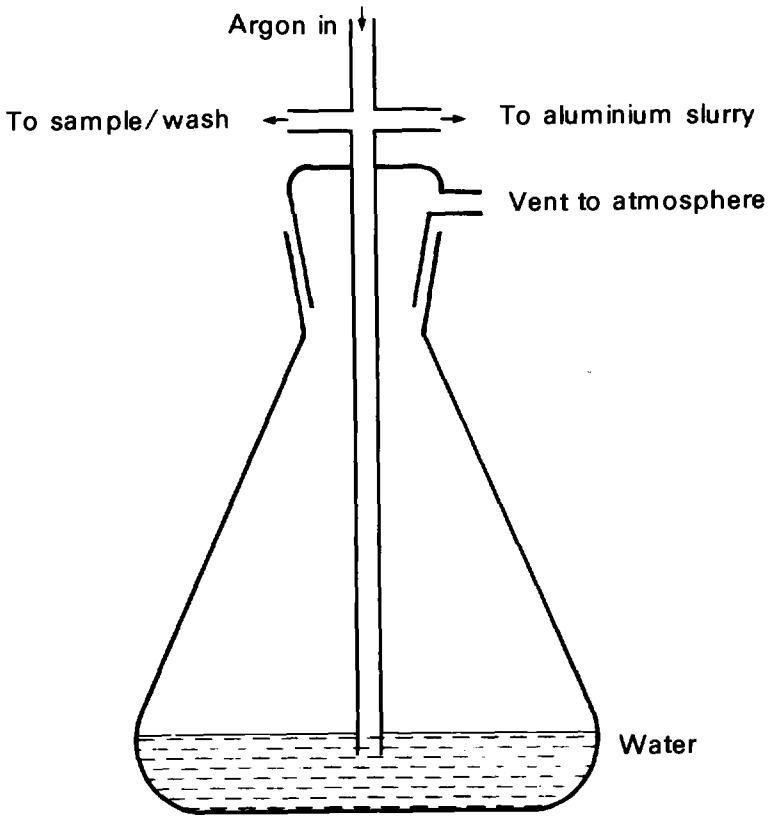
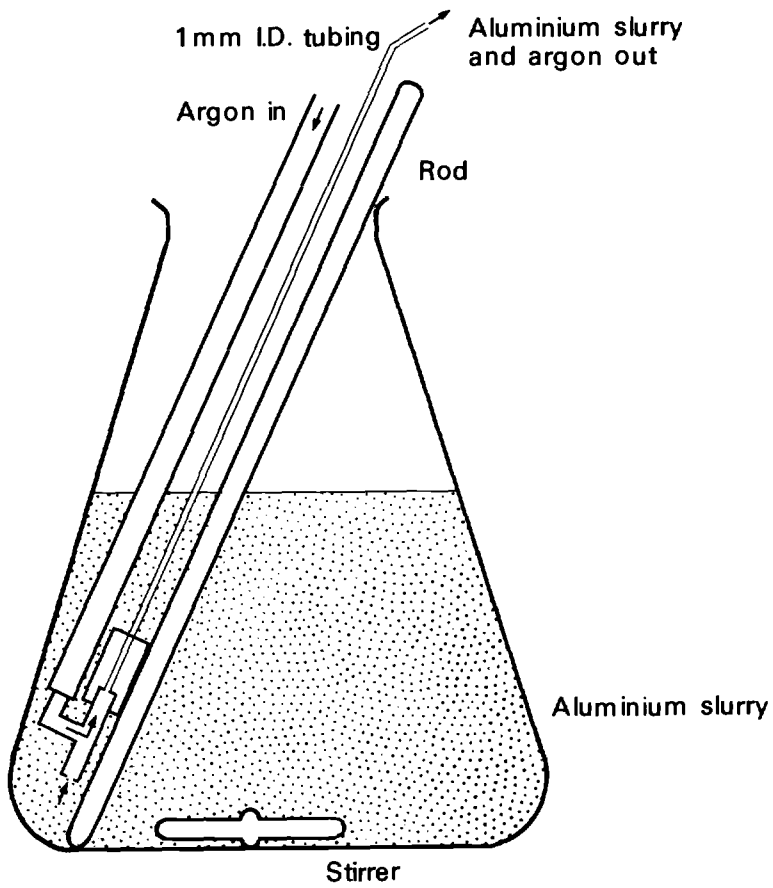


Figure 4 ALUMINIUM SLURRY DISPENSER



tube is wound with resistance wire (20 ohms) and thermally insulated. A potential of about 40 volts is applied to the wire through a variable transformer to give an indicated temperature of 850 ± 50°C, measured by a thermocouple placed on the tube under the heating wire. Connection is made to the silica tubing using heat shrink polytetrafluoroethylene (PTFE) sleeve.

