Mercury in Waters, Effluents and Sludges by Flameless Atomic Absorption Spectrophotometry 1978

Methods for the Examination of Waters and Associated Materials

London Her Majesty's Stationery Office £1 net

Mercury in Waters, Effluents and Sludges

by Flameless Atomic Absorption Spectrophotometry (1978 version)

Two Methods, both Tentative

Methods for the Examination of Waters and Associated Materials

This booklet contains two methods: the first (A) for non-saline waters, effluents and sludges; the second (B) for saline waters; both methods are tentative. Not quite all forms of organomercury are determined in all types of sample at all ranges (see Sections A2 and B2). For the few mercury compounds which might not be determinable by these methods, it is suggested that methods for the specific compound be used.

Contents

London Her Majesty's Stationery Office

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. Where the Committee has 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 or goggles, removal of toxic fumes and wastes, containment in the event of breakages, 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 than to assume that no hazard exists until proved otherwise.

First published 1978

ISBN 0 11 751326 1

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

Method A Mercury in Non-saline Waters, Effluents and Sludges by Flameless Atomic Absorption Spectrophotometry

Tentative Method (1978 version)

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

A1 Performance Characteristics of the Method

(For further information on the determination and definition of performance characteristics see another publication in this series.)

A1.1	Substance determined	All forms of mercury (See Section A2).
A1.2	Types of sample	Non-saline waters, sewages, effluents, sludges and sediments.
A1.3	Basis of method	Digestion and oxidation of sample to inorganic mercury followed by flameless atomic absorption spectrophotometry.
A1.4	Range of application (a)	Up to 2.0 μg/l for liquid samples. Up to 2.0 μg/g for solid samples (b) (See Section A11).
A1.5	Calibration curve (a)	Linear to 20 μg/l for liquid samples. Linear to 20 μg/g for solid samples (b).
A1.6	Within batch standard deviation (a) for liquid samples	Mercury concentration (μg/l) / Standard deviation (μg/l): 0.0 / 0.025 (c) 0.2 / 0.022 (c) 2.0 / 0.024 (c) 0.0 / 0.078 (d) 0.2 / 0.032 (d) 2.0 / 0.104 (d) (All with 9 degrees of freedom)
	for solid samples	Not known.
A1.7	Limit of detection (a)	0.1 to 0.2 μg/l (with 9 degrees of freedom) for liquid samples depending on their nature. Not known for solid samples.
A1.8	Sensitivity (a)	10 μg/l for liquid samples and 10 μg/g for solid samples (b) are equivalent to an absorbance of approximately 0.3.
A1.9	Bias	Not known.
A1.10	Interferences	See Section A3.
A1.11	Time required for analysis (a)	For 10 liquid samples the total analytical and operator times are approximately 36 and 4 hours respectively. For 10 solid samples the times are approximately 72 and 7 hours respectively.

(a) These data were obtained at Water Research Centre (Stevenage Laboratory)[1] using this method and a single beam atomic absorption spectrophotometer and the open circuit technique.
(b) For a sample size of 0.1 g.
(c) Distilled water spiked with the stated mercury concentration.
(d) Sewage effluent spiked with the stated mercury concentration.

A2 Principle

A2.1 The method described is based on experimental work carried out by the Water Research Centre (Stevenage Laboratory)[1].

A2.2 It is essential to convert all forms of mercury to inorganic mercury. The main method for liquid samples (Section A8), which is based on a prolonged oxidation with potassium permanganate which converts methyl mercury to inorganic mercury, is a modification of the Omang procedure[2]. An alternative method with a shorter analytical time, which is satisfactory for potable waters and for some raw waters but is unsatisfactory for sewages and sewage effluents, is mentioned in Section A14.1. Solid samples require a more prolonged and vigorous oxidation to bring the mercury completely into solution in the inorganic form. A modification of the Uthé digestion procedure[3] is given for such samples (Section A9). An alternative reference method for solid samples is mentioned in Section A14.2.

A2.3 The inorganic mercury is determined by the flameless atomic absorption spectrophotometric technique using a method similar to that described by Osland[4]. Acid stannous chloride is added to the sample to produce elemental mercury:

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

The mercury vapour is carried by a stream of air or nitrogen 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 mercury vapour is measured (see Figure 1).

A3 Interferences

There is no detailed information concerning the effect of interfering substances on the method described. Many substances are reported in the literature as causing interference with the flameless atomic absorption spectrophotometric determination of mercury. However, it is apparent that many of these interference effects are removed by the preliminary digestion/oxidation procedure. The most significant group of interfering substances is volatile organic compounds which absorb radiation in the ultra-violet[5]. Most of these are removed by the pretreatment procedure and the effect of any that remain can be overcome by pre-aeration as described in step A8.7 note (e). Bromide and iodide ions may cause interference[6]. Substances which are reduced to the elemental state by stannous chloride and then form a stable compound with mercury may cause interference; eg selenium, gold, palladium and platinum[6]. The effects of various anions, including bromide and iodide, on a similar experimental procedure have been investigated[7] and it is thought that they are not likely to be important in the method described.

A4 Hazards

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

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. Goggles and gloves must be worn when handling this material and any spillage should be washed away with copious quantities of water.

Samples and standard solutions (Section A5.8) 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 and buffering agent. Do not delay seeking medical advice.

A5 Reagents

All reagents and standard solutions should be stored in glass bottles (see Section A6.3). Polyethylene must *not* be used. Analytical reagent grade chemicals are suitable unless otherwise specified.

A5.1 **Water**
The water used for blank determinations and for preparing standard and reagent solutions should have a mercury content that is negligible compared with the smallest concentration to be determined in the samples (see Section A12.2). Distilled water is suitable.

A5.2 **Sulphuric acid** (d_{20} 1.84)

A5.3 **50% V/V Sulphuric acid**
Add slowly and cautiously with continuous stirring 500 ± 10 ml of sulphuric acid (d_{20} 1.84) to 500 ± 10 ml of water in a 2-litre beaker immersed in cold water.

