Mercury in Waters, Effluents, Soils and Sediments etc, additional methods 1985

Methods for the Examination of Waters and Associated Materials

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Methods for the Examination of Waters of Associated Materials

This booklet supplements, but does not supercede (see below) Mercury in Waters, Effluents and Sludges by Flameless Atomic Absorption Spectrophotometry 1978 (Ref 24). It contains a comparative table of methods and the following additional methods:

A. Mercury in Raw, Potable and Saline Waters and Effluents by Bromine Oxidation (concentration using Gold) and Flameless Atomic Absorption Spectrophotometry.
B. Mercury in Suspended Matter and Sediments by Aqua Regia Oxidation (concentration using Gold) and Flameless Atomic Absorption Spectrophotometry.
C. Mercury in Waters by Flameless Atomic Fluorescence Spectrophotometry.
D. Mercury in Soils, Sediments and Related materials by permanganate oxidation and Flameless Atomic Absorption Spectrophotometry.

Note: Throughout this booklet mercury is expressed as the element (Hg).

Contents

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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 These volumes inevitably took some years to prepare, so that they were often partially out of date before they appeared in print.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 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 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

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

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

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

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

Comparative Summary of 1978 and 1986 Booklet Methods

Method	Sample Type	Limit of Detection	Range	Time for 10 Samples unsupervised and operator times	Types of Mercury determined	Outline
1985 A	Raw Potable and Saline Water	c1ng/l	0–200 ng/l	4+4 hrs	All	Acidic Bromine Oxidation, Tin II Reduction, Gold Concentration, Flameless AAS
B	Suspended Matter Sediments	0.01 µg/g	no upper limit	5+2 hrs	All	Aqua Regia Oxidation, Tin II Reduction, Gold Concentration, Flameless AAS
C	All Waters also Sludge Digests	cl–2ng/l but a one hundred fold concentration step can be added	no upper limit	1+2 hrs	All	Acidic Bromine Oxidation, Tin II Reduction, (Similar concentration step), Atomic Fluorescence Spectrophotometry
D	Solids and Sediments	0.02 µg/g	0–c 0.5 µg/g	2+12 hrs + overnight	All	Nitric-Sulphuric Acid Permangamate digestion, Tin II Reduction, Flameless AAS
1978 A	Non saline Waters Effluents Sludges	0.1–0.2 µg/l	(0–20 µg/l (or 0–20 µg/g	32+4 hrs) 65+7 hrs)	All	Sulphuric Acid Permangate Digestion, Tin II Reduction, Flameless AAS
A14	Clean Waters			5+2 hrs	All	Nitric-Sulphuric Acid – Permangamate – Persulphate Digestion, Tin II Reduction, Flameless AAS
B	Saline and Other Waters	4 ng/l	0–250 ng/l	$1\frac{1}{2}$+1 hrs	not all organic forms (not all disubstituted)	Dithizone Carbon Tetrachloride Extraction, Hydrochloric – Nitrite Back Extraction, Tin II Reduction, Flameless AAS.

A Mercury in Raw, Potable and Saline Waters and Effluents by Bromine Oxidation, Gold Concentration and Flameless Atomic Absorption Spectrophotometry Tentative Method

A1 Performance Characteristics of the Method

(For further information on the determination and definition of performance characteristics see Ref 6.)

A1.1	Substance determined	All forms of mercury (see Section A2)
A1.2	Type of sample	Raw, potable and saline water and effluents
A1.3	Basis of the method	Oxidation of all forms of mercury to inorganic mercury with bromine, followed by flameless atomic absorption spectrophotometry
A1.4	Range of application (a)	Up to 200 ng/l (see Section A10)
A1.5	Calibration curve (a)	Linear to 200 ng/l

A1.6 Within batch standard deviation (a)

Type of sample	Mercury Concentration (ng/l)	Standard deviation	Degrees of Freedom
Tap water (Liverpool)	40	1.5	6
Stripped, spiked tap water (Liverpool) (b)	42	1.6	5
Sea water (Irish)	33	1.5	11
Stripped, spiked sea water (Irish) (c)	43	2.5	2
Stripped, spiked sea water (Irish) (d)	42	3.0	2
Stripped, spiked river water (Mersey) (b)	39	1.2	5
Spiked distilled water (c)	39	1.2	5
Spiked distilled water (d)	41	1.8	5
Stripped, spiked oil refinery effluent			
(9.5 mg DOC/l) (c)	37	6.0	2
(9.5 mg DOC/l) (d)	33	2.0	3
Stripped, spiked chemical plant effluent			
(16.0 mg DOC/l) (c)	41	4.0	3
(16.0 mg DOC/l) (d)	42	3.0	3
Stripped, spiked sewage effluent			
(11.0 mg DOC/l) (c)	38	3.0	3
(11.0 mg DOC/l) (d)	38	3.0	3
Stripped, spiked petrochemical plant effluent			
(250.0 mg DOC/l) (c)	44	6.0	2
(250.0 mg DOC/l) (d)	46	6.0	2
Stripped, spiked detergent factory effluent			
(3.5 mg DOC/l) (c)	37	5.0	3
(3.5 mg DOC/l) (d)	36	3.0	3

A1.7	Limit of detection (a)	0.7 ng/l with 6 degrees of freedom for distilled water 1.3 ng/l with 12 degrees of freedom for river water (Mersey)

A1.8	Sensivity (a)	75 ng/l are equivalent to an absorbance of approximately 0.2
A1.9	Bias	See Section A1.6
A1.10	Interferences	Section A3
A1.11	Time required for lanalysis (a)	The total analytical and operator times for 10 samples are 8 and 4 hours respectively including pretreatment time.

(a) These data were obtained by the Department of Oceanography, University of Liverpool[1] using this method and a single beam atomic absorption spectrophotometer with 1.7 time range expansion and using a 250 ml sample.
(b) Spiked with 40 ng Hg/l added as mercuric chloride
(c) Spiked with 40 ng Hg/l added as methyl mercuric chloride
(d) Spiked with 40 ng Hg/l added as phenyl mercuric acetate.

A2 Principle

A2.1 The method described is based on experimental work carried out at the Department of Oceanography, University of Liverpool.[1]

A2.2 It is essential to convert all forms of mercury to inorganic mercury. This is achieved by treating the acidified sample with a solution containing potassium bromide and bromate. The bromine which is formed rapidly converts both alkyl and aryl mercury compounds to inorganic mercury.[2,3] This treatment also gives approximately 90% recovery of mercury from suspended particulate matter. Before proceeding with the analysis, excess bromine is removed by addition of hydroxyammonium chloride.

A2.3 The inorganic mercury is determined by a flameless atomic absorption procedure based on that of Olafsson.[3] An acidic solution of tin (II) chloride is added to the sample to produce elemental mercury:

$$Hg^{2+} + Sn^{2+} \rightarrow Hg^{0} + Sn^{4+}$$

The mercury vapour is swept from the sample with a stream of nitrogen and concentrated in a trap containing elemental gold deposited on pumice. Subsequently, the trap is heated rapidly to 450°C. The volatilized mercury is transferred with a constant flow of nitrogen to a gas cuvette placed in the optical path of an atomic absorption spectrophotometer fitted with a mercury hollow cathode lamp. Absorption by the mercury vapour is measured at 253.7 nm (see Figure 1).

A3 Interferences

The effects of a variety of other substances on the determination of 40 ng/l of mercury are shown in Tables 1–3. The concentrations of many of these components were set at, or above, the levels recommended by the Standing Committee of Analysts.[4] However, the major cations and anions present in sea water are omitted from the Tables as complete recoveries of mercury spikes are achieved from this medium. Of the substances tested significant interference at the 95% confidence level is only found with gold (>10μg/l), and silver (>100μg/l). Because it complexes mercury very strongly fulvic acid at a concentration of 12 mg/l causes considerable interference if the bromination stage is omitted, but does not interfere if this preliminary reaction is employed.

Table 1 Effect of other substances on the determination of Mercury (a)

Other substance	Other substance added as	Concentration of other substance (mg/l)	Effect of other substances in ng Hg/l at a mercury concentration of 40 ng/l (b)
Silver (as Ag^{+})	nitrate	0.1	−5
Silver (as Ag^{+})	nitrate	1.0	−25
Aluminium (as Al^{3+})	nitrate	10.0	+2
Arsenic (as As^{3+})	arsenious oxide	1.0	−2
Gold (as Au^{3+})	chloroauric acid	0.01	−3
Gold (as Au^{3+})	chloroauric acid	0.05	−21
Gold (as Au^{3+})	chloroauric acid	0.10	−32
Barium (as Ba^{2+})	nitrate	10.0	−2
Beryllium (as Be^{2+})	sulphate	10.0	0
Bismuth (as Bi^{3+})	nitrate	10.0	0
Cadmium (as Cd^{2+})	nitrate	10.0	−1
Cobalt (as Co^{2+})	sulphate	10.0	−2
Chromium (as Cr^{3+})	chloride	10.0	−2
Copper (as Cu^{2+})	nitrate	10.0	−1
Iron (as Fe^{2+})	sulphate	10.0	0
Molybdenum (as Mo^{6+})	sodium molybdate	10.0	+1
Nickel (as Ni^{2+})	nitrate	10.0	−2
Lead (as Pb^{2+})	nitrate	10.0	−1
Antimony (as Sb^{3+})	potassium antimonyl tartrate	10.0	+1
Selenium (as Se^{4+})	selenium dioxide	0.5	−1
Strontium (as Sr^{2+})	chloride	10.0	+2
Vanadium (as V^{5+})	ammonium vanadate	10.0	−1
Zinc (as Zn^{2+})	sulphate	10.0	+2
Bromide (as Br^{-})	potassium	10.0	−2
Fluoride (as F^{-})	sodium	10.0	−2
Iodine (as I^{-})	potassium	10.0	+1
Nitrite (as N)	sodium	1.0	+2
Phosphate (as PO_4^{3-})	dipotassium hydrogen	10.0	0
Pyrophosphate (as $P_2O_7^{4-}$)	tetrapotassium	10.0	0
Thiosulphate (as $S_2O_3^{2-}$)	sodium	10.0	−2
Ethylenediamine tetra acetic acid	disodium	10.0	−1
Nitrilotriacetic acid	acid	10.0	−1
Lauryl sulphate	sodium	10.0	+2
Urea	substance	20.0	0
Acetic acid	substance	25.0	0
Acetone	substance	35.0	+2
Benzene	substance	35.0	+1
Chloroform	substance	23.0	−2
Ethanol	substance	25.0	−2
Ethyl acetate	substance	22.0	0
n-Hexane	substance	26.0	+3
Methanol	substance	25.0	−3
Phenol	substance	10.0	−3
Toluene	substance	26.0	+3

(a) These data were obtained by the Department of Oceanography, University of Liverpool[1] using this method.