6.3 Cleanliness

Cleanliness is essential for this determination. If possible, apparatus should be reserved solely for arsenic 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 following by rinsing with water after each determination should suffice.

7 Sample Collection and Preservation

Clean a polyethylene bottle by the procedure described in Section 6.3, add 2.0 ± 0.1 ml of 6M hydrochloric acid per litre of sample to be collected and then collect the sample.

8 Analytical Procedure

SEE SECTION 4 ON HAZARDS BEFORE STARTING THIS PROCEDURE

Step	Procedure	Notes
8.1	Pretreatment (note a) (Conversion of arsenic compounds to inorganic arsenic.)	(a) Some volatile arsenic compounds may be lost by this treatment but this has not been checked. If pretreatment is not required (see Section 2.3) start at step 8.2.
8.1.1	Transfer 50 ± 1 ml of the sample into a beaker, add 5.0 ± 0.1 ml of 2% m/V potassium persulphate solution and 0.5 ± 0.1 ml of 20% V/V sulphuric acid. Heat to boiling on a hot plate and continue to boil vigorously for 60 ± 5 minutes, topping up with water as required. Cool and dilute with water to 50 ± 1 ml.	
8.2	Preparation of apparatus.	
8.2.1	Connect the special apparatus (Section 6.2) as shown in Figures 1 and 2 (note b).	(b) The effluent from the stripping column can be pumped to waste if the layout of the apparatus makes it necessary.
8.2.2	Switch on the heating bath.	
8.2.3	Switch on the atomic absorption spectrophotometer. Adjust the lamp wattage or current to the recommended value. Set up the instrument for arsenic determinations at a wavelength of 193.7 nm (note c).	(c) Refer to the manufacturer's instructions.
8.2.4	Adjust the position of the tube furnace so that the radiation from the lamp passes through the tube and gives minimum absorbance.	
8.2.5	Switch on the tube furnace heater. Start the flow of water to the condenser and turn on the argon and air.	
8.2.6	Switch on the stripping column heater.	
8.2.7	Place the sulphuric acid line in its reservoir (note d).	(d) It is possible to cycle the sulphuric acid continuously from a Winchester bottle. If this is done, the acid should be discarded after 500 samples or when it becomes badly discoloured.
8.2.8	Place all the other lines pumping liquid into water. Start the proportioning pump.	

Step	Procedure	Notes
8.2.9	When the temperature of the tube furnace heater, stripping column heater, and oil bath have equilibrated, place the stannous chloride/ hydrochloric acid line and potassium iodide line into their respective solutions. Leave for at least 5 minutes.	
8.2.10	Place the aluminium slurry line into the stirred suspension. Leave for at least 5 minutes.	
8.2.11	Switch on the recorder and adjust the atomic absorption spectrophotometer to give an appropriate zero response.	
8.2.12	Put the sample line into calibration solution J.	
8.2.13	Optimise the flow rates of argon and air (see Sections 6.2.2.1 and 6.2.2).	
8.2.14	Replace the sample line into water.	
8.2.15	Adjust the zero response and flow rates of argon and air if necessary.	
8.3	Determination of inorganic arsenic.	
8.3.1	The following order of presentation of samples and standards has been found to be satisfactory.	
	Calibration solutions D E F G H I and J (note e) are followed by the samples in batches of 5 interspersed with standard G. The solutions are presented until a stable plateau is obtained. The system is flushed with water for about 120 seconds between each sample.	(e) If the samples have been pretreated the calibration solutions must also be taken through step 8.1.
8.4	Shut down procedure.	
8.4.1	Turn off the electrodeless discharge lamp or hollow cathode lamp, tube furnace and stripping column heaters, atomic absorption spectrophotometer and recorder.	
8.4.2	Replace the aluminium slurry with water and flush for about 2 minutes.	
8.4.3	Replace the stannous chloride/hydrochloric acid and potassium iodide with water and flush for about 2 minutes.	
8.4.4	Turn off the proportioning pump, and the argon and air.	
8.4.5	Turn off the distilled and condenser waters and switch off the oil bath.	
8.5	Calculation of results.	
8.5.1	Measure the response for each standard and plot a calibration curve of response against concentration expressed as μg As/1.	
8.5.2	Measure the response for each sample and read off the concentration in μg As/1 for each sample from the calibration curve. The standard solution G between each batch of 5 samples can be used to check for any instrument drift.	

9 Change of Concentration Range of the Method

The procedure given can be used to determine arsenic in the range 0 to 5 μg/l without modification. When higher concentrations of arsenic are encountered it is recommended that the samples are diluted with water containing 2.0 ± 0.1 ml of 6M hydrochloric acid per litre and the appropriate factor used in the calculation of the result.

