Arsenic in Potable and Sea Water by Spectrophotometry

(arsenomolybdenum blue procedure)

1978

Methods for the Examination of Waters and Associated Materials

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Tentative Method

Methods for the Examination of Waters and Associated Materials

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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 a properly equipped laboratory. Field operations should be conducted with due regard to possible local hazards, and portable safety equipment should be carried. Care should be taken against creating hazards for others. Lone working, whether in the laboratory or field, should be discouraged. Reagents of adequate purity must be used, along with properly maintained apparatus and equipment of correct specification. Specifications for reagents, apparatus and equipment are given in manufacturers' catalogues and various published standards. If contamination is suspected, reagent purity should be checked before use.

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

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

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

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About this series

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

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

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

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

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

TA DICK
Chairman

LR PITTWELL
Secretary

20 July 1977

Arsenic in Potable Waters and Sea Water by Spectrophotometry

(Arsenomolybdenum blue procedure) Tentative Method (1978 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 another publication in this series)

1.1	Substance determined	All forms of arsenic (see Section 2.2).		
1.2	Types of sample	Potable waters and sea water.		
1.3	Basis of the method	Evolution of arsine which is trapped, and converted to an arsenomolybdenum blue complex which is measured spectrophotometrically.		
1.4	Range of application (a)	Up to 40 µg/l (b) (see Section 11). Up to 2 µg/l (c) (see Section 11).		
1.5	Calibration curve (a)	Linear to 60 µg/l (b) (see Section 10). Linear to 15 µg/l (c) (see Section 10).		
1.6	Standard deviation (a) (within batch)	Arsenic concentration (µg/l)	Standard deviation (µg/l)	Degrees freedom
	potable waters	0.0	0.18 (b)	7
		4.0	0.05 (b)	7
		20.0	0.12 (b)	7
		40.0	0.24 (b)	7
	sea water	0.00	0.048 (c)	9
		2.49	0.050 (c)	9
		2.63	0.050 (c)	9
1.7	Limit of detection (a)	0.67 µg/l (b) (7 degrees of freedom). 0.19 µg/l (c) (9 degrees of freedom).		
1.8	Sensitivity (a)	10 µg/l (b) gives an absorbance of approximately 0.22. 1 µg/l (c) gives an absorbance of approximately 0.064.		
1.9	Bias (a)	Not known.		
1.10	Interference (a)	See Section 3.		
1.11	Time required for analysis	For six samples the total analytical time is about 100 min of which about 30 min is operator time. These figures exclude any pre-treatment time.		

(a) These data were obtained at the Department of Oceanography, University of Liverpool[1] using a spectrophotometer at 866 nm and a cell of pathlength 40 mm.
(b) Potable waters spiked with the stated concentration of arsenic (with no pre-treatment).
(c) Sea water (with no pre-treatment).

2 Principle

2.1 The method described is based on experimental work carried out at the Department of Oceanography, University of Liverpool.[1]

2.2 Inorganic arsenic (As III and As V) is converted to arsine using sodium borohydride which is added slowly to the acidified samples by means of a peristaltic pump. The evolved hydrogen and entrained arsine are bubbled through and iodine/potassium iodide solution and the resultant arsenate is determined spectrophotometrically as an arseno-molybdenum blue complex at 866 nm. It is possible that some samples may contain organo-arsenic derivatives which may not be determined by this procedure; however, at present the level of such compounds has not been generally established. The total arsenic content can be determined after preliminary oxidation of the sample (see Section 8.1 and 8.2) and the application of this technique to representative samples will indicate whether the pre-treatment stage is necessary.

3 Interferences

Table 1 gives details of the potential interfering substances which have been tested. Of the substances investigated only copper, silver and selenium interfere at the 0.5 mg/l level. Some other cations interfere at concentrations greater than 0.5 mg/l but such concentrations are unlikely to be found in potable and sea waters. These interfering cations can be removed by the ion exchange procedure described in steps 8.1.5 to 8.1.7. Alkali and alkaline earth elements, chloride and sulphate cause no interference at their normal concentrations in seawater.