(b) If the other substances did not interfere the effect would be expected to be within 0.0±3.0 ng Hg/l.

A4 Hazards

A4.1 The exhaust fumes from the cuvette of the atomic absorption spectrophotometer are toxic and must be ducted away.

A4.2 The reagent described in Section A5.5 should be regarded as a special hazard. Hydroxyammonium chloride is a skin and eye irritant and continued contact may cause dermatitis. A face-shield and gloves must be worn when handling this material and any spillage should be washed away with copious amounts of water.

A4.3 Samples and standard solutions containing mercury are toxic and care must be taken handling them. If any of these solutions is swallowed give water to dilute and milk as a soothing and buffering agent. Do not delay seeking medical advice.

A4.4 Magnesium perchlorate is a strong oxidant and should not be exposed to inflammable vapours or liquids. Spent material should be disposed of by dissolving in water and flushing down the drain.

A5 Reagents

All reagents and standards must be stored in glass bottles (See Section A6). Polyethylene must *not* be used because of its permeability to mercury vapour. Analytical reagent grade chemicals are suitable unless otherwise specified.

A5.1 Water

The water used for blank determinations and for preparing standards and reagents should have a mercury content that is negligible compared with the smallest concentration to be determined in the samples (see Section A12). Redistilled water which has been passed through a 25 cm×1.5 cm^2 column of strongly acidic cation exchanger is suitable.

A5.2 0.28% m/V Potassium bromate solution

Heat potassium bromate overnight in a silica basin at 350°C in a muffle furnace to remove mercury. After cooling, dissolve 0.28±0.05 g of it in 100 ml of water. Prepare this solution weekly.

A5.3 1% m/V Potassium bromide solution

Heat potassium bromide overnight in a silica basin to 350°C in a muffle furnace. After cooling, dissolve 1.0±0.05 g of it in 100 ml water. Prepare this solution weekly.

A5.4 Bromate-bromide mixture

Mix 50±2 ml of potassium bromate solution (Section A5.2) with 50±2ml of potassium bromide solution (Section A5.3).

A5.5 30% m/V Hydroxyammonium chloride

This reagent is hazardous (see Section A4.2). Dissolve 30±1 g of hydroxyammonium chloride in water and dilute to 100 ml with water. This solution is stable indefinitely.

A5.6 Hydrochloric acid (d_{20} 1.18)

If necessary, purify by passing through a 10 cm by $1\frac{1}{2}$ cm^2 column of strongly basic anion exchange resin in the chloride form.

A5.7 10% V/V Hydrochloric acid

Dilute 100±2 ml of hydrochloric acid (d_{20} 1.18) to 1 litre with water.

A5.8 5% m/V Tin (II) chloride solution

Dissolve by warming, 5.0±0.3 g of tin (II) chloride ($SnCl_2.2H_2O$) in 90±2 ml of 10% V/V hydrochloric acid in the presence of a granule of tin, cool and dilute to 100±5 ml with 10% V/V hydrochloric acid. Prepare this reagent freshly each day and purge it by bubbling with nitrogen for 20 minutes before use.

A5.9 2% m/V Chloroauric acid ($HAuCl_4$) solution

If not available commercially, prepare by quantitative dilution of a commercially available solution.

A5.10 Gold Coated pumice

Wash approximately 10 g of pumice (60–80 mesh) by decantation with acetone and then with water. Digest it with 10% V/V hydochloric acid at room temperature for 1 hour and then wash thoroughly by decantation. Dry overnight at approximately 200°C. Place 5.0±0.5 g of it in a silica basin and add 25± ml of 2% m/V chloroauric acid. Stir well and evaporate to dryness on a water bath. Heat the pumice at 450°C for 8 hours in a muffle furnace. Cool, and transfer to a well-stoppered bottle. Pack an approximately 4 cm length of the pumice into the silica trap (Section A6.2) retainining it in place with plugs of silica wool.

A5.11 Standard mercury solutions

These solutions are hazardous (See Section A4.3).

A5.11.1 *Solution A* 1 ml contains 100 μg Hg

Weigh 0.1354±0.0005 g of mercuric chloride and dissolve it in approximately 100 ml of water, add 60±5 ml of nitric acid (d_{20} 1.42) and dilute to 1 litre in a calibrated flask. Store in a refrigerator. This solution is stable for at least 1 year.

A5.11.2 *Solution B* 1 ml contains 1 μg Hg

Dilute 5.00±0.05 ml of solution A with water to approximately 300 ml. Add 30±1 ml of nitric acid (d_{20} 1.42) and dilute with water to 500 ml in a calibrated flask. Prepare freshly when required.

A5.11.3 *Solution C* 1 ml contains 10 ng Hg

Dilute 5 ml of solution B to approximately 300 ml, add 30±1 ml of nitric acid (d_{20} 1.42) and dilute with water to 500 ml in a calibrated flask. Prepare freshly when required.

A5.12 Nitrogen

From a cylinder. Purify by passage through a 10 cm by 1.5 cm^2 tube packed with gold coated pumice (Section A6.2).

A5.13 Magnesium Perchlorate (anhydrous)

This substance is strongly deliquescent and also absorbs ammonia. It may be dried by heating in clean air to 200–210°C to constant weight. It decomposes if heated above 250°C. See Hazards Section A4.

A5.14 Nitric acid d_{20} 1.42

A6 Apparatus

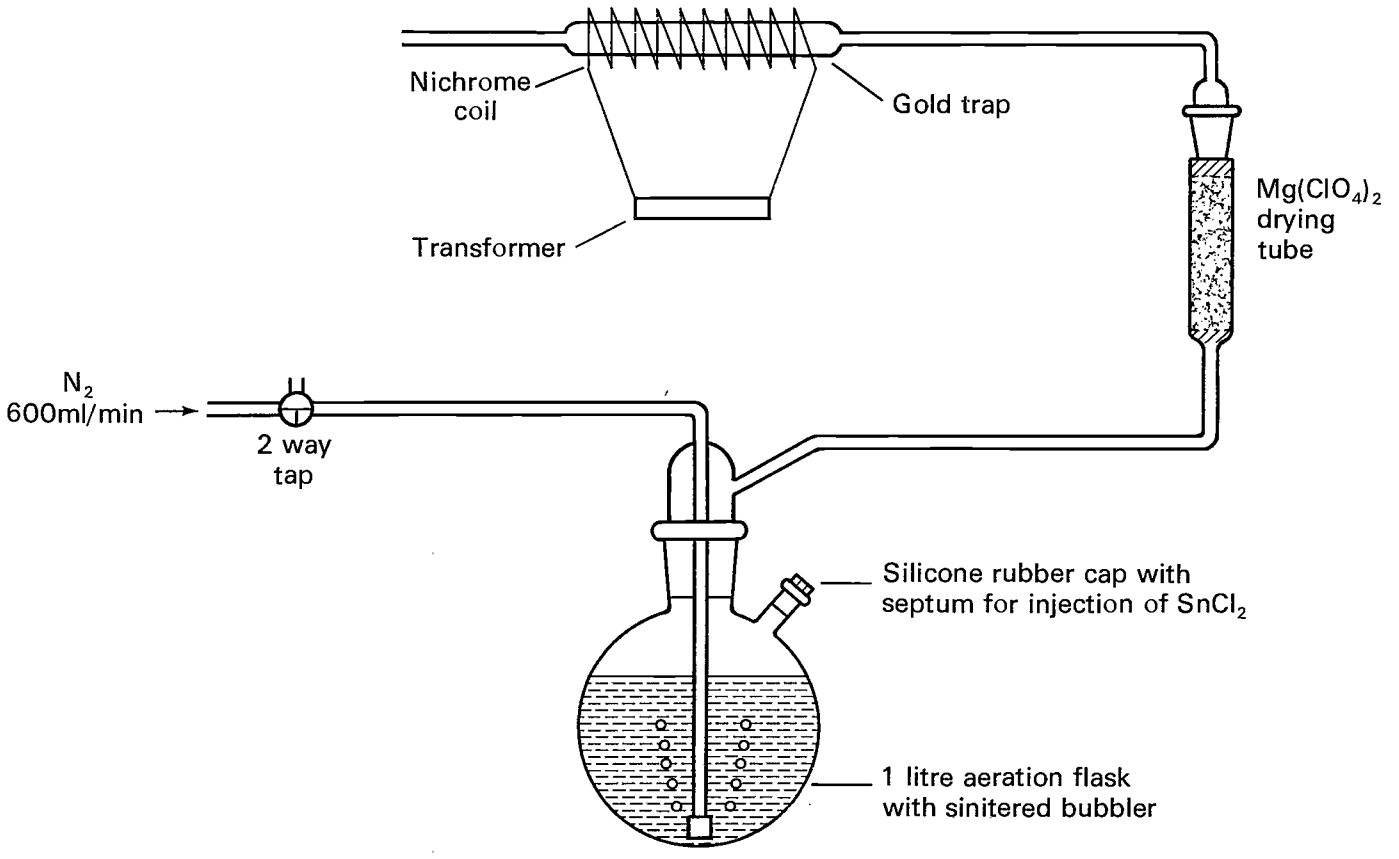
A6.1 An atomic absorption spectrophotometer

With a mercury hollow cathode lamp. A chart recorder with a rapid response item (0.5s) can be used for read-out, or alternatively a digital indicator or printer which triggers at maximum response can be used.

A6.2 The gold trap

Is constructed of fused silica tubing and consists of an approximately 7 cm length of 6 mm internal diameter (i.d.) tubing sealed at one end to a 5 cm length of 4 mm i.d. tubing and at its other to a 4 cm length of 2 mm i.d. tubing which serves as the exit tube. The central portion of the trap, which contains approximately 4 cm of gold coated pumice, is heated by means of a spiral of 34 turns of 0.6 mm nichrome wire (3.34 ohm/m) which is wound closely round it and connected to the 20V tapping of a transformer rated at at least 6A.