A5.4 **5% m/V Potassium permanganate**
Dissolve with stirring 50 ± 1 g of potassium permanganate in water and dilute with water to 1 litre.

A5.5 **12% m/V Hydroxyammonium chloride/12% m/V sodium chloride solution**
This reagent is hazardous (see Section A4). Dissolve 12.0 ± 0.5 g of hydroxyammonium chloride and 12.0 ± 0.5 g of sodium chloride in water and dilute with water to 100 ml.

A5.6 **2% m/V Stannous chloride dihydrate**
Dissolve 20.0 ± 0.5 g of stannous chloride dihydrate in a mixture of 20 ± 1 ml of hydrochloric acid (d_{20} 1.18) and approximately 20 ml water and dilute with water to approximately 100 ml. Transfer to a 1-litre cylinder, add cautiously 5.0 ± 0.5 ml of sulphuric acid (d_{20} 1.84) and dilute with water to 1 litre. Bubble oil-free air or nitrogen through the solution for at least 10 minutes to ensure that the solution is mercury free.

A5.7 **Nitric acid** (d_{20} 1.42)

A5.8 **Standard mercury solutions**
These solutions are hazardous (see Section A4).

A5.8.1 *Solution A* 1 ml contains 1 mg Hg.
Weigh 0.1354 ± 0.0005 g of mercuric chloride and dissolve in approximately 70 ml of water, add 6.0 ± 0.5 ml of nitric acid (d_{20} 1.42) and dilute with water to 100 ml in a calibrated flask. Store in a refrigerator. This solution is stable for at least 1 year.

A5.8.2 *Solution B* 1 ml contains 10 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. Store in a refrigerator. This solution is stable for several months.

A5.8.3 *Solution C* 1 ml contains 1 μg Hg.
Dilute 10.00 ± 0.05 ml of *solution B* with water to approximately 80 ml, add 5.0 ± 0.5 ml nitric acid (d_{20} 1.42) and dilute with water to 100 ml in a calibrated flask. Prepare freshly when required.

A5.8.4 *Solution D* 1 ml contains 0.1 μg Hg.
Dilute 5.00 ± 0.05 ml of *solution B* 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.

A5.9 **Oil-free air or nitrogen**

A6 Apparatus

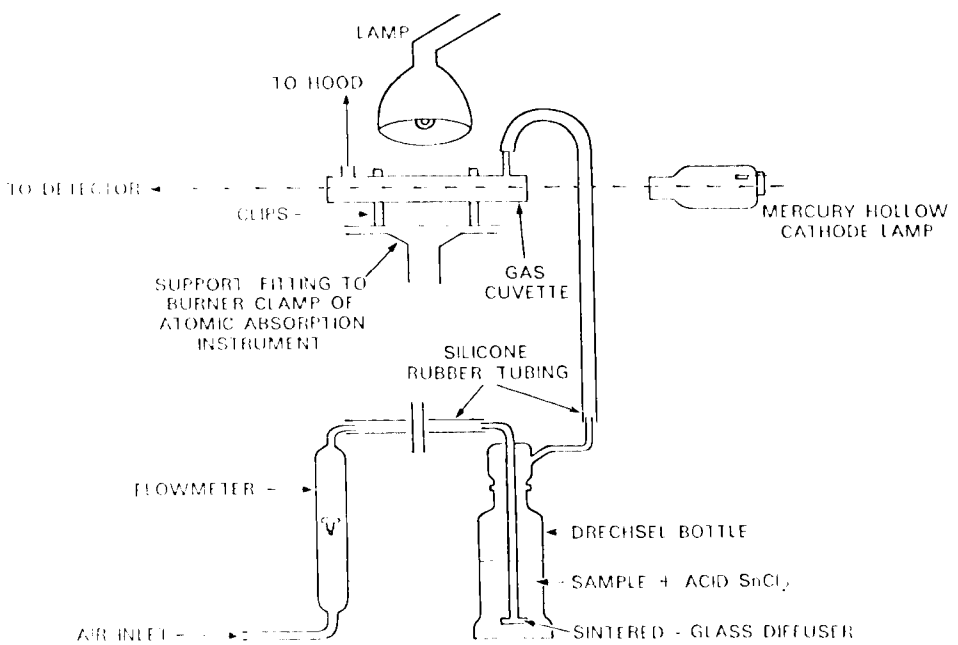

FIG. 1 DETAIL OF SAMPLE VAPORIZER

A6.1 An atomic absorption spectrophotometer with a mercury hollow cathode lamp. A chart recorder having a fast response time (0.5 s) is 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.

A6.2 **Special apparatus for aspirating samples**

A diagram of the apparatus is shown in Figure 1. A stream of oil-free air or nitrogen (see Section A12.1) at a steady flow rate of approximately 2 l/min is bubbled through the treated sample mixture in a 125-ml Drechsel bottle. This carries the mercury vapour to a gas cuvette of 100 mm length, 25 mm internal diameter and with fused silica end windows which is placed in the path of the radiation from the mercury hollow cathode lamp. Heat from a 60W electric light bulb placed near the cuvette prevents condensation of the vapour. The sintered glass diffuser (porosity 1) in the Drechsel bottle may become blocked with tin salts and it is essential that it is cleaned at frequent intervals by soaking in hydrochloric acid (d_{20} 1.18).

Alternatively, a closed circuit technique may be used in which the air is recirculated by means of a peristaltic pump through the Drechsel bottle and the gas cuvette.

A6.3 **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. Clean all glassware by filling with or soaking in water containing 1% sulphuric acid and 0.05% m/V potassium permanganate overnight. Rinse thoroughly with 50% V/V hydrochloric acid and then with water, then cover the clean glassware to protect it from the atmosphere.