Table 1
Effect of other substances on the determination of arsenic≠

Other substance	Substance added as	Concentration of other substance mg/l	Effect* of other substances in µg/l As at an arsenic concentration of 20 µg/l
Ag^{+}	nitrate	0.5	– 5.36
		2.5	–10.20
		50.0	–17.70
		250.0	–18.40
Bi^{3+}	nitrate	0.5	– 0.12
		2.5	+ 0.24
		50.0	– 4.00
		250.0	– 6.28
Cd^{2+}	chloride	0.5	+ 0.16
		2.5	– 0.06
		50.0	– 1.12
		250.0	– 6.86
Cr^{3+}	chloride	250.0	– 0.16
Co^{2+}	chloride	0.5	– 0.16
		2.5	– 0.16
		50.0	– 0.12
		250.0	– 9.24
Cu^{2+}	chloride	0.5	– 1.50
		2.5	– 3.68
		50.0	–17.90
		250.0	–18.68
Fe^{3+}	sulphate	250.0	– 0.36
Ge^{4+}	sodium germanate	0.5	+ 0.16
		2.5	– 0.02
		50.0	+ 0.36
		250.0	– 1.74
Hg^{2+}	chloride	0.5	– 0.22
		2.5	– 0.24
		50.0	– 0.16
		250.0	– 0.64
Mn^{2+}	chloride	250.0	– 0.36
Mo^{6+}	ammonium molybdate	50.0 (c)	– 0.34
Ni^{2+}	chloride	0.5	+ 0.16
		2.5	+ 0.16
		50.0	–17.20
		250.0	–18.58
Pb^{2+}	nitrate	250.0	– 0.02
Sb^{3+}	antimony potassium tartrate	0.5	+ 0.28
		2.5	+ 0.44
		50.0	(a)
		250.0	(a)
Se^{4+}	sodium selenate	0.5	– 3.90
		2.5	– 6.18
		50.0	(b)
		250.0	(b)
Sn^{2+}	chloride	0.5	+ 0.16
		2.5	– 0.72
		50.0	– 9.74
		250.0	–12.66

Table 1
Effect of other substances on the determination of arsenic≠

Other substance	Substance added as	Concentration of other substance mg/l	Effect* of other substances in µg/l As at an arsenic concentration of 20 µg/l
ClO_3^-	potassium chlorate	0.5	+ 0.16
		2.5	− 0.38
		50.0	− 0.38
		250.0	− 1.22
NO_3^-	sodium nitrate	2000.0	− 0.10
PO_4^{3-}	disodium hydrogen phosphate	1.0	− 0.30
		5.0	+ 0.16
		100.0	+ 0.44
		500.0	+ 0.76
SiO_4^{4-}	sodium silicate	0.4	+ 0.24
		4.0	+ 0.02
		40.0	+ 0.24
		100	− 0.42
chloroform	—	2000.0	+ 0.02
methanol	—	1000.0	− 0.12
sodium dodecyl sulphate	—	50.0	+ 0.06

* If the other substances had no effect, results would be expected (95% confidence) to lie within the following range:

0.00±0.42 for 20 µg As/l

When only one concentration is given tests were made at lower concentrations and the effects shown to be statistically not significant.

(a) white turbidity in final solution

(b) elemental selenium precipitated in final solution

(c) final solution had a yellowish green colour instead of the usual faint blue.

≠ These determinations were carried out in distilled water spiked with the stated concentrations of other substances using the procedure given in Section 8.3.

4 Hazards

4.1 Particular care must be taken to avoid exposure to the intense ultra violet radiation produced by the mercury lamp because this can cause permanent eye and skin damage. Also the photolysis process produces copious quantities of ozone which is toxic and it is essential that the cooling air from this apparatus is vented to a fume hood. (See Sections 6.2 and 8.2).

4.2 Addition of sulphuric acid (d_{20} 1.84) to water must be carried out with care and gentle swirling of the contents of the flask. (See Section 5.2.1).

4.3 Sodium borohydride (see Section 5.17) is caustic and can react violently with water and extra care should be taken to avoid contact with the eyes, skin and clothing. Gloves and goggles must be worn when handling this compound. In the event of accidental spillage or contact immediate copious washing with water is the simplest and most effective remedy. Subsequently treat the affected areas as a caustic burn. If the compound gets into the eyes, irrigate with water immediately and obtain medical attention as quickly as possible.

4.4 Care is required when preparing and handling solutions containing arsenic (see Section 5.20) or potassium antimonyl tartrate (see Section 5.11) as these are toxic. If any of these compounds have been ingested immediately carry out gastric aspiration and lavage and obtain medical attention.

4.5 Very small quantities of arsine which is toxic are produced in steps 8.3.4 and 8.4.4. These steps must be carried out in a fume cupboard.

5 Reagents

All reagents and standard solutions should be kept in either glass or polyethylene bottles which have been cleaned by the procedure described in Section 6.6. Except where otherwise stated analytical grade chemicals are suitable.

5.1 Water

5.1.1 The water used for blank determinations and for preparing standard and reagent solutions should have an arsenic content that is negligible compared with the smallest concentration to be determined in the samples (see Section 12.2). Water distilled from an all glass apparatus has been found to be satisfactory.

5.1.2 *Arsenic-free seawater* is prepared by passing seawater at approximately 2 ml/min through a 5 cm x 1.5 cm^2 bed of hydrous zirconium oxide previously prepared by heating zirconyl chloride octahydrate in a muffle furnace at 260±20°C for 12 hours followed by sieving to 80–100 mesh. The bed should be sufficient to produce 20 litres of arsenic-free sea water. It is recommended that each batch of sea water be checked by carrying out a blank determination (step 8.4.7).

5.2 Sulphuric acid (d_{20} 1.84)

5.2.1 *2.5M Sulphuric acid (approximately)*
Add slowly and cautiously with stirring 135±3 ml of sulphuric acid (d_{20} 1.84) to 750 ml of water in a 2-litre beaker which is standing in cold water. When thoroughly mixed and cooled make up to 1 litre with water in a measuring cylinder.