FIG 1a APPARATUS FOR STRIPPING AND TRAPPING MERCURY



A6.3 Special apparatus for analysis of samples

A diagram of the apparatus used is shown in Figures 1a and 1b. A stream of purified nitrogen at a flow rate of 600±100 ml/min (measured by means of a flow meter) is passed through a sintered glass bubbler (Porosity 1) into the sample contained in a suitable sized two-necked flask (up to 1 L). The B 10 neck of this flask is fitted with a silicon rubber cap bearing a gas chromatographic septum through which tin (II) chloride is injected with a syringe. The outlet tube of the Drechsel bottle head is connected by means of 4 mm i.d. polyvinyl chloride tubing to a 12 cm × 1.5 cm i.d. drying tube packed with anhydrous magnesium perchlorate, which must be replaced when it becomes wet for half its length. The outlet of the drying tube is connected to the gold trap (Sections A5.8 and A6.2). A removable 2.5 mm i.d. polyvinylchloride (PVC) tube is used to connect the exit tube of the trap to a gas cuvette 150 cm in length and 1 cm i.d. with silica windows. The cuvette is mounted in a holder on the burner head of the atomic absorption spectrophotometer and accurately aligned with the light beam. Note: It is important to keep the lengths of the PVC connecting tubing to a minimum.

A6.4 Glassware

Cleanliness is essential in this determination. Apparatus must be reserved solely for mercury determination. Clean all glassware, both before and after use, by filling it with 50% V/V hydrochloric acid. Immediately before use rinse it with water.

A7 Sample Collection and Preservation

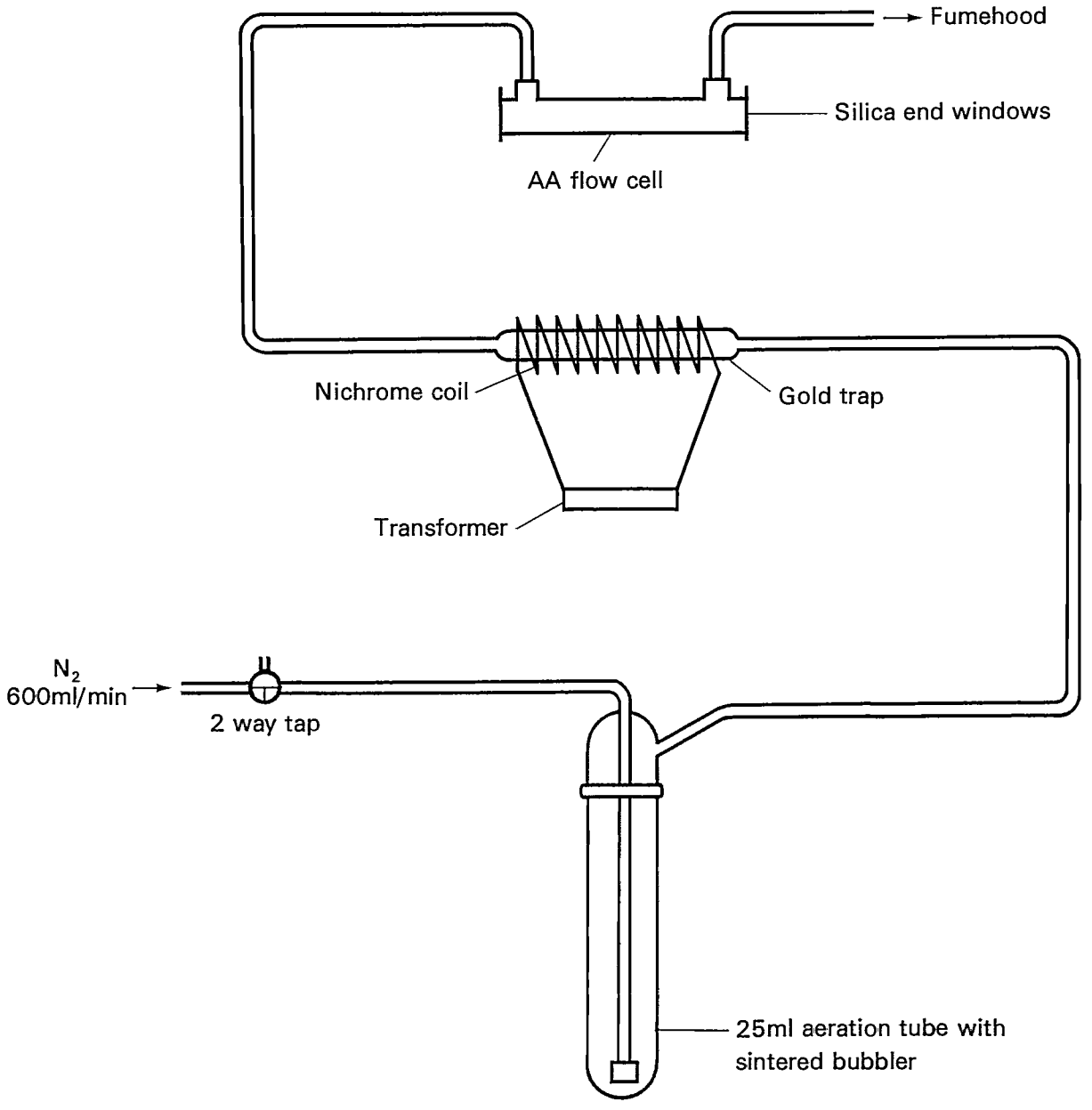
Samples must be collected in clean glass-stoppered bottles (Section A6.4) whose quality (freedom from mercury) has been proved by carrying out a blank determination on a sample of clean water stored in the bottle prior to use.

Unsatisfactory bottles should not be used.

A7.1 If only soluble mercury is required, proceed as in Section B7.1, but collect the filtrates, not the washings. Use this undiluted filtrate in step A7.2.

If a division between soluble and insoluble mercury is required procedures A7.1 and B7.1 can be combined in one operation.

FIG 1b APPARATUS FOR TRANSFERRING MERCURY FROM THE GOLD TRAP TO THE FLOW CELL OF THE ATOMIC ABSORPTION SPECTROPHOTOMETER



A7.2 To each 250±1 ml sample add 5.0±0.2 ml of concentrated hydrochloric acid (d_{20} 1.18) and 5.0±0.1 ml of bromate-bromide reagent (5.4). Stopper the bottle and allow the reaction to proceed for 3 hours to ensure complete breakdown of organo-mercury compounds. Proceed with the analysis as soon as possible thereafter. Samples should be collected directly into the bottle, but may be transferred to it **immediately** after collection. In the latter case precaution must be taken to ensure that the primary collection apparatus does not alter the mercury content of the sample.

A.8 Analytical Procedure

Read Section A4 on hazards before starting this procedure.

Step	Procedure	Notes
	Analysis of sample	
A8.1	Place 250±2 ml of the sample in a 500 ml two-necked flask (note a).	(a) For samples containing less than 20 ng/1 the volume of sample should be increased to 1 L.
A8.2	Add 1.00±0.05 ml of 30% m/V hydroxyammonium chloride solution (5.6) and mix well (note b).	(b) The brown colour due to bromine should be completely discharged.
A8.3	Insert the head of the bubbler into the neck of the flask and connect it to the gold trap.	
A8.4	By means of a syringe inject 2.0±0.1 ml of 5% m/V tin (II) chloride solution through the septum.	
A8.5	Pass nitrogen through the solution at a flow rate of 600±100 ml/min. Turn off the gas flow after 30 min.	
A8.6	Remove the two necked flask and replace it by a dry 25 ml boiling tube with a B24 socket.	
A8.7	Connect the outlet tube of the gold trap to the gas cuvette.	
A8.8	Turn on the nitrogen again and adjust its flow rate to 50±5 ml/min.	
A8.9	Set up the atomic absorption spectrophotometer according to the manufacturer's instructions and adjust it to a wavelength of 253.7 nm: Set it and the chart recorder to zero (note c).	(c) Range expansion may be used if necessary.
A8.10	Start the chart recorder and then switch on the heating current for the gold trap. Measure the maximum instrument response of the sample (S) (note d).	(d) The maximum absorbance should be reached 35–40 s after switching on the current.
A8.11	Continue heating and passing nitrogen until the instrument response returns to the baseline.	
A8.12	Turn off the current to the heater and, after a further 30 seconds, the nitrogen flow.	
	Blank determination	
A8.13	A blank must be included with each batch of determinations.	

A8.14 Carry out steps A8.1 to A8.5 using the same volume of distilled water instead of the sample. Add to the flask 5.0±0.2 ml of concentrated hydrochloric acid (d_{20} 1.18), 5.0±0.1 ml of bromate-bromide reagent (A5.4), and 1.00±0.05 ml of hydroxyammonium chloride solution (A5.6).

A8.15 Insert the head of the bubbler into the neck of the flask and connect it to a fresh gold trap.

A8.16 Carry out steps A8.4 to A8.12 inclusive. Let the maximum instrumental response of the blank be B.

Calibration standards

A8.17 Duplicate calibration standards must be included with each batch of determinations.

A8.18 Carry out steps A8.1 to A8.5 inclusive using 250 ml of water instead of the sample and continue thereafter as detailed in step A8.14.

A8.19 Carry out step A8.15.

A8.20 Through the septum inject 2 ml of standard mercury *solution C* (20 ng).

A8.21 Carry out steps A8.4 to A8.12 inclusive. Let this maximum instrument responses be C_1 and C_2, if these are in satisfactory agreement calculate their mean C.

Calculation of the results (see Section A10)

A8.22 Calculate the concentration, A, of mercury in 250 ml of the sample containing preservative from

$$A = \frac{S - B}{C - B} \times 80 \times 1.04 \text{ ng/l}$$

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

This calculation assumes a linear calibration curve.
Linearity must be checked (See Section A9).

(e) The factor 1.04 allows for the dilution of the sample with the preserving reagents.

A9 Checking the linearity of the Calibration Curve

The procedure given below must be carried out on at least two independent occasions before application of the method to any samples and regularly thereafter. To do this, inject aliquots (1.0, 2.0, 3.0, 4.0 and 5.0 ml) of standard mercury **solution C** (corresponding with 10, 20, 30, 40 and 50 ng Hg respectively) into a stripped water sample as described in Sections A8.20–A8.21. Plot the maximum instrument response (e.g. chart peak height) against ng of mercury. The calibration curve should be linear to at least 50 ng of mercury.

A10 Changing the concentration. Range of the Method.

The procedure can be used to determine mercury in the concentration range given in Section A1.6 without modification but with appropriate instrument settings. When the mercury content of the sample exceeds 200 ng/Hg/l an appropriately smaller aliquot of the sample must be taken for analysis. Conversely if the concentration is less than 20 ng/Hg/l it is advanatgeous to increase the sample volume to 1 L (it is not necessary to increase the time of sparging with nitrogen (step A8.5)). When the volume of sample used is changed an appropriate factor must be incorporated in the calculation of the result.