10 Sources of Error

The attention to be paid to sources of error depends on the accuracy required of the analytical results. The following sub-sections summarise the main sources of error.

10.1 Contamination

The technique and working conditions should be critically examined to minimise any possibility of contamination. In particular, it is desirable to reserve the glass apparatus used for the determination of arsenic solely for this purpose.

10.2 Arsenic content of the water used for the determination

If the water used contains arsenic the results for samples will be falsely low by an amount equal to the concentration of arsenic in the water. The importance of this error depends on the arsenic content of the water and the concentrations of interest in the samples. Ideally, the arsenic content of the water used would be measured and an appropriate correction made. However, at present a technique for this particular determination has not been established and reliance is therefore placed on the preparation of water with a negligible arsenic content.

10.3 Arsenic content of the reagents used in the automated determination of arsenic

If the reagents used for the determination contain significant quantities of arsenic the calibration curve may deviate appreciably from linearity or near-linearity. The importance of the error depends on the concentrations of interest in the samples.

10.4 Non-stoichiometric reduction of arsenic (V) to arsenic (III)

If arsenic (V) is not quantitatively reduced to arsenic (III) the results for samples may be falsely low. It is recommended that an As (V) standard, containing 2.0 μg As per litre, is run at intervals.

10.5 Interfering substances

See Section 3. The effect of possible interfering substances may be determined by analysing samples spiked with various concentrations of the potential interfering substance.

11 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 the analytical results. It is recommended that experimental tests to check certain sources of inaccuracy should be made regularly. Many types of test are possible and they should be used as appropriate(4). It is recommended that a standard solution of arsenic of suitable concentration be analysed at the same time and in exactly the same way as normal samples. The results obtained should then be plotted on a quality control chart which will help to determine whether errors are occurring.

12 References

(1) Department of the Environment, File WS/646/47, paper SCA/4.1/As2/3.

(2) Goulden, P. D. and Brooksbank, P., *Anal. Chem.*, 1974, *46*, 1431.

(3) Department of the Environment, File WS/646/47, paper SCA/4.1/As2/5.

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

Appendix

Estimation of the Accuracy of Analytical Results using the Arsenic Method

1 Introduction

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

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

2 Basis of suggested Tests

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

Solution No	Description
1	Blank
2	Another blank
3	Standard solution 0.5 μg/l As
4	Standard solution 5.0 μg/l As
5	Typical sample
6	Same sample spiked with 2.5 μg/l As

It is essential that these solutions be treated exactly as if they were samples and the procedure specified in Section 8 of the method be rigidly followed. These solutions should be analysed in random order in each batch of analyses. Solutions 1 to 4 should be prepared each day exactly as described in the method and should contain the same amount of hydrochloric acid as is present in the samples. The same batch of water should be used on each day to prepare all four solutions. For solutions 5 and 6 a total of 1 litre of typical sample are required. Prepare solution 6 each day when required by spiking solution 5 as follows: add with a bulb pipette 2.50 ml of standard arsenic solution C to 100 ml of solution 5. When analysing solution 6 it may be necessary to take into account Section 9 and to take an appropriately smaller aliquot. The total period of the tests may be any convenient time so long as the arsenic concentration in solution 5 does not change appreciably (up to 2 weeks). The results of the analyses of solutions 5 and 6 will provide a check on the effect of sample type on precision. Any deviation of the recovery of spiked arsenic from 100% may give an indication of the presence of interfering substances.

3 Evaluation of Results

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

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

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

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

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

where x_i = the result from the ith batch
x = the mean value of x_i.

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

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

where x_{1i} = the 1st blank result (solution 1) from the ith batch
x_{2i} = the 2nd blank result (solution 2) from the ith batch.

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

$$R = \frac{(1.025\,\bar{x}_6 - \bar{x}_5)}{10} \times 100$$

where $\bar{X}_6$ = the mean result for solution 6

and $\bar{X}_5$ = the mean result for solution 5

3.6 Summarize the results as in the following table:

Solution	No of results n	Mean arsenic concentration µg/l	Standard deviation µg/l	Mean recovery %
2 Blank				-
3 Standard, 0.5µg/l As				-
4 Standard, 5.0µg/l As				-
5 Sample				-
6 Solution 5 + 2.5µg/l As				

The appropriate sample description should be entered in the space for solution 5. The standard deviation from step 3.4 is entered for the blank solution 2 and the standard deviations from step 3.3 are entered for solutions 3 to 6.

* Results to be sent to the following:

The Technical Secretary
The Metals and Metalloids Working Group
The Standing Committee of Analysts
The Department of the Environment
Romney House
43 Marsham Street
London SW1P 3PY.

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 method are requested to write to:

The Technical Secretary
The Standing Committee of Analysts
The Department of the Environment
Romney House
43 Marsham Street
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