5.3 Hydrochloric acid (d_{20} 1.18)

5.3.1 *6M hydrochloric acid (approximately)*
Dilute 53±1 ml of hydrochloric acid (d_{20} 1.18) with water to 100 ml in a measuring cylinder.

5.3.2 *1M Hydrochloric acid (approximately)*
Dilute 9.0±0.5 ml hydrochloric acid (d_{20} 1.18) with water to 100 ml in a measuring cylinder.

5.3.3 *0.1M Hydrochloric acid (approximately)*
Dilute 10.0±0.5 ml of 1M hydrochloric acid with water to 100 ml in a measuring cylinder.

5.4 Nitric acid (d_{20} 1.42)

5.5 Ammonia (d_{20} 0.91)

5.5.1 *2M Ammonia solution (approximately)*
Dilute, cautiously, 14.0±0.5 ml of ammonia solution (d_{20} 0.91) with water to 100 ml in a measuring cylinder. Carry out this operation in a fume cupboard.

5.6 1M Sodium chloride solution (approximately)

Dissolve 5.85±0.01g of sodium chloride in water in a beaker and dilute with water to 100 ml in a measuring cylinder.

5.7 4.2% m/V Sodium hydrogen carbonate solution

Dissolve 4.2±0.1g of sodium hydrogen carbonate in water in a beaker and dilute with water to 100 ml in a measuring cylinder.

5.8 2% m/V Disodium dihydrogen ethylene diamine tetra-acetate (EDTA) solution

Dissolve 2.0±0.1 g of disodium EDTA in water in a beaker and dilute with water to 100 ml in a measuring cylinder.

5.9 **4.8% m/V Ammonium molybdate solution**

Dissolve 4.8±0.1g of ammonium molybdate tetrahydrate in water in a beaker and dilute with water to 100 ml in a measuring cylinder. Store in a polyethylene bottle and reject if it becomes discoloured, or if a precipitate forms.

5.10 **1.76% m/V *L*– Ascorbic acid solution**

Dissolve 1.76±0.01g of L-ascorbic acid in water in a beaker and dilute with water to 100 ml in a measuring cylinder. Store at 0 to 5°C and reject the solution if it becomes discoloured.

5.11 **0.274% m/V Potassium antimonyl tartrate (PAT) solution**

Dissolve 0.274±0.001g of PAT in water in a beaker and dilute with water to 100 ml in a measuring cylinder.

5.12 **Mixed reagent solution**

Mix 10.0±0.1 ml of 2.5M sulphuric acid, 3.00±0.05 ml ammonium molybdate solution, 1.00±0.01 ml of PAT solution and 6.00±0.05 ml of ascorbic acid solution in a 25-ml stoppered flask. This reagent is NOT stable and should be used within 1 hour of preparation.

5.13 **Iodine**

5.14 **8% m/V Potassium iodide solution**

Dissolve 8.0±0.1g of potassium iodide in water in a beaker and dilute with water to 100 ml in a measuring cylinder.

5.15 **Iodine/potassium iodide solution (absorption solution)**

Dissolve 0.25g±0.02g of iodine in 5.0±0.1 ml of 8% m/V potassium iodide solution and when dissolution is complete dilute with water to 100 ml in a measuring cylinder.

5.16 **Calcium hydroxide**

5.17 **10% m/V Sodium borohydride solution**

Dissolve 25±1g of powdered sodium borohydride in 100±5 ml water and filter the solution through a qualitative analytical grade paper capable of retaining 5 μm particles into a 150-ml flask. To purify the solution add 2.0±0.1g of calcium hydroxide, loosely stopper the flask and place in a water bath in a fume cupboard at 75±3°C for 20 minutes; under these conditions a small proportion of the borohydride decomposes rapidly, thus removing traces of arsenic as arsine (this operation is hazardous, see Section 4). Cool the solution to room temperature, filter through a qualitative analytical grade filter paper capable of retaining 5 μm particles and dilute to 250±5 ml with water. This solution decomposes slowly and therefore it should be discarded after two days.

5.18 **4% m/V Sodium hydroxide solution**

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

5.19 **Cation exchange resin**

Digest a strongly acidic cation exchange resin of 50–100 mesh contained in a beaker in a water bath at 80°C with approximately 20 times its own volume of 6M hydrochloric acid. After 1 hour decant the acid and wash the resin several times with water until the resin is free from acid. Store as a slurry in water in a polyethylene bottle (pH greater than 5.0).

5.20 **Standard arsenic solutions:**

5.20.1 *Solution A* 1 ml contains 1 mg As

Dissolve 1.321±0.001g of arsenic trioxide in 100 ml of 4% m/V sodium hydroxide solution in a 1-litre calibrated flask. When dissolution is complete dilute with water to the mark and mix well.

5.20.2 *Solution B* 1 ml contains 10 µg As
Dilute 10.00±0.02 ml of *solution A* to 600 ml with water in a 1-litre calibrated flask, add 3.0±0.1 ml 6M hydrochloric acid, dilute with water to the mark and mix well. This solution should be freshly prepared before use.