A11 Sources of Error

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

A11.1 Contamination

Mercury is a source of contamination in most laboratories and it is advisable to carry out the analysis in a laboratory in which no appreciable amounts of mercury or its compounds are used. Any sources of contamination should be identified and eliminated or minimized. It should be borne in mind that many types of plastic bottles are permeable to mercury vapour and their use for samples and reagents must be avoided. Glass apparatus used in the determination of mercury should be reserved solely for this purpose. Before carrying out a series of determinations it is essential to carry out a series of blank analyses. If any unusually high and/or variable blank values are found they indicate contamination and steps must be taken to eliminate the problem.

A11.2 Mercury content of the water used for blanks and standards

Because of the way in which the blank is determined slight contamination of the water used is of no consequence. It is, however, important that water employed in the preparation of reagents and the dilute standard mercury solution is of acceptable quality. The concentration of mercury in this water can be determined by analysing it in the same way as a sample.

A11.3 Interfering substances

See Section A3.

A11.4 Calibration curve

The calibration curve for this method has been found to be linear although its slope may vary from one set of determinations to another. Such variations may arise (i) from changes in the sensitivity of the atomic absorption spectrophotometer, or (ii) from differences in the sharpness with which mercury is stripped from the gold trap if the flow rate of nitrogen falls outside the recommended range of 50±5 ml/min.

A12 Checking the Accuracy of the Analytical Results

(For further information see Refs 6, 21 and 22.) Once the method has been put into normal routine operation many factors may subsequently adversely affect the accuracy of the analytical results. It is recommended that experimental tests to check certain sources of inaccuracy should be made regularly. Many types of test are possible and should be used as appropriate.[5] As a minimum, however, it is suggested that a standard solution of mercury of suitable concentration should be analysed at the same time and in exactly the same way as normal samples. The results obtained should then be plotted on a quality control chart which will facilitate detection of inadequate accuracy, and will also allow the standard deviation of routine analytical results to be estimated.

B Mercury in Suspended Matter and Sediments by Flameless Atomic Absorption Spectrophotometry Tentative Method

B0

In aquatic systems mercury appears to be associated mainly with the suspended particulate matter and sediments. For this reason, it is often helpful to determine this fraction separately, although generally more than 85% of the mercury in the suspended particulate matter is released by the bromination technique (see Method A) used for the preservation of aquatic samples. Mercury in sediments or separated particulate matter is determined by digestion with aqua regia followed by a modification of the flameless atomic absorption technique described in Method A for waters.

B1 Performance Characteristics of the Method

(For further information on the determination and definition of performance characteristics see Ref 6.)

B1.1	Substance determined	All forms of mercury (see Section B2).
B1.2	Types of sample	Sediments and aquatic suspended matter.
B1.3	Basis of the method	Digestion and oxidation of the sample to inorganic mercury with aqua regia followed by flameless atomic absorption spectrophotometry.
B1.4	Range of application (a)	Up to 5 μg/g depending only the size of the sample and the aliquot of the digest taken.
B1.5	Calibration curve (a)	Linear up to at least 0.050 μg Hg.

B1.6 Within batch standard deviation (a)

Type of Sample	Mercury concentration (μg/g)	Standard deviation (μg/g)	Degrees of freedom
(i) Particulate matter			
Mersey estuary	3.0	0.36	8
Manchester Ship Canal	5.5	0.61	8
(ii) Fresh water sediments			
River Tawe	1.6	0.10	4
Whittle Brook (Mersey)	0.43	0.01	10
River Tamar (Calstock)	0.67	0.05	5
River Tamar (Morwellham Quay)	0.25	0.01	4
Leeds–Liverpool Canal	0.69	0.05	4
Leeds–Liverpool Canal	1.83	0.06	4
(iii) Estuarine/Marine sediments			
River Tamar (Cargreen)	2.7	0.06	5
Mersey (Hale Head)	5.1	0.29	5
Bauer Deep (Pacific Ocean)	0.52	0.02	3
East Pacific Rise (core 365 cm)	3.3	0.07	4
East Pacific Rise (core 445 cm)	2.3	0.10	8
East Pacific Rise (core 445 cm)	3.3	0.00	4

B1.7	Limit of detection (a)	0.01 μg/g with 6 degrees of freedom using a 0.05 g sample.
B1.8	Sensitivity (a)	0.005 μg Hg gives an absorbance of approximately 0.1.
B1.9	Bias (a)	see Section B3.
B1.10	Interferences (a)	see Sections B3 and A3.
B1.11	Time required for analysis (a)	For 10 samples the total analytical and operator times are approximately 5 and 2 hours respectively.

(a) These data were obtained by the Department of Oceanography, University of Liverpool[1] using this method and a single beam atomic absorption spectrophotometer.

B2 Principle

B2.1 The method described is based on experimental work carried out in the Department of Oceanography, University of Liverpool.[1]

B2.2 The sample of sediment of particulate matter is digested with aqua regia to extract mercury from it and to break down any organo-mercury compounds. Mercury in the resultant solution is reduced to the elemental state with tin (II) chloride, stripped into a gold-trap with a current of nitrogen and subsequently determined by flameless atomic absorption spectrophotometry.

B3 Interferences

No detailed information is available about the effect of interfering substances on this method. However, samples of suspended matter from the Mersey estuary and Manchester Ship Canal, which were found to contain 3.0 and 5.5 μg Hg/g respectively when analysed by this procedure, were analysed by an independent procedure [7], which has been shown to determine total mercury, and found to contain 3.4 and 6.0 μg Hg/g. In addition 30 mg portions of a deep sea sediment containing 0.15 μg Hg/g were analysed alone and after spiking with 10.1 and 0.2 μg of inorganic mercury whereupon recoveries of 90±3% and 99±1% were obtained respectively. This suggests that interferences are slight with most samples. The effect of other substances of the evolution and atomic absorption stages of the procedure can be judged from Table 1 in Section A3.

B4 Hazards

See Method A Section A4.

B5 Reagents

All reagents and standard solutions must be stored in glass bottles.
(See Method A, Section A5.)

B5.1 Water

See Method A, Section A5.1.

B5.2 5% m/V Tin (II) chloride solution

See Method A, Section A5.8.

B5.3 Standard Mercury solutions

See Method A, Sections A5.11.1 to A5.11.3.

B5.4 Nitrogen

See Method A, Section A5.12.

B5.5 Hydrochloride acid (d_{20} 1.18)

B5.6 Nitric acid (d_{20} 1.42)

B6 Apparatus

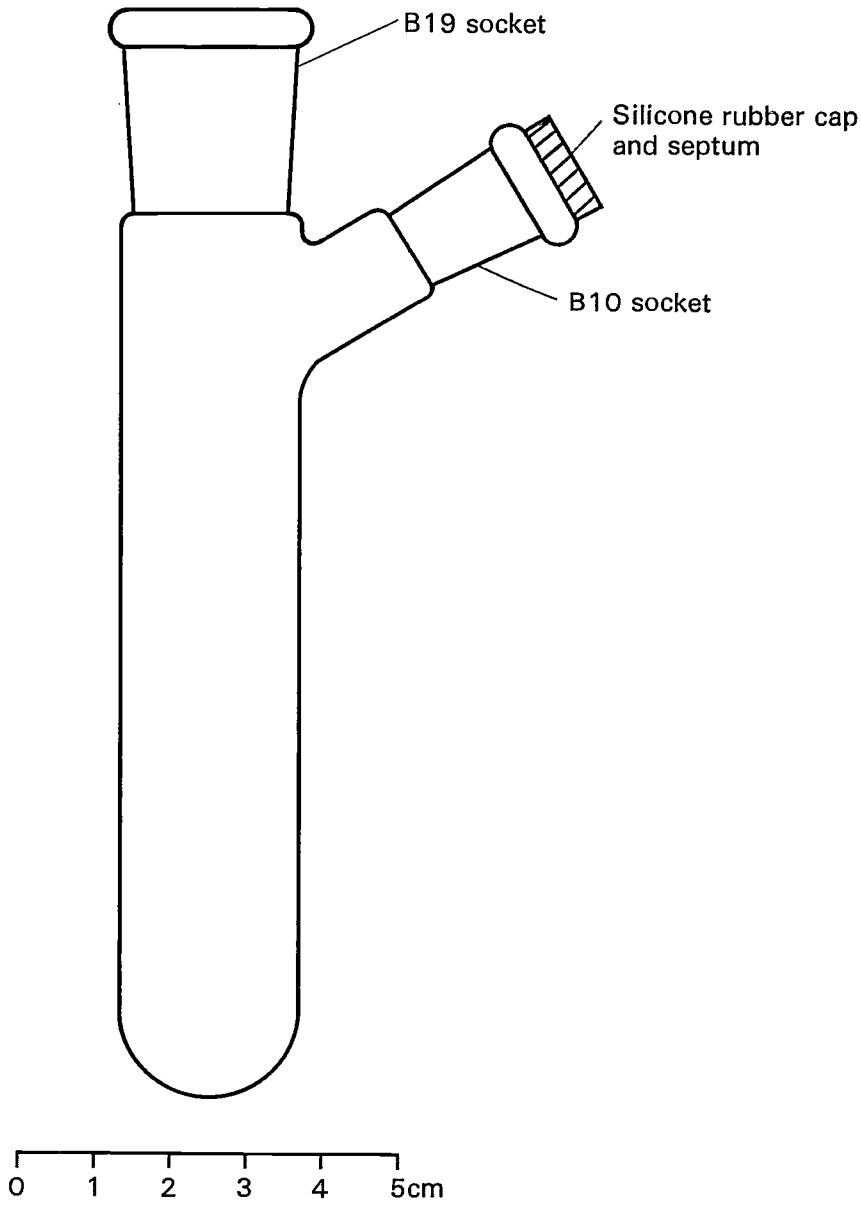
B6.1 Filtration apparatus

A Millipore or equivalent in-line filter holder capable of holding 47 mm filters is connected to the outlet of a 500 ml polypropylene separatory funnel. Filtration is carried out using pre-ignited (450°/c) tared Whatman GF/F glass fibre filters or equivalent which are stored in sealed petri dishes until required. Flow of the sample through the filter is induced by application of approximately 1 atmosphere of purified nitrogen to the top of the separatory funnel.

B6.2 Special apparatus for aspiration

The apparatus used is basically similar to that shown in Figure 1a, with the exception that the two-necked flask is replaced by a 25 ml B24 boiling tube (Figure 2). This has a B10 socket fused to it at an angle of approximately 45° close to the top and closed with a silicone rubber cap into which a gas chromatographic septum is inserted.