A7 Sample Collection and Preservation

A7.1 Samples must preferably be collected in all glass containers and analysed as soon as practical. It is advisable to have at least 300 ml of liquid samples (see step A8.7 note c), or 25g of solid sample (see step A9.8 note j).

A7.2 **Liquid samples**

Liquid samples must be collected in glass stoppered bottles whose quality (freedom from mercury) has been proven by carrying out blank determinations. The bottles must have been cleaned with acid permanganate (see Section A6.3) and then thoroughly rinsed with water. Acidic strongly oxidising conditions must be established in the sample immediately after taking it and maintained until the analysis is started[8].

Add to the sample bottle sufficient nitric acid (d_{20} 1.42) to ensure an acidity equivalent to about 0.1 N when the sample has been collected and sufficient 5% m/V potassium dichromate (A5.5) to maintain an excess until the analysis of the sample is started. 5 ± 1 ml of each reagent per litre of sample will usually be sufficient, but with some samples the volumes of these reagents may need to be determined by a previous trial. If necessary add more potassium dichromate if the sample becomes reduced (green) before the analysis can be started.

Samples should be collected directly into the bottle, but may be transferred to it *immediately* after collection. In the latter case precautions must be taken to ensure that the primary collection apparatus does not cause contamination of the sample.

Note the volumes of nitric acid (d_{20} 1.42) and 5% m/V potassium dichromate (A5.5) used.

A7.3 **Solid samples**

Solid samples must be collected in a clean glass bottle with a closure. These samples should be kept as cool as possible and preferably refrigerated.

Step	Experimental Procedure	Notes
	Analysis of sample	
A8.1	Add 100 ± 1 ml of the sample to a 250-ml conical flask (note a).	(a) See Section A11 for concentration range of the method.
A8.2	Add 5.0 ± 0.1 ml of 50% V/V sulphuric acid followed by 5.0 ± 0.1 ml of 5% m/V potassium permanganate and mix by swirling.	
A8.3	Cover the neck of the flask with an inverted beaker and place it on a thermostatically controlled water bath for at least 7 to 8 h and maintain the liquid at a temperature of 80 ± 2°C. Ensure that excess potassium permanganate is always present by adding further 5.0 ± 0.1 ml aliquots of 5% m/V potassium permanganate as required to keep the solution deeply coloured. Note the total amount of potassium permanganate which has been added.	
A8.4	Remove the flask. Allow to cool to ambient temperature by standing overnight.	
A8.5	Add 1.00 ± 0.05 ml of hydroxyammonium chloride/ sodium chloride reagent and mix by swirling. Stand for at least 5 min until the solution has decolorized and all the suspended matter has dissolved. Transfer to a 250-ml measuring cylinder and dilute with water to 150 ml. Quantitatively transfer back to the original 250-ml conical flask (note b).	(b) The batch of samples may be processed to this step but each sample must be treated as in steps A8.6, A8.7 and A8.8 before proceeding to the next sample.
A8.6	Set up the atomic absorption spectrophotometer and related apparatus ready to carry out the determination. Place 75 ± 1 ml of this solution in a 125-ml Drechsel bottle. Add 10.0 ± 0.5 ml of 2% m/V stannous chloride. Replace the Drechsel bottle head immediately.	
A8.7	Bubble air or nitrogen through the solution (see Section A6.2) and measure the maximum instrument response, S (eg peak height), at 253.7 nm (notes c, d and e).	(c) If foaming occurs discard and start again from step A8.1 as digestion/oxidation is incomplete. (d) If the instrument response is too high take a smaller aliquot from the conical flask (step A8.5) and dilute to 75 ml. Proceed from step A8.6 and make an appropriate allowance in the calculation of the result.
A8.8	Continue bubbling air or nitrogen until the instrument response returns to the baseline.	(e) If the shape of the peak deviates noticeably from that obtained with the standard this indicates possible interference from volatile organic compounds. These may be removed by bubbling air or nitrogen through the solution for 5 min prior to step A8.5.
	Blank determination	
A8.9	A blank must be included with each batch of determinations. Add 100 ± 1 ml of water to a 250-ml conical flask. Add the same amount of nitric acid (d_{20} 1.42) as is present in 100 ml of sample.	

Step	Experimental Procedure	Notes
A8.10	Carry out steps A8.2 to A8.8 inclusive (note f). Let the maximum instrument response be B.	(f) If additional potassium permanganate was added to a sample during step A8.3 an additional blank must be run with a similar amount of potassium permanganate present.
	Calibration standards	
A8.11	Duplicate calibration standards must be included with each batch of determinations (see Section A12.4). Add 2.00 ml of standard mercury *solution D* into each of two 250-ml conical flasks containing 98 ± 1ml of water and the same amount of nitric acid (d_{20} 1.42) as is present in 100 ml of sample.	
A8.12	Carry out steps A8.2 to A8.8 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 $\bar{C}$.	
	Calculation of results (see Section A11)	
A8.13	Calculate the concentration, A, of mercury in the sample from $A = \frac{S - B}{\bar{C} - B} \times 2\ \mu g/l$ Where $\bar{C} = \frac{C_1 + C_2}{2}$ This calculation assumes a linear calibration curve. Linearity must be checked (see Section A10).	

A9 Procedure for Solid Samples

If the sample is excessively wet, an aliquot should be centrifuged to remove as much of the aqueous phase as possible. Determine the moisture content of a separate aliquot of the centrifuged sample by a suitable method. On the limited evidence available, the majority of the mercury is normally present in the solid phase; however, oil contaminated sludges may require separate examination of the liquid phase in order to obtain an accurate estimate of the total concentration of mercury present in the sludge.