5.20.3 *Solution C* 1 ml contains 1 µg As
Dilute 10.00±0.02 ml of *solution B* to 60 ml with water in a 100-ml calibrated flask, add 2.0±0.1 ml of 1M hydrochloric acid, dilute with water to the mark and mix well. This solution should be prepared freshly before use.

5.20.4 *Solution D* 1 ml contains 0.1 µg As
Dilute 10.00±0.02 ml of *solution B* to 600 ml with water in a 1-litre calibrated flask, add 3.0±0.1 ml of 6M hydrochloric acid, dilute with water to the mark and mix well. This solution should be freshly prepared before use.

6 Apparatus

6.1 **A spectrophotometer** of prism or grating type or using narrow band pass optical filters and fitted with 40-mm micro cuvettes with a capacity of not greater than 1.5 ml.

6.2 **Ultra violet photolysis apparatus**

The apparatus which is used for pre-treatment of seawater samples (Section 8.2) is shown diagrammatically in figure 1. 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 photolysis tubes, each at a distance of 10 cm from the lamp. Cooling, to the optimum temperature of 60±3°C, is provided by an externally mounted fan and the expelled air is vented to a fume cupboard to remove ozone which is toxic at the concentrations encountered. The lid of the photolysis apparatus is fitted with an interlocked micro-switch so that the mercury lamp cannot be operated when the lid is open.

6.3 **Cation exchange column for removal of heavy metals**

Place a wad of silica wool (glass wool should not be used for supporting the resin since it tends to retain arsenic) at the bottom of a 5 cm × 0.8 cm^2 ion exchange column and fill the column with a slurry of approximately 5 ml of cation exchange resin in the hydrogen form (see Section 5.19) taking care to avoid air bubbles and channeling. Convert the resin to the sodium form by passing through it 50±1 ml of 1M sodium chloride at approximately 2 ml/min. Finally, wash the resin column with 50±1 ml of water. After use, the column can be regenerated by washing it with 50±1 ml of 1M hydrochloric acid and then reconverting to the sodium form as described above.

6.4 **Apparatus for the evolution and collection of arsine**

The apparatus used for the evolution of arsine is shown diagrammatically in figure 2. 10% m/V sodium borohydride solution is delivered from the reservoir via a manifold to a multichannel peristaltic pump fitted with acid resistant tubing which serves to inject the reagent at a controlled rate (10±1 and 15±1 ml/h for potable water and seawater samples respectively) into the 250-ml evolution flask mounted at an angle of approximately 35° on a stand. The evolved hydrogen, along with the entrained arsine, passes through the delivery tube jet (bore 0.5 mm) into the absorption tube (figure 3) which has been calibrated at a volume of 2.50±0.02 ml and which contains the absorption solution.

6.5 **Ultrasonic bath**

6.6 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 in 10% V/V nitric acid followed by a thorough rinse with water after each determination should suffice.

7 Sample Collection and Preservation

Seawater samples can be stored in either glass or polyethylene containers with or without acidification (pH 1–8) for up to at least seven days without significant change. Potable water samples also appear to be stable under similar conditions. Clean either a glass or polyethylene bottle by the procedure described in Section 6.6, add 2.0±0.1 ml of 6M hydrochloric acid per litre of sample to be collected and then collect the sample.