FIG 2 BUBBLER TUBE FOR THE DETERMINATION OF MERCURY IN SEDIMENTS AND PARTICULATE MATTER



B6.3 An atomic absorption spectrophotometer

With a mercury hollow cathode lamp. A chart recorder with a rapid response time can be used for read-out, or alternatively, a digital indicator or printer triggered at maximum response can be used.

B6.4 Glassware

Cleanliness is essential in this determination. Apparatus must be reserved solely for mercury determination. Clean all glassware, both before and after use, by filling it with 50% V/V hydrochloric acid. Immediately before use rinse it with water.

B7 Sample Collection and Preservation

If soluble mercury values are also required, read Method A Section A7.1 prior to filtering the sample. Both procedures can then be combined in one operation.

B7.1 Suspended particulates

Samples must be collected in 500 ml glass-stoppered bottles and filtered within 30 min of collection (see Section B6.1). Shake the bottle well to resuspend the sample and with a measuring cylinder transfer 500±10 ml to the separatory funnel. Replace the stopper of the funnel and force the sample through the filter using nitrogen pressure. Release the pressure and wash the walls of the funnel and the filter with water and again apply pressure to drain the filter. Transfer the filter back to its petri dish and dry to constant weight at 40°C to determine the load of suspended matter. Replace the lid of the petri dish and seal with adhesive plastic tape. Analyse the sample as soon as possible to minimize contamination by atmospheric mercury.

B7.2 Sediments

After collection, sediments should be washed by resuspension in water, centrifuged and dried in an oven at 40°C. The dried sediment should be stored in a well sealed glass tube and analysed as soon as possible.

B7.3 For the soluble mercury see method A

B8 Analytical Procedure

Read Section A4 on hazards before starting this procedure.

Step	Procedure	Notes
	Samples of particulate matter and sediments	
B8.1	Transfer the filter containing the particulate matter to a 25 ml conical flask using a pair of plastic tweezers (note a). For sediments weigh the dry sediment (note b) into a 25 ml conical flask.	(a) Care must be taken to avoid losing particulate material. (b) 30–200 mg according to the expected mercury content.
B8.2	Add 0.50±0.05 ml of nitric acid (d_{20} 1.42) and 1.50±0.05 ml of hydrochloric acid (d_{20} 1.18). Close the flask with a loosely fitting bulb stopper and heat to 70–75°C on a hot plate for 180±10 min.	
B8.3	After cooling, transfer the digest quantitatively to a 25 ml calibrated flask and dilute to volume with water.	
B8.4	Transfer a suitable aliquot of the solution (note c) to the 25 ml boiling tube and dilute to approximately 20 ml with water.	(c) 0.5–10 ml according to the expected mercury concentration in the particulate matter and the loading on the filter.

B8.5 Fit the Drechsel bottle head and connect the gold trap (A6.2). Using a syringe inject 1.0±0.1 ml of 5% m/V tin (II) chloride solution (B5.2) through the septum in the side arm.

B8.6 Transfer the liberated mercury to the gold trap with a current of nitrogen at a flow rate of 100±20 ml/min.

B8.7 Turn off the gas after 10±1 min and replace the boiling tube with a dry boiling tube.

B8.8 Continue the analysis as described in Sections A8.8 to A8.12. Let the maximum instrumental response be S.

Blank determination

B8.9 A blank must be included with each batch of determinations.

B8.10 Carry out steps B8.1 to B8.8 and A8 to A12 inclusive using a pre-ignited glass fibre filter. Let the maximum instrumental response be B.
Calibration standards.

B8.11 Duplicate standards and an associated blank must be included with each batch of determinations.

B8.12 Pipette 2 ml of standard mercury solution C (A5.11.3) into a 25 ml side-arm boiling tube and dilute to approximately 20 ml with water.

B8.13 Carry out Steps B8.5 to B8.8 and A8 to A12 inclusive. Let the maximum instrument responses be C_1 and C_2; if these are in satisfactory agreement calculate their mean C.

B8.14 Determine the associated blank by carrying out Steps B8.1 and B8.13, but omitting the addition of the standard mercury solution. Let the maximum instrument response be B_S.

Calculation of the results.

B8.15 Calculate the concentration A, of mercury in the suspended matter or sediment sample from

$$A = \frac{S - B}{C - B_S} \times \frac{1000}{W} \times \frac{25}{V} \times 0.02 \ \mu g/g$$

where W is the weight m mg of suspended matter taken in and V is the volume in ml of digest used.
The concentration, R, of particulate mercury in the water sample from

$$R = \frac{S - B}{C - B_S} \times \frac{1}{V} \ \mu g/l$$

when a 500 ml sample of water is filtered.
These calculations assume a linear calibration curve. Linearity must be checked (see Section B9).

B9 Checking the Linearity of the Calibration Curve

The procedure described below must be carried out on at least two independent occasions before application of the method to any samples and regularly thereafter. To do this add aliquots (0.0, 1.0, 2.0, 3.0 and 4.0 ml) of standard mercury solution C (corresponding to 0.00, 0.01, 0.02, 0.03 and 0.04 μg Hg) to a series of 25 ml conical flasks. Carry out Steps B8.1 to B8.8 and A8 to A12 inclusive. Plot the maximum instrument response against μg of mercury. The calibration curve should be linear to at least 0.04 μg.

B10 Sources of Error

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

B10.1 Contamination

(See also Method A, Section A11.1.) Sediments and particulate matter tend to absorb mercury from the atmosphere and analyses should be carried out as soon as practicable.

B10.2 Mercury content of the water used for blanks and standards

It is important that water used in the analysis and for the preparation of the standard mercury solution C is of acceptable quality. This can be checked as described in Method A, Sections A8.1 to A8.12 inclusive.

B10.3 Interfering substances

See Section B3.

B10.4 Calibration standards

See Method A, Section A11.4.

B11 Checking the Accuracy of the Analytical results

See Method A, Section A.12.

C Mercury in Waters and Effluents by Flameless Atomic Fluorescence Spectrophotometer Tentative Method

C1 Performance Characteristics of the Method

(For further information on the determination and definition of performance characteristics see Ref 6.)

C1.1	Substance determined	All forms of mercury (see Section C2).
C1.2	Type of sample	Saline and non-saline waters and effluents.
C1.3	Basis of the method	Oxidation of all forms of mercury in the sample to inorganic mercury, conversion to mercury vapour, concentration in a brominating solution followed by flameless atomic flurorescence spectrophotometry, after addition of a reducing agent.
C1.4	Range of application (a)	There is no fixed upper concentration limit.
C1.5	Calibration curve (a)	Linear without preconcentration to at least 100 µg/l.
C1.6	Within batch standard deviation	

C1.6.1 **Water samples**

Sample type	Mercury concentration (ng/l)	Standard deviation (ng/l)	Degrees of Freedom
Standard (a)	10.0	0.8	9
Oceanic Seawater[8] (a)	2.4	0.4	3
Spiked oceanic Seawaters[8] (a)	17.2	2.9	4
	145.0	5.0	4
Seawater (c)	10.0	1.22	9

C1.6.2 Sludge samples digested by Method A of Ref 23 (b).

Sample	Mean mercury concentration µg/g dry wgt	Standard deviation µg/g dry wgt	Degrees of freedom
BCR144	1.35	0.105	5
BCR145	8.2	0.38	5
BCR146	8.5	0.22	5

C1.7	Limit of detection (a)	0.5 ng/l with 9 degrees of freedom without preconcentration.
C1.7	Limit of detection (b)	0.04 µg/g with 5 degrees of freedom. 2.79 ng/l with 10 degrees of freedom, without preconcentration.
C1.8	Effects of Preconcentration (Steps C8.1 to C8.4)	The effect of preconcentration as given is to lower the values given in C1.5 and C1.7 one hundred fold. Recovery tests indicate 80% recovery at stage C8.3.

C1.9	Bias (a)	See Section C3.
C1.10	Interferences (a)	See Section C3.
C1.11	Time required for analysis (a)	For a batch of 10 samples the pretreatment and total analytical times are approximately 1 and 2 hours respectively.

(a) These data were obtained at Thames Water Authority[9].
(b) These data were obtained at MAFF Fisheries Laboratory, Burnham on Crouch. (BCR stands for Community Bureau of Reference Sample.)
(c) Clyde River Purification Board.

C2 Principle

C2.1 The method described is based on experimental work carried out at the Thames Water Authority.[10,11]

C2.2 It is essential to convert all forms of mercury to inorganic mercury. This is achieved by treating the sample with a brominating solution and an acid. Stannous chloride is added to reduce the excess bromine and to liberate elemental mercury

$$Hg^{2+} + Sn^{2+} \rightarrow Hg^{0} + Sn^{4+}$$

The mercury vapour is transferred by purging with argon gas into a preconcentration trap containing a brominating solution. The mercury in this solution is then determined by flameless atomic fluorescence spectrophotometer.

C3 Interferences

C3.1 No general tests on the effect of other substances on this method have been carried out; from the data in table 1 and method similarity, interferences are deemed to be unlikely. Analysis of 10 μg/l mercury standards containing various amounts of the brominating solution showed that there was no interference from bromate/bromide in the atomic fluorescence state.[10] Also up to 24 mg/l of sulphide does not interfere.[11]

C3.2 Table 2 shows the recovery of mercury from distilled water spiked with various organic mercury compounds using this method. The table also shows the recovery of mercury from various types of water sample spiked with 14.8 μg/l of mercury added as methyl mercuric chloride and allowed to equilibrate for 24 hours. These results were obtained by Thames Water Authority.

Table 2 Recovery of mercury from spiked samples

Type of sample	Organo mercury compound added	Concentration added (μg/Hg/l)	Concentration found * (μg/Hg/l)	Recovery (%)
Distilled water	phenylmercuric chloride	15.1	14.9	99
Distilled water	p-tolymercuric chloride	11.9	11.8	99
Distilled water	thiomersal ($C_2H_5HgSC_6H_4CO_2Na$)	9.7	9.9	102
Distilled water	phenylmercuric acetate	10.0	10.0	100
Distilled water	ethylmercuric chloride	15.0	14.4	96
Distilled water	methylmercuric chloride	14.0	14.2	101
Tap water	methylmercuric chloride	14.8	13.9	94
River water	methylmercuric chloride	14.8	13.6	92
River water	methylmercuric chloride	14.8	14.4	97
River water	methylmercuric chloride	14.8	13.3	90
Sewage effluent	methylmercuric chloride	14.8	14.5	98
Sewage effluent	methylmercuric chloride	14.8	13.9	94
Thames Water Authority data				
With sea water samples recovery is never less than 80% and should be much higher (IMER information).				
Sea Water (stripped)		100 ng/l		91.57
		100 ng/l		92.5
Clyde River Purification Board data				

* mean results obtained from duplicate experiment without preconcentration.