READ SECTION A4 ON HAZARDS BEFORE STARTING THIS PROCEDURE

Step	Experimental Procedure	Notes
	Analysis of sample	
A9.1	Weigh accurately 0.1 to not more than 0.25 g (± 0.001 g) of solid on a dry weight basis in to a 50-ml Kjeldahl flask (note g). Let the dry weight be W g.	(g) See Section A11 for concentration range of the method.
A9.2	Place the flask in an ice bath. Add slowly and carefully with swirling 10.0 ± 0.5 ml of sulphuric acid (d_{20} 1.84). Stopper the flask lightly with a pear shaped glass bulb. Leave in the ice bath for 60 ± 5 min.	
A9.3	Transfer to a water bath at 55 ± 2°C. Leave for 20 ± 4 h shaking occasionally.	

Step	Experimental Procedure	Notes
A9.4	Remove the flask, cool and place it in an ice bath. Slowly add 2.0 ± 0.1 ml of 5% m/V potassium permanganate. Cool. Gradually add 5.0 ± 0.1 ml of 5% m/V potassium permanganate. Cool. Slowly add 8.0 ± 0.1 ml of 5% m/V potassium permanganate. Ensure that excess potassium permanganate is always present by adding further 5.0 ± 0.1 ml aliquots of 5% m/V potassium permanganate as required to keep the solution deeply coloured (note h). Note the total amount of potassium permanganate which has been added.	(h) Volatilization of mercury can occur if the liquid is not kept cold—hence the slow separate additions of permanganate whilst the flask is immersed in the ice bath.
A9.5	Remove the flask and allow to stand at ambient temperature for at least 24 h.	
A9.6	Add 1.0 ± 0.1 ml of nitric acid (d_{20} 1.42) followed by 1.00 ± 0.05 ml of hydroxyammonium chloride/sodium chloride reagent and mix by swirling. Stand at least 5 min until the solution has decolorized and all the suspended matter has dissolved.	
A9.7	Quantitatively transfer to a 250-ml measuring cylinder and dilute with water to 150 ml. Then transfer to a 250-ml conical flask (note i).	(i) The batch of samples may be processed to this step but each sample must be treated as in steps A9.8, A9.9 and A9.10 before proceeding to the next sample.
A9.8	Set up the atomic absorption spectrophotometer and related apparatus ready to carry out the determinations. Place 75 ± 1 ml of solution from A9.7 in a 125-ml Drechsel bottle. Add 10.0 ± 0.5 ml of 2% m/V stannous chloride. Replace the Drechsel bottle head immediately.	
A9.9	Bubble air or nitrogen through the solution (see Section A6.2) and measure the maximum instrument response, S (eg peak height), at 253.7 nm (notes j, k and l).	(j) If foaming occurs discard and start again from step A9.1 as digestion/oxidation is incomplete. (k) If the instrument response is too high take a smaller aliquot from the conical flask (step A9.7) and dilute to 75 ml, proceed from step A9.8 and make an appropriate allowance in the calculation of the result.
A9.10	Continue bubbling air or nitrogen until the instrument response returns to base line.	(l) If the shape of the peak deviates noticeably from that obtained with the standard this indicates possible interference from volatile organic compounds. These may be removed by bubbling air or nitrogen through the solution for 5 min prior to step A9.6.
	Blank determination	
A9.11	A blank must be included with each batch of determinations. Place a 50-ml Kjeldahl flask in an ice bath.	
A9.12	Carry out steps A9.2 to A9.10 inclusive (note m). Let the maximum instrument response be B.	(m) If additional potassium permanganate was added to a sample during steps A9.4 and A9.5 an additional blank must be run with similar amount of potassium permanganate present.
	Calibration standards	
A9.13	Duplicate calibration standards must be included with each batch of determinations (see Section A12.4). Add 2.00 ml of standard mercury *solution D* into each of two-50 ml Kjeldahl flasks.	

Step	Experimental Procedure	Notes
A9.14	Carry out steps A9.2 to A9.10 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 $\bar{C}$.	
	Calculation of results (see Section A11)	
A9.15	Calculate the concentration, A, of mercury in the original sample (dry weight basis) from $A = \frac{S}{\bar{C}} \frac{B}{B} \times \frac{0.2}{W}$ $\mu g/g$ Where $\bar{C} = \frac{C_1 + C_2}{2}$ This calculation assumes a linear calibration curve. Linearity must be checked (see Section A10).	

A10 Checking the Linearity of the Calibration Curve

The procedure given in Sections A10.1 and A10.2, as appropriate, must be carried out on at least two independent occasions before application of these methods to any samples and regularly thereafter.

A10.1 Procedure for liquid samples

Acidify 1 litre of water with the same amount of nitric acid (d_{20} 1.42) as would be present in 1 litre of sample. To each of a series of 250-ml conical flasks add 100 ml of the acidified water. Pipette into these flasks 0.0, 0.2, 0.5, 1.0, 1.5, and 2.0 ml of standard mercury *solution D*, which correspond with 0.00, 0.02, 0.05, 0.10, 0.15 and 0.20 μg mercury respectively. Carry out the procedure given in steps 8.2 to 8.8 inclusive. Plot the maximum instrument response (eg peak height) against μg mercury. The calibration curve should be linear to at least 2 μg mercury; therefore when higher concentrations of mercury are encountered a calibration curve covering a higher range, eg 0 to 2.0 μg mercury, should be prepared using standard mercury *solution C*.

A10.2 Procedure for solid samples

Pipette into a series of 50-ml Kjeldahl flasks 0.0, 0.2, 0.5, 1.0, 1.5 and 2.0 ml of standard mercury *solution* D. These flasks contain 0.00, 0.02, 0.05, 0.10, 0.15 and 0.20 μg mercury respectively. Carry out the procedure given in steps A9.2 to A9.10 inclusive. Plot the maximum instrument response (eg peak height) against μg mercury. The calibration curve should be linear to at least 2 μg mercury. When higher concentrations of mercury are encountered a calibration curve covering a higher range, eg 0 to 2.0 μg mercury should be prepared using standard mercury *solution C*.