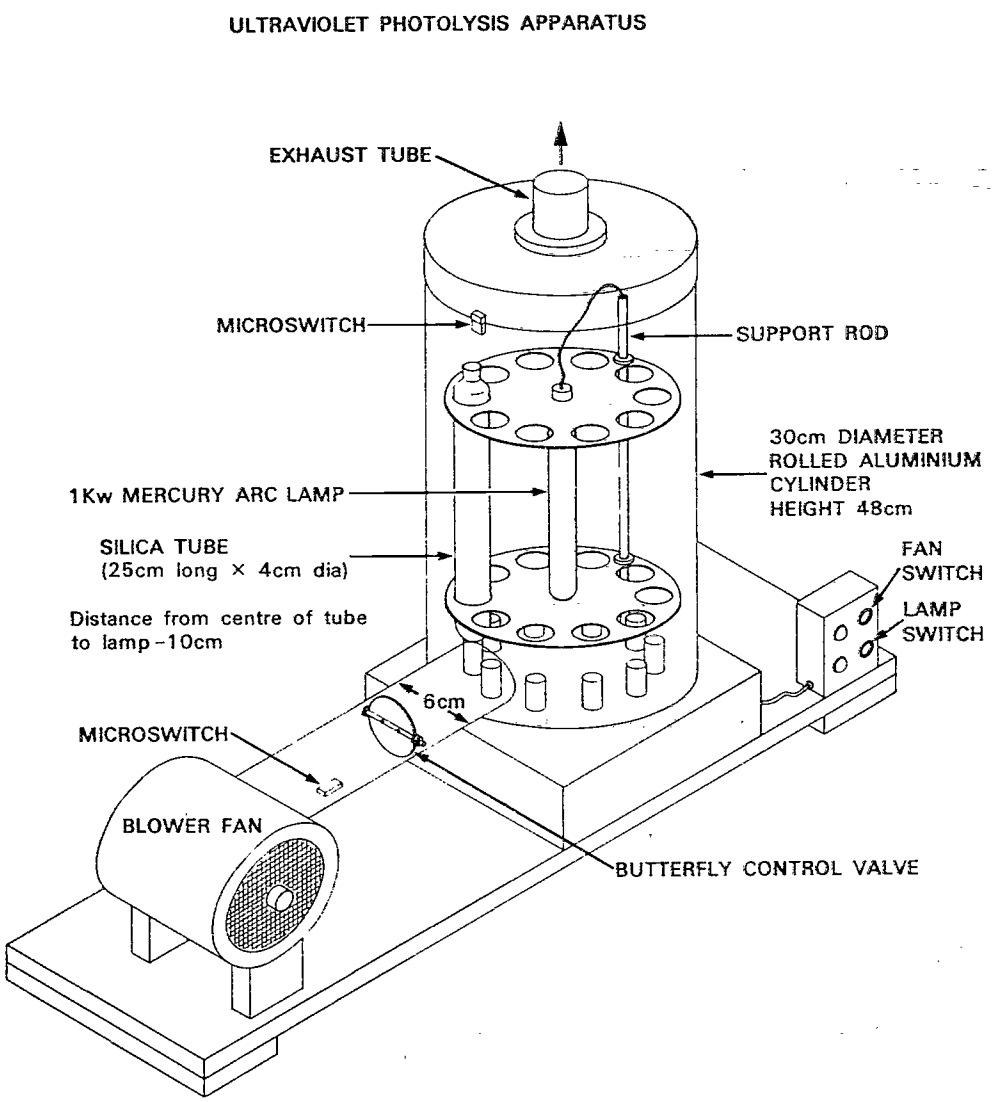

Figure 1

APPARATUS FOR THE EVOLUTION AND COLLECTION OF ARSINE

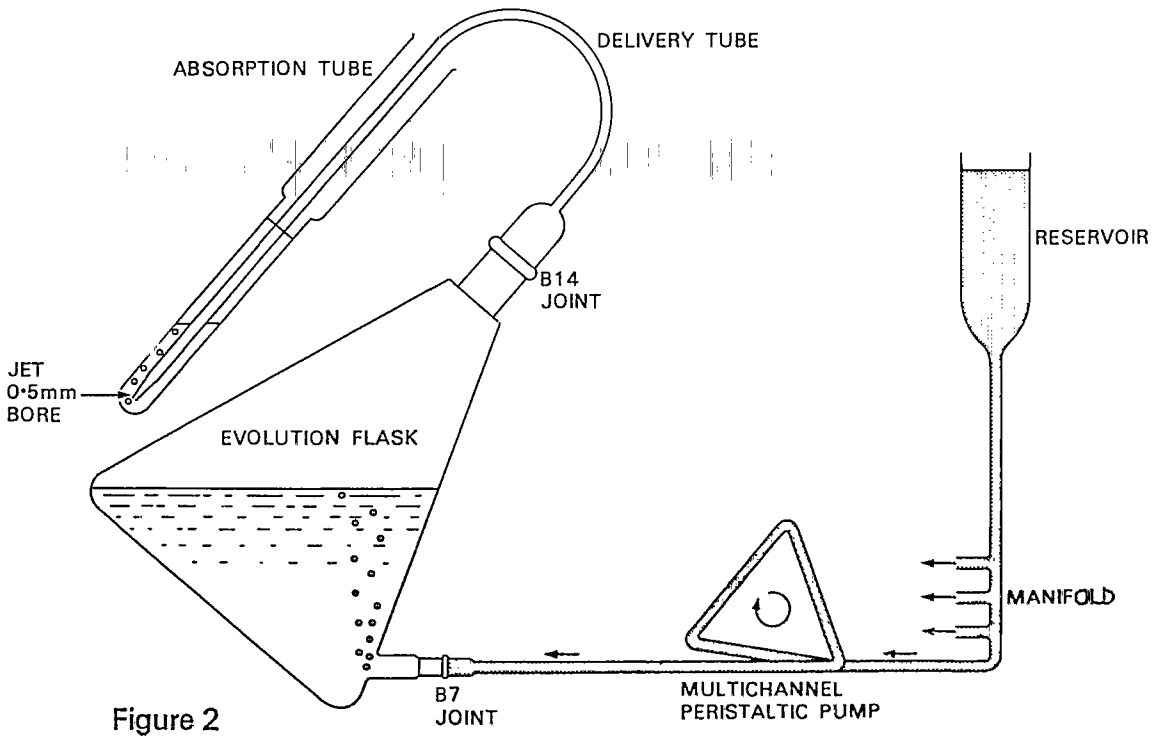

Figure 2

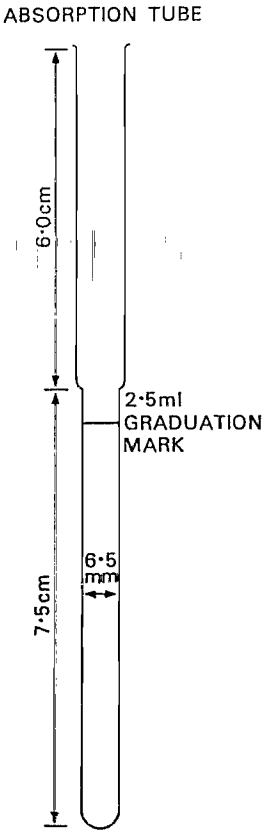

Figure 3

READ SECTION 4 ON HAZARDS BEFORE STARTING THIS PROCEDURE

8 Analytical Procedure

Pre-treatment procedures are described for potable waters and sea water followed by the method for the determination of the inorganic arsenic in potable waters and sea waters.