C4 Hazards

C4.1 Mercury fumes are toxic and must be ducted away.

C4.2 Samples and standard solutions containing mercury are toxic and care must be taken handling them. If any of these solutions is swallowed give water to dilute, then milk as a soothing and buffering agent. Do not delay seeking medical advice.

C4.3 The ultraviolet light from mercury lamps is harmful to the eyes. Enclose lamps or wear UV-absorbing goggles. Screen to protect all in the room.

C5 Reagents

All reagents and standard solutions must be stored in glass bottles (see Section C6). Polyethylene must not be used. Analytical reagent grade chemicals are suitable unless otherwise stated.

C5.1 Water

See Method A, Section A5.1.

C5.2 0.28% m/v Potassium bromate/1.0% m/v potassium bromide solution

Heat 2.78±0.01 g of potassium bromate and 10.0±0.1 g of potassium bromide in a furnace of 350±20°C overnight to remove any residual mercury. Then dissolve them in water and dilute with water to 1 litre. Prepare afresh if discoloured.

C5.3 10 M Hydrochloric acid (approximately)

2.5 litres of hydrochloric acid (d_{20} 1.18) are cleaned of mercury by dissolving 2.0±0.1 g of stannous chloride dihydrate in it and bubbling argon gas through the solution at 2.0±0.2 litres/minute for 15±2 minutes. Then add 200±10 mls of 0.28% m/v potassium bromate/1.0% m/v potassium bromide solution to oxidize the stannous chloride. Properly stored this solution keeps indefinitely.

C5.4 Brominating solution for preconcentration

Add 20.0±0.1 ml of 10 M hydrochloric acid and 40.0±0.5 ml of 0.28% m/v potassium bromate/1.0% m/v potassium bromide solution to approximately 700 ml of water and then dilute with water to 1 litre. Prepare freshly before use.

C5.5 50% V/V sulphuric acid

Slowly and carefully with continuous stirring add 50±1 ml of sulphuric acid (d_{20} 1.84) to 50±1 ml of water contained in a beaker partially immersed in cold water.

C5.6 20% m/v stannous chloride dihydrate (for sample reduction)

Dissolve 20.0±0.1 g of stannous chloride dihydrate in 10.0±0.1 ml of hydrochloric acid (d_{20} 1.18). A small particle of metallic tin is added and the solution warmed. After cooling 10.0±0.1 ml of 50% v/v sulphuric acid is added and the solution diluted with water to 100 ml. The solution is then purged with argon at 2.0±0.2 litres/minute for 15±2 minutes to remove any residual mercury. This solution may be kept for one day.

C5.7 2% m/v stannous chloride dihydrate (for atomic fluorescence stage)

Dissolve 2.00±001 g of stannous chloride dihydrate in 8.0±0.1 ml of hydrochloric acid (d_{20} 1.18). A small particle of metallic tin is added and the solution warmed. After cooling add 10.0±0.1 ml of 50% v/v sulphuric acid and dilute with water to 100 ml. Purge the solution with argon at 2.0±0.2 litres/minute for 15±2 minutes to remove any residual mercury. Prepare freshly before use (may be kept overnight at c4°C).

C5.8 Standard mercury solutions

If accurate equipment is available smaller stocks of solutions C5.8.2 and C5.8.3 should be prepared, based on usage.

C5.8.1 ***Solution A*** **1 ml contains 1 mg Hg**

Dissolve 1.354±0.005 g of mercuric chloride in approximately 100 ml of water, add 60±5 ml of nitric acid (d_{20} 1.42) and dilute with water to 1 litre in a calibrated flask. Store in a refrigerator. This solution is stable for a least 1 year.

C5.8.2 ***Solution B*** **1 ml contains 10 μg Hg**

Dilute 10.0±0.1 ml of solution A with water to approximately 600 ml. Add 10.0±0.1 ml of 0.28% m/v potassium bromate/1.0% m/v potassium bromide solution and 10.0+0.1 ml of 10 M hydrochloric acid and dilute with water to 1 litre in a calibrated flask. Prepare freshly before use.

C5.8.3 ***Solution C*** **1 ml contains 100 ng Hg**

Dilute 5.0±0.05 ml of solution B with water to approximately 300 ml. Add 5.0±0.1 ml of 0.28% m/v potassium bromate/1.0% m/v potassium bromide solution and 5.0±0.1 ml of 10 M hydrochloride acid and dilute with water to 500 ml in a calibrated flask.

C5.8.4 If lower concentration standards are required at step C8.8, repeat the C5.8.3 dilution using Solution C to obtain Solution D (1 ml contains 1ng Hg).

C5.9 Silica gel — non indicating

C5.10 Glassware cleaning solution – see Section C6.3.

C6 Apparatus

C6.1 An atomic fluorescence spectrophotometer

with ancillary equipment necessary to determine mercury by the flameless technique. This equipment can readily be built, see references 12–15.

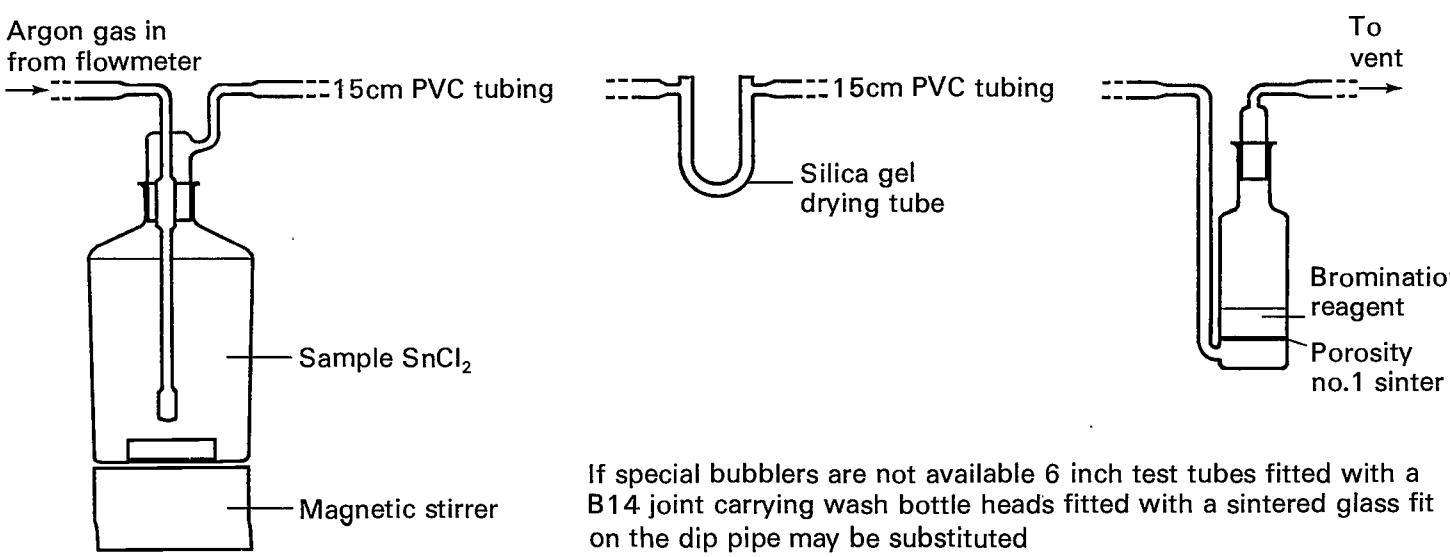
C6.1.1 A flameless atomic absorption spectrophotometer

without the hollow cathode lamp, with a powerful mercury discharge tube lamp mounted parallel with the absorption tube has proved satisfactory. Check tube position for maximum fluorescent signal.

C6.2 Special apparatus for the preconcentration of mercury

The apparatus used is shown in Figure 3. 500 ml of the brominated sample is treated with stannous chloride and purged with argon at 2.0±0.2 litres/minute. The argon gas stream containing the mercury vapour is dried by passing through silica gel and then the mercury vapour is absorbed in 5.0±0.1 ml of dilute brominating solution, (thus giving a concentration factor of 100). The silica gel trap is necessary to prevent any stannous chloride getting into the brominating solution.

FIG 3 MERCURY PRECONCENTRATION APPARATUS



If special bubblers are not available 6 inch test tubes fitted with a B14 joint carrying wash bottle heads fitted with a sintered glass fit on the dip pipe may be substituted

C6.3 Glassware

Cleanliness is essential for this determination. Apparatus must be reserved solely for mercury determinations. Clean all glassware, both before and after use, by filling with a solution containing 0.1 M hydrochloric acid (1% v/v of reagent C5.3) and 0.3% m/v potassium bromate/0.1% m/v potassium bromide (10% v/v of reagent C5.2). If convenient, keep all glassware used soaking in this brominating solution. Immediately before use rinse the glassware thoroughly with water.

If special bottles are not available 6 inch test tubes fitted with a B14 joint carrying wash bottle heads fitted with a sintered glass fit on the dip pipe may be substituted.

C7 Sample Collection and Preservation

Users of the method suggest that at least 2 litres of sample be collected.

Samples must be collected in clean glass stoppered bottles (see Section C6.3) whose quality (freedom from mercury) has been proved by carrying out blank determination. To each 1 litre of sample collected immediately add 10.0±0.1 ml of 0.28% m/v potassium bromate/1.0 m/v potassium bromide solution and 10.0±0.1 ml of 10 M hydrochloric acid. Stopper the bottle and allow at least 45 minutes reaction time to ensure complete breakdown of organo mercury compounds before proceeding to Section C8.

If sufficient free bromine remains, the sample may be stored for at least two days if protected from any possible contamination by mercury or organic materials.

If the samples contain much organic matter it may require more reagent than is given above. If this amount is excessive, a preliminary nitrate acid digestion (see Ref 23) may be advisable.

C8 Analytical Procedure

READ SECTION C4 ON HAZARDS BEFORE STARTING THIS PROCEDURE

If the preconcentration step is omitted, use an appropriate size of sample and connect the Drechsel Bottle directly to the instrument instead of to the trap at C8.2. Omit steps C8.3 and C8.4. Treat standards and blanks in the same manner.