A11 Change of Concentration Range of the Methods

The procedures can be used to determine mercury in the concentration ranges given in Section A1.4 without modification, but with appropriate instrumental settings. When higher concentrations of mercury (up to 20 μg/l) are encountered it is only necessary to prepare a calibration curve for a higher range (see Sections A10.1 and A10.2). Note that in such circumstances the calibration standard required (step A8.11 and step A9.13) would be different and hence the calculation (step A8.13 and step A9.15) would also be different. For example, if a 2 μg mercury calibration standard had been run in step A8.11 then the multiplication factor in the calculation step A8.13 would be 20.

When the mercury concentration in a liquid sample exceeds 20 μg/l an appropriately smaller aliquot of the sample must be taken for analysis. It is often convenient to take a smaller aliquot from the 250-ml conical flask at step A8.6 or step A9.8 and to dilute with water to 75 ml before proceeding. An appropriate factor must be incorporated in the calculation of the result. When the concentration of mercury is lower than 0.1 μg/l a larger initial aliquot of the sample may be taken.

A12 Sources of Error

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

A12.1 Contamination

Mercury is a contaminant in most laboratories. It is desirable to carry out the analysis in a laboratory in which no appreciable amounts of mercury or its compounds are handled. The technique and working conditions should be critically examined and any sources of contamination eliminated or minimized. In particular, it is desirable to reserve the glass apparatus used for the determination of mercury solely for this purpose and to carry out a preliminary series of blank determinations before analysing any samples. If any unusually high and/or variable blank values are detected, they indicate contamination and steps must be taken to eliminate the problem.

A12.2 Mercury content of the water used for blank determination

If the water used for blank determinations contains mercury the results for samples will be falsely low by an amount equal to the concentration of mercury in the blank water. Clearly, the importance of this error depends on the mercury content of the blank water and the concentrations of interest in the samples. Ideally, the mercury content of the water used for each blank determination would be measured and an appropriate correction made. However, at present, a technique for this particular determination has not been established and reliance is therefore, placed on the preparation of blank water with a negligible mercury content (see Saline water method, Section B5).

A12.3 Interfering substances

See Section A3.

A12.4 Calibration standards

The calibration curve for this method has been found to be linear though its slope may vary from one set of determinations to another. Such variations can be caused by changes either in the rate at which mercury is stripped from the solutions by the air or nitrogen stream or in the sensitivity of the atomic absorption spectrophotometer. Therefore, a calibration standard must be run for each batch of analyses and step A8.11 and step A9.13 give the necessary procedures. These procedures assume a linear calibration curve and the linearity must be checked (see Section A10).

The accuracy with which the batch calibrations are established affects the accuracy of the results for the samples and the procedures given in step A8.11 and step A9.13 will usually ensure sufficient accuracy. More calibration standards may be analysed if desired.

A13 Checking the Accuracy of the Analytical Results

(For further information see another publication in this series.)

Once the methods have been put into normal routine operation many factors may subsequently adversely affect the accuracy of the analytical results. It is recommended that experimental tests to check certain sources of inaccuracy should be made regularly. Many types of test are possible and should be used as appropriate. 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 (see Section A5.8.4 and steps A8.11 and A9.13). 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.

A14 Alternative Methods

A14.1 Determination of mercury in non-saline waters

The method developed by the US Environmental Protection Agency[9] is suggested as an alternative method for potable waters and some raw waters. The method, however, does not work satisfactorily for sewages and sewage effluents[1]. The time for analysis is shorter than that of the method described in Section A8 viz for 10 samples the total analytical and operator times are approximately 5 and 2 h respectively. The method is based on the same principle of oxidation of organic matter and conversion of mercury to inorganic mercury followed by flameless atomic absorption spectrophotometry. The essential difference is the much shorter oxidation procedure using nitric acid as well as sulphuric acid and potassium peroxydisulphate in addition to potassium permanganate.

A14.2 Determination of mercury in solids

As a reference method for solid samples and also as an alternative method the procedure developed by the Water Research Centre (Stevenage Laboratory)[1] is recommended. This is a modification of the method described by the Analytical Methods Committee[10] in which the dithizone/spectrophotometric finish is replaced by a flameless atomic absorption spectrophotometric one. The sample pretreatment in both of these procedures involves a distillation step and is much more rigorous than that described in Section A9.

A15 References

(1) Water Pollution Research Laboratory, Stevenage, *Report 1272*, May 1972.
(2) Omang SH, Analyt Chim Acta, 1972, **53**, 415.
(3) Uthé JF, Armstrong FAJ and Stainton MP, J Fish Res. Bd, Can 1970, **27**, 805.
(4) Osland R, Pye Unicam Spectrovision, No 24, 1970, p 11.
(5) Kopp JF, Longbottom MC and Lobring LB, Wat. Technol./Qual., January 1972.
(6) Lindstedt G, Analyst, Lond., 1970, **95**, 264.
(7) Rains TC and Menis O, J Ass Off agric Chem, 1972, **55**, No 6, 1339.
(8) Batley GE, and Gardner D, Water Research, 1977, **11**, 745.
(9) US Environmental Protection Agency, EPA–R4–72–003, Sept 1972.
(10) Analytical Methods Committee, Analyst, Lond, 1965, **90**, 515.