8.1 Pre-treatment of potable waters

This pre-treatment procedure should be carried out on all samples unless the analyst, from knowledge and experience of his particular waters and confirmation by testing, has shown that the procedure is not necessary. (See Section 2.2).

Step	Experimental Procedure	Notes
	Pre-treatment stage (Note a)	
8.1.1	Add 50.00±0.05 ml of the sample to a borosilicate glass beaker and evaporate to approximately 10 ml on a hot plate in a fume cupboard.	(a) It is possible that some volatile arsenic compounds may be lost by this procedure. If pre-treatment is not required start at step 8.3.1.
8.1.2	Cool to ambient temperature and add cautiously 2.0±0.1 ml of nitric acid (d_{20} 1.42) and 1.0±0.1 ml of sulphuric acid (d_{20} 1.84). Continue to evaporate until dense white fumes of sulphur trioxide begin to be evolved. Cool to ambient temperature.	
8.1.3	Dissolve the residue cautiously in approximately 25 ml of water (note b).	(b) When the concentration of certain individual heavy metals in the original sample exceeds 0.1 mg/l (see Section 3 and Table 1) these elements must be removed prior to the evolution stage. The removal technique, steps 8.1.5 to 8.1.7 can be used for heavy metal concentrations of up to a total of 2 g/l. Application of this technique to representative samples will show whether this separation is necessary and, if so, proceed to step 8.1.5.
8.1.4	If removal of heavy metals is not necessary, transfer the solution of the residue to a 50-ml calibrated flask and dilute with water to the mark. Proceed to step 8.3.1.	
	Removal of heavy metals	
8.1.5	Using a pH meter adjust the solution of the residue from step 8.1.3 to pH 3.0±0.5 by careful addition of 2M ammonia solution.	
8.1.6	Pass the solution through a column of cation exchange resin in the sodium form at a rate of approximately 2 ml/min (see Section 6.3) and wash the column with four 5 ml aliquots of water.	
8.1.7	Combine the percolate and washings, dilute with water to 50 ±1 ml transfer to an evolution flask, and proceed to step 8.3.2.	

8.2 Pre-treatment of seawater

This pretreatment procedure should be carried out on all samples unless the analyst, from knowledge and experience of his particular water and confirmation by testing, has shown that the procedure is not necessary (see Section 2.2).

Step	Experimental Procedure	Notes
	Pre-treatment stage (note c)	
8.2.1	Using a pH meter adjust the pH of 200 ± 1 ml of sample to pH 6.0 ± 0.3 by cautious addition of 4% m/V sodium hydroxide solution.	(c) Experience has shown that organic arsenic constitutes less than 0.5% of the total arsenic in seawater. Some estuarine waters may contain a greater proportion of organic arsenic. Application of this procedure to representative samples will indicate whether the pretreatment stage is necessary. If pre-treatment is not necessary proceed to step 8.4.1.
8.2.2	Transfer 150 ± 1 ml of the solution to a 25 × 4 cm fused silica tube and loosely stopper.	
8.2.3	Irradiate the silica tube for 2 hours in the photolysis apparatus adjusting the flow of air from the fan by means of the butterfly valve (see fig. 1) so that an optimum solution temperature of 60 ± 3°C is achieved.	
8.2.4	Cool to ambient temperature and quantitatively transfer the solution to an evolution flask using 2 ml portions of water to rinse the tube. Proceed to step 8.4.2.	
8.3	Determination of inorganic arsenic in potable waters	
8.3.1	Place 50 ± 0.05 ml of the sample in the evolution flask (fig. 2).	
8.3.2	Add 5.0 ± 0.1 ml of 2.5M sulphuric acid and 5.0 ± 0.1 ml of 2% m/V EDTA solution. Place the flask on the stand and fit the delivery tube.	
8.3.3	To the absorption tube add 1.2 ± 0.1 ml of the absorption solution and 0.20 ± 0.02 ml of 4.2% m/V sodium hydrogen carbonate solution. Insert the delivery tube into the absorption tube until the jet is close to the bottom.	
8.3.4	Using a peristaltic pump add 10% m/V sodium borohydride solution at a rate of 10 ± 1 ml/hr. After one hour lower the absorption tube and rinse the tip of the delivery tube into it with not more than 0.3 ml water.	
8.3.5	Add 0.5 ± 0.1 ml of the mixed reagent to the absorption tube and dilute with water to 2.50 ± 0.02 ml. Mix thoroughly (note d) to release carbon dioxide. Stand for 30 ± 1 min.	(d) An ultra-sonic bath is suitable.
8.3.6	Set up the spectrophotometer according to the manufacturer's instructions and measure the absorbance of the solution at 866 nm in a 40-mm micro-cuvette against a reference cuvette containing water. Let the absorbance of the sample be S.	
	Blank determination	
8.3.7	A blank must be run with each batch of determinations in an identical manner with that used for the samples. To 50.00 ± 0.01 ml of water add 0.10 ± 0.02 ml of 6M hydrochloric acid. If pre-treatment was used, carry out steps 8.1.1 to 8.1.7 and 8.3.1 to 8.3.6; if pre-treatment was not used carry out steps 8.3.1 to 8.3.6. Let the absorbance of the blank be B.	