Step	Procedure	Notes
	Analysis of samples	
C8.1	Add 500±5 ml of the brominated sample (see Section C7) to the Drechsel bottle as shown in Figure 3. Add 2.5±0.5 ml of 20% m/v stannous chloride dihydrate. Replace the Drechsel head.	
C8.2	Connect the Drechsel bottle to the preconcentration trap. Place 5.0±0.1 ml of the brominating solution for preconcentration into the trap as shown in figure 3. Stir the contents of the Drechsel bottle rapidly for about 1 minute (note a).	(a) Ensure that all free bromine, which might interfere with transfer of mercury vapour, has been reduced.
C8.3	Bubble argon through the apparatus at 2.0±0.2 litres/minute for 10±1 minutes (note b). Pour off the brominating solution into a glass flask and retain.	(b) Prior to pouring off the brominating solution, allow it to work through the Diffuser to remove any traces of mercury absorbed in the underside of the sinter. Recovery is always about 80%.
C8.4	To prevent cross contamination, before proceeding with the next sample, wash the sinter twice with 5.0+0.1 ml of fresh brominating solution. Be sure to wash through the sintered glass frit. Discard unless needed for Section C10.	(c) For other ranges see C10.

C8.5 Set up the atomic fluorescence spectrophotometer and associated equipment according to the manufacturer instructions for determining mercury by the flameless technique (note d). Adjust for optimum conditions. The fluorescence is measured at 253.7 nm.

(d) The biggest source of error found with this method is instrument contamination. The apparatus including all tubing needs to be scrupulously clean. Before analysing any samples repeatedly analyse blank samples until a consistent value of less than 2 ng/l is obtained using the procedure given in step C8.6 and water prepared as in step C8.7. Prior to the analysis of a batch of samples always check the calibration of the instrument using standards (see step C8.8) and if necessary recheck the blank until satisfactory.

C8.6 Set the argon flow at 1.0±0.1 litres/minute. Add 1.0±0.1 ml of the brominating solution from step C8.3 and 1.0±0.1 ml 2% m/v stannous chloride (C5.7) to the reaction vessel and measure the instrument response, S. (Note c.)

Blank determination

C8.7 A blank must be included with each batch of determinations. Carry out steps C7 and C8.1 to C8.6 using either water or an aliquot of the sample which has already been stripped of its mercury (by carrying out steps C7 and C8.1 to C8.4). Let the instrument response be B (note e).

(e) The blank should be less than 2 ng Hg/l.

Calibration standards

C8.8 Duplicate calibration standards should be run with each batch of samples. The concentration of mercury in the standard used will depend on the mercury concentration expected in the samples. Suitable aliquots (yml) of standard mercury solution C are added to 500 ml of water or 500 ml of sample which has been stripped of mercury (by carrying out steps C7 and C8.1 to C8.3) and steps C7 and C8.1 to C8.4 carried out. The measurement is made as in steps C8.1 to C8.6. Let the mean instrument response be C (note f).

(f) y ml of solution C will give 0.2y µg/l mercury in the calibration standards. For very low concentrations use Solution D, then y ml will give 2y ng Hg/l.

Calculation of result

C8.9 The concentration, A ng/l, of mercury in the sample is calculated from:

$$\frac{y\,(S - B)}{C - B}\ \text{ng/l}$$

(Note g)

(g) This calculation assumes a linear calibration curve Linearity must be checked (see Section C9).

C9 Checking the Linearity of the Calibration Curve

The procedure given below must be carried out on two independent occasions before application of the method to any samples and regularly thereafter. Suitable aliquots (at least 5) of standard mercury solution C, chosen to cover the expected mercury concentrations in samples, are added to 500 ml aliquots of water (or a stripped sample as described in step C8.8) and the procedure described in C8.8 is carried out. Plot the instrument response against ng/l mercury. The calibration curve should be linear over a wide range of mercury concentrations.

C10 Changing the Concentration Range of the Methods

Somewhat lower concentrations might be determinable by using a larger initial sample and either correcting the calculation in step C8.9 accordingly, or treating the standard sample in like manner.

If the concentration is too high, make up the combined sample plus double washings at step C8.4 to 25 ml with water and take a suitable aliquot. Either correct the calculation in step C8.9 accordingly or treat the standard sample in like manner. Alternatively use the initial brominated sample from step C7 in step C8.6, and compare with standards treated in like manner.

C11 Sources of Error

See Method A, Section A.11.

C.12 Checking the Accuracy of Analytical Results

See Method A, Section A.12.

D Mercury in Soils, Sediments and Related Materials by Flameless Atomic Absorption Spectrophotometry Tenative Method

D1 Performance Characteristics of the Method

(For further information on the determination and definition of performance characteristics see Ref 6).
Note: Throughout this method mercury is expressed as the element (Hg)

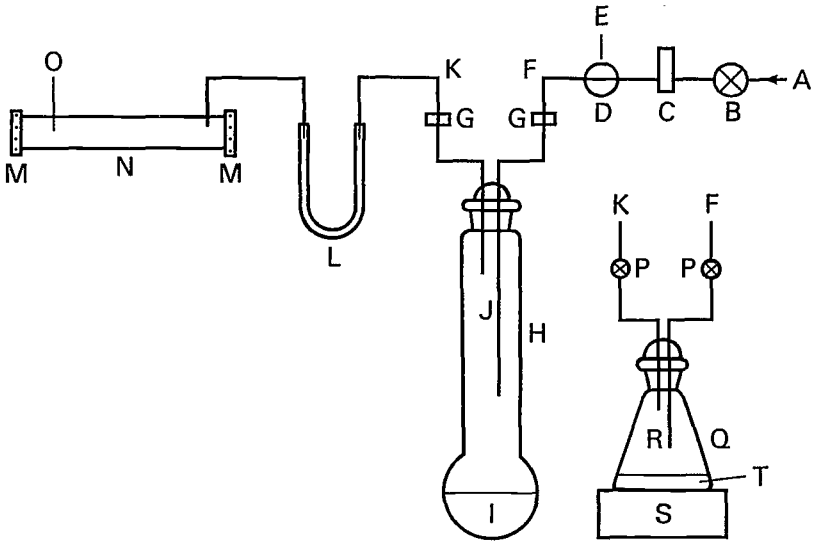
D1.1	Substance determined	All forms of mercury (see Section D2).
D1.2	Type of sample	Soils, sediments and related materials.
D1.3	Basis of the method	Digestion in acid solution and oxidation with permanganate to convert mercury to inorganic mercury followed by flameless atomic absorption spectrophotometry
D1.4	Range of application (a)	0.01 to 0.50 mg/kg in the dry sample.
D1.5	Calibration curve (a)	Linear up to 0.3 mg/kg with slight curvature from 0.3 to 0.5 mg/kg.
D1.6	Within batch standard deviation (a)	

Sample type	Mercury concentration (mg/kg)	Standard deviation (mg/kg)	Degrees of Freedom
Soil 1	0.073	0.005	9
Soil 2	0.134	0.008	9
Soil 3	0.184	0.012	9
Peat	0.082	0.004	9

D1.7	Limit of detection (a)	0.02 mg/kg with 9 Degrees of Freedom.
D1.8	Sensitivity (a)	0.10 mg/kg is equivalent to an absorbance of approximately 0.17.
D1.9	Bias	Not known.
D1.10	Interference	See Section D.3
D1.11	Time required for analysis (a)	For 16 samples the total analytical and operator times are 14 and 12 hours respectively, excluding standing overnight.

(a) These data were obtained at the Macaulay Institute for Soil Research, Aberdeen[16] using this method and a single beam atomic absorption spectrophotometer.

FIG 4 APPARATUS FOR THE DETERMINATION OF MERCURY BY COLD-VAPOUR ATOMIC ABSORPTION



A Compressed nitrogen or air line 105 KN m^{-2} (15lb/in^2)
B Needle valve
C Flow meter
D Two-way tap
E Vent
F and K Connection points
G Silicone rubber tubing with Mohr spring-clips to H
H Kjeldahl flask
I Sample
J Plain glass tubes, o.d. 0.5cm
L Empty U-tube
N 25cm Pyrex absorption tube o.d. 19cm with removable fused-silica end windows
M O-ring seals
O Exhaust
Q Alternative conical flask
R Plain glass tubes
P Nylon stop-cocks
T Sample
S Magnetic stirrer

D2 Principle

D2.1 The method is based on experimental work carried out by the Macaulay Institute for Soil Research, Aberdeen[16].

D2.2 It is essential to convert all forms of mercury into inorganic mercury. The objective of the method is to ensure that all the mercury, organically bound or elemental, is brought into solution in a form readily released as atomic vapour by reduction and aeration. A digestion and wet oxidation procedure using a nitric and sulphuric acid mixture followed by potassium permanganate treatment was found to be satisfactory. The method is similar to that devised by Iskander et al (1972).[17]

D2.3 The inorganic mercury is determined by the cold vapour atomic absorption spectrometric technique. Acid stannous chloride is added to the sample to produce elemental mercury:

$$Hg^{2+} + Sn^{2+} \rightarrow Hg^{0} + Sn^{4+}$$

The mercury vapour is carried by a stream of air into a gas cuvette placed in the path of the radiation from a mercury hollow cathode lamp and the absorption of this radiation at 253.7 nm by the atomic mercury vapour is measured (see Figure 4).

D3 Interferences

See Table 3 and references therein. Molecular absorption and light scattering interference effects were found to be insignificant for solutions of soils and rocks.

Table 3

Substance added	Amount added per 0.1 μg Hg	Interference effect
Aluminium chloride	0.5 g	not over 5% variation
Calcium carbonate	0.5 g	not over 5% variation
Calcium chloride	0.5 g	not over 5% variation
Magnesium oxide	0.5 g	not over 5% variation
Calcium phosphate	0.5 g	depression but under 10%
Copper Sulphate	250 μg Cu	not over 5% variation
Silver Nitrate	100 μg Ag	not over 5% variation
Sodium sulphide	1 mg S	not over 5% variation
Selenous acid	200 μg Se	depression of 90% (actually 400 μg Se + 0.2 μg Hg) etc
Selenous acid	20 μg Se	depression of 8%
Selenous acid	2 μg Se	not over 5% variation
Iodine	100 μg I	depression of 10%
Gold, Platinum, Palladium		depress, see ref 16
Iron	over 20% of sample	depresses, see ref 18 (lower amounts do not significantly depress)

D4 Hazards

D4.1 The exhaust fumes from the atomic absorption spectrometer are toxic and must be ducted away. Samples and standard solution (Section D5.8) containing mercury are toxic and care must be taken when handling them. If any of these solutions is swallowed give water to dilute and milk as a soothing buffering agent. Do not delay in seeking medical advice.

D4.2 The reagent described in Section D5.6 should be regarded as a special hazard. Hydroxy-ammonium chloride is a skin and eye irritant and continued contact may cause dermatitis. Goggles and gloves must be worn when handling this material and any spillage should be washed away with copious quantities of water.