Method B Dissolved Mercury in Saline Waters by Flameless Atomic Absorption Spectrophotometry

Tentative Method (1978 version)

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

B1 Performance Characteristics of the Method

(For further information on the determination and definition of performance characteristics see another publication in this series)

B1.1	Substance determined	Inorganic mercury and those organo-mercury compounds which form dithizonates (see Section B2).
B1.2	Types of sample	Sea, estuarine and some other waters (a)
B1.3	Basis of Method	Concentration of mercury by extraction with dithizone in carbon tetrachloride followed by back extraction and flameless atomic absorption spectrophotometry.
B1.4	Range of application (b)	Up to 100 ng/l
B1.5	Calibration curve (b)	Linear to 250 ng/l
B1.6	Standard deviation (b)	Mercury concentration (ng/l) 0.0 — Standard deviation (ng/l) 1.30 (c) 50.0 — 1.15 (d) (each with 9 degrees of freedom)
B1.7	Limit of detection (b)	4 ng/l (with 9 degrees of freedom)
B1.8	Sensitivity (b)	100 ng/l is equivalent to an absorbance of approximately 0.1.
B1.9	Bias (b)	None detected
B1.10	Interferences (b)	See Section B3.
B1.11	Time required for (b) analysis	For 6 samples the total analytical and operator times are approximately 140 minutes and 60 minutes respectively.

(a) For adaptation to other waters, see Section B13.
(b) These data were obtained at the Department of Oceanography, University of Liverpool[1] using this method and a single beam atomic absorption spectrophotometer and the closed circuit technique.
(c) Distilled water spiked with the stated mercury concentration.
(d) Irish Sea Water.

B2 Principle

Inorganic mercury is extracted from the acidified saline water as its dithizonate into carbon tetrachloride. Organo-mercury compounds may also be extracted by the carbon tetrachloride, but not all these compounds form dithizonates and those which do not may not be determined by this method. In general organo-mercury compounds of the type R-Hg-X in which X is a simple anion form dithizonates, whereas the type R_1-Hg-R_2 does not. Monomethyl mercury ion is extracted though it only appears to have a transient existence in aerobic saline water. The dithizonates are decomposed by the addition of hydrochloric acid and sodium nitrite and the mercury or organo-mercury compound returned to the aqueous phase. Some organo-mercury compounds may not be completely re-extracted into the aqueous phase. The mercury in this aqueous phase is determined by the procedure described in Section A2.3. The method is based on that used at the Department of Oceanography, University of Liverpool[1].

B3 Interferences

The combined effect of the commonly present ions in estuarine and sea waters at the concentrations normally encountered in these waters is less than 1 ng/l at a mercury concentration of 30 ng/l.

B4 Hazards

As Section A4 except that the hydroxyammonium chloride solution is here described in Section B5.7 and the standard solutions containing mercury are here described in Section B5.9. Additional hazards are the use of dithizone and carbon tetrachloride (B5.4 etc) which are toxic. Avoid inhalation, skin contact and ingestion. Carbon tetrachloride can be an anaesthetic and repeated heavy exposure can cause liver damage.

B5 Reagents

All reagents and standard solutions should be stored in glass bottles (see Section A6.3). Polyethylene must *not* be used. Analytical reagent grade chemicals are suitable unless otherwise specified.

B5.1 Water

The water used for preparing the reagent solutions should have a mercury content which is negligible compared with the smallest concentration to be determined in the samples. Water which has been doubly distilled in an all glass apparatus and then passed through a column of the sodium form of a strongly acidic cation exchanger is suitable. The water must be freshly prepared immediately before use.

B5.2 4.5M Sulphuric acid (approximately)

This operation contains a potential hazard (see Section B4).
Cautiously add with continuous stirring 240 ± 5 ml of sulphuric acid (d_{20} 1.84) to approximately 700 ml of water. When cool, dilute with water to 1 litre. Purify by repeated extraction with 25 ± 1 ml aliquots of 0.05 % m/V solution of dithizone in carbon tetrachloride until the extract remains green. Wash sequentially with two 25 ± 1 ml aliquots of carbon tetrachloride. Store the purified acid in a well stoppered, acid washed glass bottle.

B5.3 5M Hydrochloric acid (approximately)

Add 415 ± 5 ml of hydrochloric acid (d_{20} 1.18) to approximately 400 ml of water, mix, cool and dilute to 1 litre. Purify by passing through a column containing a strongly basic anion exchanger in the chloride form. Reject the first 2 bed volumes of percolate and retain the remainder.

B5.4 0.005 % m/V Dithizone solution

This reagent is hazardous (see Section B4).
Dissolve 25 ± 1 mg of dithizone in 500 ± 5 ml of redistilled carbon tetrachloride. Store in a dark glass bottle in a refrigerator. This solution is stable for 2 weeks. If necessary the dithizone solution may be purified by extraction with 5M hydrochloric acid and washing thoroughly with water.

B5.5 **Stripped sea water**

This operation contains a potential hazard (see Section B4).

Prepare freshly stripped sea water for blanks and calibrations in batches as follows.

To 2 litres ± 10 ml of sea water in a separating funnel add 15 ± 1 ml of 0.005 m/V dithizone solution. Shake mechanically for 5 min. Separate and discard the dithizone layer. Add a further 15 ± 1 ml of dithizone solution, shake for 5 min, separate and discard the dithizone layer.

B5.6 **10% m/V Sodium nitrite**

Dissolve 10.0 ± 0.5 g of sodium nitrite in approximately 80 ml of water and dilute with water to 100 ml.

B5.7 **20% m/V Hydroxyammonium chloride**

This reagent is hazardous (see Section B4). Dissolve 20.0 ± 0.5 g of hydroxyammonium chloride in approximately 80 ml of water and dilute with water to 100 ml.

B5.8 **30% m/V Stannous chloride dihydrate**

Dissolve 15.0 ± 0.5 g of stannous chloride dihydrate in 30 ± 1 ml of purified 5M hydrochloric acid and dilute with water to 50 ml. Bubble air or nitrogen through the solution for at least 10 min to ensure that the solution is mercury free. Prepare freshly when required.

B5.9 **Standard mercury solutions**

These solutions are hazardous (see Section B4).

B5.9.1 *Solution A* 1 ml contains 1 mg Hg—as Section A5.8.1.

B5.9.2 *Solution B* 1 ml contains 10 μg Hg—as Section A5.8.2.

B5.9.3 *Solution E* 1 ml contains 100 ng Hg.