Step	Experimental Procedure	Notes

Calibration standards

8.3.8 A duplicate calibration standard must be run with each batch of determinations in an identical manner to that used for the samples.
Add 20.00 ± 0.02 ml of standard arsenic *solution D* and 0.10 ± 0.02 ml of 6M hydrochloric acid to each of two 50-ml calibrated flasks and dilute with water to the mark. If pre-treatment was used carry out steps 8.1.1 to 8.1.7 and 8.3.1 to 8.3.6; if pre-treatment was not used carry out steps 8.3.1 to 8.3.6. Let the absorbance of the calibration standards be C_1 and C_2. These contain 40 µg/l As.

Calculation of results

8.3.9 Calculate the concentration A of arsenic from

$$A = \frac{S - B}{\bar{C} - B} \times 40\ \mu g/l$$

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

This calculation assumes a linear calibration curve and linearity must be checked (see Section 10).

8.4 Determination of inorganic arsenic in sea waters

8.4.1 Place 150 ± 1 ml of sample in the evolution flask (fig 2).

8.4.2 Add 5.0 ± 0.1 ml of 2.5M sulphuric acid and 5.0 ± 0.1 ml of 2% m/V EDTA solution. Place the flask on the stand and fit the delivery tube.

8.4.3 To the absorption tube add 1.2 ± 0.1 ml of the absorption solution and 0.20 ± 0.02 ml of 4.2% m/V sodium hydrogen carbonate solution. Insert the delivery tube into the absorption tube until the jet is close to the bottom.

8.4.4 Using a peristaltic pump add 10% m/V sodium borohydride solution at a rate of 15 ± 1 ml/hr. After one hour lower the absorption tube and rinse the tip of the delivery tube into it with not more than 0.3 ml of water.

8.4.5 Add 0.5 ± 0.1 ml of the mixed reagent to the absorption tube and dilute with water to 2.50 ± 0.02 ml. Mix thoroughly (note d) to release carbon dioxide. Stand for 30 ± 1 min.

(d) An ultrasonic bath is suitable.

8.4.6 Set up the spectrophotometer according to the manufacturer's instructions and measure the absorbance of the solution at 866 nm in a 40-mm micro-cuvette against a reference cuvette containing water. Let the absorbance of the sample be S_1.

Step	Experimental procedure	Notes

Blank determination

8.4.7 A blank must be run with each batch of determinations in a similar manner to that used for samples. To 150 ± 1 ml of arsenic-free sea water add 0.30 ± 0.02 ml of 6M hydrochloric acid. If pre-treatment was used carry out steps 8.2.1 to 8.2.4 and 8.4.1 to 8.4.6; if pre-treatment was not used carry out steps 8.4.1 to 8.4.6. Let the absorbance of the blank be B_1.

Calibration standards

8.4.8 A duplicate calibration standard must be run with each batch of determinations in a similar manner to that used for the samples.
Add 4.00 ± 0.02 ml of standard arsenic *solution D* 0.40 ± 0.02 ml of 6M hydrochloric acid and 196 ± 1 ml of water to each of two beakers. If pretreatment was used carry out steps 8.2.1 to 8.2.4 and 8.4.1 to 8.4.6; if pre-treatment was not used carry out steps 8.4.1 to 8.4.6. Let the absorbance of the calibration standards be C_3 and C_4. These contain 2 µg/l As.

Calculation of results

8.4.9 Calculate the concentration A_1 of arsenic from

$$A_1 = \frac{S_1 - B_1}{\bar{C}_1 - B_1} \times 2\ \mu g/l$$

where $\bar{C}_1 = \frac{C_3 + C_4}{2}$

This calculation assumes a linear calibration curve and linearity must be checked (see Section 10).

9 Measurement of Absorbance

The procedure used for measuring absorbance should be rigorously controlled to ensure satisfactory precision of measurement. The same cells should always be used for the reference and sample solutions, and they should always be placed in the same position in the cell holder with the same face towards the light source.

It is difficult to ensure reproducible alignment of cells with chipped corners, and therefore they should be discarded. Similarly the movement of the cell carrier should be kept scrupulously clean. Before every set of measurements the sample cell should be measured against the reference cell when both are filled with water. This will help indicate when the cells need cleaning and it will also enable the true absorbance of the blank to be determined.

10 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 applied to any samples and regularly thereafter.