D5 Reagents

All reagents and standard solutions should be stored in glass bottles (see Section D 6.3). **Polyethylene must *not* be used**. Analytical reagent grade chemicals are suitable unless otherwise specified.

D5.1 Sulphuric acid (d_{20} 1.84)

D5.3 Nitric acid (d_{20} 1.42), distilled

D5.4 50% V/V distilled Nitric acid/Sulphuric acid mixture

Add slowly and cautiously 250±5 ml of sulphuric acid (d_{20} 1.84) to 250±5 ml of distilled nitric acid (d_{20} 1.42). This should be carried out in a fume cupboard and protective equipment should be worn. This reagent should be made up as required and not stored.

D5.5 6% m/V Potassium permanganate

Dissolve with stirring 60±1 g potassium permanganate in hot water and dilute with water to 1000±25 ml. Filter through a glass fibre filter to remove any manganese dioxide. This reagent must be kept stoppered at all times when not in use because it can absorb mercury from the laboratory atmosphere.

D5.6 20% m/V Hydroxy-ammonium chloride

This reagent is hazardous (see Section D4). Dissolve 20.0±0.5 g of hydroxy-ammonium chloride in water and dilute with water to 100±2 ml.

D5.7 20% m/V Stannous chloride dihydrate

Dissolve 20.0±0.5 g of stannous chloride dihydrate in 6 M hydrochloric acid and dilute with 6 M hydrochloric acid to 100±2 ml. If mercury is present in the solution bubble oil-free air or nitrogen through for at least 10 minutes to ensure that the solution is mercury free.

D5.8 Standard mercury solutions

These solutions are hazardous (see Section D4).

D5.8.1 ***Solution A*** **1 ml contains 1 mg Hg**
Weigh 0.1354±0.0005 g of mercuric chloride and dissolve in approximately 70 ml of 0.5 M sulphuric acid. Dilute with further 0.5 M sulphuric acid to 100 ml in a calibrated flask. Store in a refrigerator. This solution is stable for at least 1 year.

D5.8.2 ***Solution B*** **1 ml contains 10 μg Hg**
Dilute 5.00±0.05 ml of Solution A with 0.5 M sulphuric acid to 500 ml in a calibrated flask. Store in a refrigerator. This solution is stable for several months.

D5.8.3 ***Solution C*** **1 ml contains 0.1 μg Hg**
Dilute 5.00±0.05 ml of Solution B with 0.5 M sulphuric acid to 500 ml in a calibrated flask. Prepare freshly when required.

D5.9 An oil-free air or nitrogen supply

D6 Apparatus

See Figure 4.

D6.1 An atomic absorption spectrophotometer

with a mercury hollow cathode lamp. A chart recorder having a fast response time (0.5 s) is now the most desirable form of read out. Scale expansion should be used to ensure that adequate recorder response is achieved with the highest calibration standard used.

D6.2 Special apparatus for aspirating samples

A diagram of the apparatus is shown in Figure 4. Bubbling techniques have two disadvantages with digested soils. Firstly, frothing can occur and secondly, it is necessary to insert a drier containing magnesium perchlorate, calcium chloride or silica gel to remove aqueous spray and vapour. The use of such driers has been found to give rise to variable memory effects both positive and negative. For these reasons, the bubbling technique was replaced by an agitation procedure in which the mercury in the reduced sample solution is partitioned between a fixed volume of air and the liquid phase in a closed vessel by hand-shaking. The mercury-laden air is then blown by air at a flow rate of 3±0.2 litres per minute directly, without drying, through the absorption cell for the atomic absorption measurement.

D6.3 Glassware

Cleanliness is essential for this determination. If possible apparatus should be reserved solely for mercury determinations: all residual mercury from previous determinations must be removed. Glassware is washed in tap-water, followed by 6 M hydrochloric acid, 8 M nitric acid and several rinses in glass-distilled water. Ground-glass stoppered, long-necked Kjeldahl flasks are rinsed in tap-water, brushed clean using a liquid detergent, then rinsed thoroughly in tap-water before being washed with acid and distilled water as above. Kjeldahl flasks in regular use are soaked once a week, or whenever stains develop, in a solution of laboratory detergent, rinsed in tap-water and washed in acid and distilled water as above. Cleaned glassware is then covered to protect it from the atmosphere.

D7 Sample Collection and Preparation

Soils and sediments should be collected and prepared as described in reference 19. Air dried and sieved soils and sediments should then be finely ground to pass 150 μm) using an agate ball mill. Samples should be kept in a mercury free area and analysed as soon as possible, as mercury pick up can occur rapidly.

Step	Procedure	Notes
	Analysis of Sample	
D8.1	Weigh accurately 1.00±0.05 g (on a dry weight basis, see Ref 20) into a 100-ml Kjeldahl flask (note a). Let the dry weight be Wg.	(a) The weight of sample taken depends upon the expected mercury content and amount of oxidizable matter. It is generaly 0.5–2.0 g for soils whereas for peats, 0.5 g is the maximum normally encountered.
D8.2	Add slowly and carefully with swirling 10.0±0.5 ml of 50% V/V distilled nitric/sulphuric acid.	
D8.3	Transfer to a water bath at 60±20°C. Leave to digest in the flask (covered with a small beaker) for 2.0±1.0 h swirling occasionally, only the bulb of the flask being immersed so that its long neck acts as an air condenser.	
D8.4	Remove the flask, cool and add 20±0.5 ml of distilled water. Cool further preferably by placing in an ice bath. Slowly add 5.0±0.1 ml of 6% m/V potassium permanganate. Cool. Slowly add further 5.0±0.1 ml aliquots of 6% m/V potassium permanganate round the neck of the flask to wash any solid particles into the solution. Cool. Ensure that excess potassium permanganate is always present by adding further 5.0±0.1 ml aliquots of 6% m/V potassium permanganate as required to keep the solution deeply coloured for at least 1 h (note b). Note the total amount of potassium permanganate which has been added.	(b) Volatilization of mercury can occur if the liquid is not kept cold – hence the slow separate additions of permanganate while the flask is kept cold. (c) If the $KMnO_4$ has been completely reduced add a further measured amount to restore the purple colour and record the amounts added.
D8.5	Remove the flask and allow to stand, whilst glass-stoppered, at ambient temperature overnight or for at least 15 h (notes c and d).	(d) A batch of samples may be processed together to this step but each sample must be taken separately through steps D8.6 to D8.10 before proceeding to the next sample.
D8.6	Add very slowly 2.0±0.1 ml of 20% m/V hydroxyammonium chloride (note e) with gentle swirling. Repeat with 2.0 ml aliquots of hydroxyammonium chloride until the brown hydrated manganese oxides and excess potassium permanganate are reduced and the solution has decolorized (note f).	(e) Hydroxyammonium chloride must be used. The sulphate is not suitable as chloride must also be present to prevent losses. (f) There is usually a residue of insoluble material.
D8.7	Allow the unstoppered flask to stand at ambient temperature for 1 h to allow the evolved gases to be liberated (notes g and h).	(g) No loss of mercury is observed at this stage.
D8.8	The apparatus is cleaned before use and between samples by attaching the Kjeldahl flask, containing 10 to 20 ml water, to the air train. The clips are attached and the flask shaken manually. After repeating with a fresh aliquot of distilled water the clips are removed, the two-way tap is opened and air is passed at 10±1 litres/minute through the flask and measuring system until no absorption is obtained using the instrument as set up under D8.9. The air flow is then reduced to 3±0.2 litres/minute, the two-way tap is set to vent, and the clips are replaced.	(h) When samples contain unusually large amounts of mercury, a suitable aliquot of the digest can be taken for analysis at this stage. The aliquot must then be diluted with appropriate volumes of the reagents D5.4, D5.5, D5.6 and water to make up to an equivalent volume of digest before proceeding to step D8.9.

D8.9 Set up the atomic absorption spectrophotometer and related apparatus ready to carry out the determinations. Add 5.0±0.1 ml of 20% m/V stannous chloride dihydrate in 6 M hydrochloric acid. Fit the flask to the apparatus immediately to prevent loss of mercury. Agitate for 2±0.5 min, remove the clips and blow air through at 3±0.2 l/min. The absorption is measured at 253.7 nm and maximum instrument response S (eg peak height) recorded with a pen recorder and chart speed of 2.5 mm/min.

If the signal is too high take a smaller weight of sample (Step D8.1) and repeat the determination. Make an appropriate allowance in the calculation of the result. Make use of the partition equilibrium effect[16] to indicate a suitable weight of sample to take.

D8.10 Continue blowing air until the instrument response returns to the baseline.

Blank Determination

D8.11 A blank must be included with each batch of determinations. Place a 100-ml Kjeldahl flask in an ice bath.

D8.12 Carry out steps D8.2 to D8.10 inclusive (note i). Let the maximum instrument response be B.

(i) If additional potassium permanganate was added to a sample during steps D8.4 and D8.5 an additional blank must be run with an equivalent amount of potassium permanganate present.

Calibration Standards

D8.13 Duplicate calibration standards must be included with each batch of determinations. Add 2.00 ml of standard mercury *solution* D into each of two 100 ml Kjeldahl flasks.

D8.14 Carry out steps D8.2 to D8.10 inclusive. Let the maximum instrument responses be C_1 and C_2. If C_1 and C_2 are in satisfactory agreement calculate the mean C.

calculation of results

D8.15 Calculate the concentration, A, of mercury in the original sample (dry weight basis) from

$$A = \frac{(S - B)}{C - B} \times \frac{0.2}{W} \text{ mg/kg}$$

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

This calculation assumes a linear calibration curve. Linearity must be checked (See Section D9).

D9 Checking the Linearity of the Calibration Curve

This must be carried out on at least two independent occasions before application of the method to any samples and regularly thereafter. Pipette into a series of 100-ml Kjeldahl flasks 0.00, 0.50, 1.00, 2.00, 3.00 and 5.00 ml of Standard solution D5.8.3. The flasks contain 0.00, 0.05, 0.1, 0.2, 0.3 and 0.5 µg mercury respectively. Carry out the procedure given in steps D8.2 to D8.10 inclusive. Plot the maximum instrument response (eg peak height) against ug mercury. The calibration curve should be linear to 0.5 µg mercury.

D10 Sources of Error

See Method A, Section A11.

D11 Checking the Accuracy of Results

See Method A, Section A12.

Estimation of the Accuracy Attainable by Various Methods

The methods given in both booklets are capable of permutation and combination. For advice on procedures for testing out a method more thoroughly than just running a standard or stable sample and plotting a quality control chart, see the 1978 booklet(24) section on Estimation of the Accuracy of Analytical Results.

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Address for Correspondence

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