Dilute 5.00 ± 0.05 ml of *solution B* to approximately 300 ml with water. Add 10.0 ± 0.5 ml of 5M hydrochloric acid and dilute with water to 500 ml in a calibrated flask. Prepare freshly when required.

B6 Apparatus

As Section A6 except that a 35-ml stoppered measuring cylinder fitted with a gas washing bottle head is used instead of a 125-ml Drechsel bottle. Particular attention must be paid to the cleanliness of all glassware used. The alternative closed circuit technique may be used.

B7 Sample Collection and Preservation

Collect a sample of at least 2.5 litres using a van Dorn[2] or similar sampler constructed of polypropylene or polymethyl-methacrylate. Transfer 2.5 litres of the sample to a glass bottle and add 50 ± 1 ml of 4.5M sulphuric acid.

B8 Analytical Procedure

READ SECTION 4 ON HAZARDS BEFORE STARTING THIS PROCEDURE

Step	Experimental Procedure	Notes
	Analysis of sample	
B8.1	Add 2 litres ± 5 ml of the sample to a separating funnel (note a).	(a) See Section B10 for concentration range.
B8.2	Add 15 ± 1 ml of 0.005% m/V dithizone solution. Shake mechanically for 5 min. Separate the lower layer into a 50-ml separating funnel.	

Step	Experimental Procedure	Notes
B8.3	Repeat step B8.2 separating the lower layer into the 50-ml separating funnel.	
B8.4	Add 15 ± 1 ml of 5M hydrochloric acid to the 50-ml separating funnel followed by 0.50 ± 0.05 ml of 10% m/V sodium nitrite. Shake mechanically for 5 min to back extract the mercury into the aqueous phase.	
B8.5	Separate the aqueous layer and place it in a 25-ml measuring cylinder fitted with a gas washing bottle head. Wash the carbon tetrachloride layer with 5 ml of water. Separate the aqueous layer and add it to the measuring cylinder.	
B8.6	Add 1.00 ± 0.01 ml of 20% m/V hydroxyammonium chloride to the measuring cylinder and dilute with water to the 25 ml mark. Allow to stand for 60 ± 5 min (note b).	(b) The batch of samples may be processed to this step but each sample must be treated as in steps B8.7, B8.8 and B8.9 before proceeding to the next sample.
B8.7	Set up the atomic absorption spectrophotometer and related apparatus ready to carry out the determinations. Add 1.0 ± 0.1 ml of 30% m/V stannous chloride dihydrate. Replace the gas washing bottle-head immediately.	
B8.8	Bubble air or nitrogen through the solution (see Section A6.2) and measure the maximum instrument response, S (eg peak height), at 253.7 nm (notes c and d).	(c) If the instrument response is too high start again from step B8.1 using a smaller aliquot of sample and make an appropriate allowance in the calculation of the result.
B8.9	Continue bubbling air or nitrogen until the instrument response returns to the baseline.	(d) It is unlikely that volatile organic compounds will cause interference because of the extraction procedure. If the shape of the peak deviates noticeably from that of the standard then bubble air or nitrogen through the solution for 5 min prior to step B8.6.
	Blank determination	
B8.10	A blank must be included with each batch of samples. Place 2 litres ± 5 ml of stripped sea water in a separating funnel. Add the same amount of 4.5M sulphuric acid as is present in 2 litres of sample.	
B8.11	Carry out steps B8.2 to B8.9 inclusive. Let the maximum instrument response of the blank be B.	
	Calibration standards	
B8.12	Duplicate calibration standards must be included with each batch of determinations. Place 2 litres ± 5 ml of stripped sea water in each of 2 separating funnels. Add the same amount of 4.5M sulphuric acid as is present in 2 litres of sample and add 2.00 ml of standard mercury *solution E* into each funnel.	
B8.13	Repeat steps 8.2 to 8.9 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 $\bar{C}$.	

Step	Experimental Procedure	Note

Calculation of results (see Section B10).

B8.14 Calculate the concentration, A, of mercury in the sample from

$$A = \frac{S - B}{C - B} \times 100 \text{ ng/l}$$

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

This calculation assumes a linear calibration curve. Linearity must be checked (see Section B9).

B9 Checking the Linearity of the Calibration Curve

This procedure must be carried out on at least two independent occasions before application of the method to any samples and regularly thereafter. Add 2 litres ± 5 ml of stripped saline water to each of a series of separating funnels.

Add to each funnel the same amount of 4.5M sulphuric acid as would be present in 2 litres of sample. Pipette into these funnels 0.0, 0.2, 0.5, 1.0, 1.5 and 2.0 ml of standard mercury *solution E*. These solutions contain respectively 0, 20, 50, 100, 150 and 200 ng of mercury (ie equivalent to 0, 10, 25, 50, 75 and 100 ng/l respectively). Carry out the procedure given in steps B8.2 to B8.9 inclusive. Plot the maximum instrument response (eg peak height) against ng mercury. The calibration curve should be linear to at least 500 ng mercury (ie equivalent to 250 ng/l). When higher concentrations of mercury are encountered a calibration curve covering a higher range, eg 0 to 250 ng/l mercury must be prepared.

B10 Change of Concentration Range of the Method

The procedure can be used to determine mercury in the concentration range given in Section B1 without modification, but with appropriate instrumental settings. When higher concentrations of mercury (up to 250 ng/l) are likely to be encountered it is only necessary to prepare a calibration curve for a higher range (see Section B9). Note that in such circumstances the calibration standard required (step B8.12) would be different and hence the calculation (step B8.14) would also be different. When the mercury concentration exceeds 250 ng/l, an appropriately smaller aliquot of the sample must be taken and an appropriate factor incorporated in the calculation of the result.

B11 Sources of Error

As Section A12 with substitution of the appropriate section and step numbers for the saline water method.