10.1 Potable waters

To each of a series of 500-ml calibrated flasks add 1.00 ± 0.01 ml of 6M hydrochloric acid and by pipette add 0.0, 5.0, 10.0, 15.0 and 20.0 ml of standard arsenic *solution C* respectively and dilute with water to the mark. These solutions contain respectively 0, 10, 20, 30 and 40 µg/l arsenic. Pipette 50.0 ml aliquots of each and carry out the procedure described in steps 8.3.1 to 8.3.6 inclusive. Plot the absorbance against µg/l arsenic for each solution.

The calibration curve for potable water is normally linear between 0 and 60 µg/l arsenic.

10.2 Seawater

To each of a series of 500-ml calibrated flasks add 1.00 ± 0.01 ml 6M of hydrochloric acid and by pipette add 0.0, 5.0, 10.0, 15.0 and 20.0 ml of standard arsenic *solution D* respectively and dilute with arsenic-free seawater to the mark. These solutions contain respectively 0, 1, 2, 3, 4 µg/l arsenic. Using a 150 ml aliquot of these solutions carry out the procedure described in steps 8.4.1 to 8.4.6 inclusive. Plot the absorbance against µg/l arsenic for each solution. The calibration curve for seawater is normally linear between 0 and 15 µg/l arsenic.

11 Concentration Range of the Method

The procedure given can be used without modification to determine arsenic in potable waters in the concentration range 0 – 40 µg/l and in seawater in the concentration range 0 – 2 µg/l. When the arsenic concentration in the sample exceeds these levels the final solution (steps 8.3.5 or 8.4.5) must be diluted to an appropriately larger volume (V ml) with water. In both cases the upper concentration limit for the method is 800 µg/l As. It is necessary to alter the calculation, steps 8.3.9 or 8.4.9, as follows

Arsenic in potable water

$$A = \frac{V(S-B)}{2.5(\bar{C}-B)} \times 40\ \mu g/l\ As$$

Arsenic in seawater

$$A_1 = \frac{V(S_1-B_1)}{2.5(\bar{C}_1-B_1)} \times 2\ \mu g/l\ As$$

12 Sources of Error

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

12.1 Contamination

The technique and working conditions should be critically examined to minimize any possibility of contamination.

12.2 Arsenic content of water used for blank when analysing potable waters

If arsenic is present in the water used for the blank the results will be falsely low. A method for the determination of arsenic in water used for blanks has not yet been evaluated. However, the following method is thought likely to be satisfactory.

Carry out arsenic determinations using exactly the procedure described in Section 8.3 with 50 ml and 150 ml aliquots of the water which is being tested. Add the 10% m/V sodium borohydride at a rate of 10 ± 1 ml/hr in both instances.

The arsenic content of the blank water is equivalent to an absorbance, Y, where

$$Y = \frac{B_{150} - B_{50}}{2}$$

where B_{150} = the absorbance obtained with 150 ml water
B_{50} = the absorbance obtained with 50 ml water

The concentration of arsenic (A_W) in the blank water is then given by

$$A_W = \frac{Y}{\bar{C}-B} \times 40\ \mu g/l\ As$$

This concentration must then be added to the arsenic concentration as determined in step 8.3.9.

12.3 Interfering substances

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

13 Checking the Accuracy of Analytical Results

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 source of inaccuracy should be made regularly. Many types of test are possible and they should be used as appropriate. As a minimum, however, it is suggested 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 facilitate detection of inadequate accuracy, and will also allow the standard deviation of routine analytical results to be estimated.

14 References

1. Heywood MG and Riley JP, *Anal. Chim. Acta*, 1976, **85**, 219–230.

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 Secretary
The Standing Committee of Analysts
The Department of the Environment
2 Marsham Street
LONDON SW1P 3EB
England

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 University of Liverpool – (Department of Oceanography). 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	For potable waters	For seawaters
1	Blank	Blank
2	Another blank	Another blank
3	Standard solution 10 µg/l As	Standard solution 0.5 µg/l As
4	Standard solution 40 µg/l As	Standard solution 2.0 µg/l As
5	Typical sample	Typical sample
6	Same sample spiked with 40 µg/l As	Same sample spiked with 2.0 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 2.5 litres of typical sample are required for potable waters and 5 litres of typical sample are required for seawaters. Prepare solution 6 each day when required by spiking solution 5 as follows: for potable waters add, using a pipette, 4.0 ml of standard arsenic *solution C* to 100 ml of solution 5; for seawaters add, using a pipette, 4.0 ml of standard arsenic *solution D* to 200 ml of solution 5. When analysing solution 6 it will be necessary to take into account Section 11 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 for 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:

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

where x_i = the result from the ith batch

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

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

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

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

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

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

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

for seawaters, $R = \frac{(1.02\,\bar{x}_6 - \bar{x}_5)}{2} \times 100$

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

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

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 %
For potable waters				
2 Blank				—
3 Standard, 10.0 µg/l As				—
4 Standard, 40.0 µg/l As				—
5 Sample.....				—
6 Solution 5 + 40.0 µg/l As				
For seawaters				
2 Blank				—
3 Standard 0.5 µg/l As				—
4 Standard 2.0 µg/l As				—
5 Sample.....				—
6 Solution 5 + 2.0 µg/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. If pre-treatment was carried out this should be stated.

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