B12 Checking the Accuracy of the Analytical Results

As Section A13 with substitution of the appropriate section and step numbers for the saline method.

B13 Use with Non-saline Waters

B13.1 This method may be used directly for non-saline waters, but will not determine those mercury complexes that will not react with dithizone to form dithizonates or back-extract.

B13.2 As most of these unreactive complexes are decomposed slowly by chloride, the following procedure may be of use:

B13.2.1 Prepare a 20% m/V sodium chloride solution by dissolving 200 ± 10 g of sodium chloride in 750 ± 10 ml of warm water, cool and make up to 1000 ± 10 ml with water. Extract with dithizone as in Section B5.5.

B13.2.2 To every 1000 ± 5 ml of sample, in a clean glass bottle add 100 ± 0.5 ml of sodium chloride solution (B13.2.1), stopper and mix thoroughly. Allow to stand overnight.

B13.2.3 Proceed with the method starting at B8.1. Correct the final result for the sodium chloride addition by multiplying the mercury concentration observed by 1.1.

B13.3 Procedure B13.1 has been tested at the University of Liverpool and found to be satisfactory. Procedure B13.2 is based on the equilibrium that occurs between most mercury complexes, and the exceptionally high stability of the tetrachloromercurate II ion in the presence of excess chloride. The performance characteristics given in Section B1 do not necessarily apply to this procedure and the analyst is advised to check its suitability for his determination using spiked or synthetic samples.

B14 References

(1) Gardner D, and Riley JP, J.Cons Int Explor Mer 1974, **35**, 202.
(2) van Dorn WG, Trans Amer Geophys Un 1956, **37**, 682.

Appendix

Estimation of the Accuracy of Analytical Results using the Mercury Methods

1 Introduction

Quantitative investigation of the accuracy achievable when the mercury Methods A (non-saline waters) and B (saline waters) are used appears to be limited to work at the Water Research Centre (Stevenage Laboratory) and the University of Liverpool respectively. Before firmly recommending the methods 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 these methods, could estimate the accuracy of its own analytical results and report the findings to 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 mercury in the sample analysed and on the type of sample, for example, worse precision may be obtained with effluents 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 5 days and preferably more, up to 10.

Solution	Method A	Method B
1	Blank	Blank
2	Another blank	Another blank
3	Standard solution 0.5 μg/l Hg	Standard solution 25 ng/l Hg
4	Standard solution 2.0 μg/l Hg	Standard solution 100 ng/l Hg
5	Typical sample	Typical sample
6	Same sample spiked with 2.0 μg/l Hg	Same sample spiked with 100 ng/l Hg

It is essential that these solutions be treated exactly as if they were samples and the procedures specified in Sections 8 of Methods A and B 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 methods and should contain the same amount of nitric or sulphuric acids and dichromate 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 Method A and 50 litres of typical sample are required for Method B. Prepare *solution 6* each day when required by spiking *solution 5* as follows: add 2.00 ml of standard mercury *solution D* to 100 ml of *solution 5* (Method A) and 2.00 ml of standard mercury *solution E* to 2 litres of *solution 5* (Method B). When analysing *solution 6* it will be necessary to take into account step 8.7 note d (Method A) and step 8.8 note c (Method B). The total period of the tests may be any convenient time so long as the mercury 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 mercury from 100% may indicate the presence of interfering substances.

3 Evaluation of Results

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

3.1 Convert all results to concentrations as described in the methods. 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 mercury in *solution 6* from,

For Method A, $$R = \frac{(\bar{x}_6 - \bar{x}_5)}{2} \times 100$$

For Method B, $$R = \frac{(\bar{x}_6 - \bar{x}_5)}{100} \times 100$$

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 tables:

Method A

Solution	No of results n	Mean Concentration µg/l	Standard Deviation µg/l	Mean Recovery %
2 Blank				—
3 Standard, 0.5 µg/l				—
4 Standard 2.0 µg/l				—
5 Sample				—
6 Solution 5 + 2.0 µg/l				

Method B

Solution	No of Results n	Mean Concentration ng/l	Standard Deviation ng/l	Mean Recovery %
2 Blank				—
3 Standard 25 ng/l				—
4 Standard 100 ng/l				—
5 Sample				—
6 Solution 5 + 100 ng/l				

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

* Results to be sent to the following:

The Technical Secretary
The Metals and Metalloids Working Group
The Standing Committee of Analysts
The Department of the Environment
2 Marsham Street
LONDON SW1P 3EB
England

4 Solid Samples

At the present time a suitable technique for the estimation of the accuracy of analytical results using the method for solid samples (Method A, Section 9) has not been established.

Address for Correspondence

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

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

Printed in England for Her Majesty's Stationery Office by McCorquodale Printers Ltd., London
HM 9675 Dd 595690 K32 11/78

Department of the Environment/National Water Council

Standing Committee of Analysts

Members of the Committee Responsible for this Method:

Mr DL Bond	until January 1974*
Mr J Borland	after June 1975*
Dr JM Carter	after June 1975*
Dr GW Clayfield	*
Dr V Collins	after June 1975*
Mr I C Conchie	†
Dr RL Cooper	after June 1975*
Dr BT Croll	after June 1975*
Mr TA Dick	after February 1975*
Mr GL Eden	until June 1975*
Mr TR Graham	after April 1977*
Mr B Gubbins	until September 1975†
Dr N Harkness	until June 1975*
Mr PJ Hewitt	†
Mr L Hodges	after June 1975*
Mr GJ Holland	after June 1975*
Dr AJ Howard	after June 1975*
Mr OD Hydes	after January 1974†‡
Mr WM Lewis	*†‡
Mr PJ Long	after June 1975*
Mr GL Lowden	†
Mr D Mercer	until June 1974*
Mr P Morries	after June 1975*‡
Mr D Myles	after June 1975*
Mr AH Nield	after January 1976*
Dr HA Painter	after June 1975*
Mr JF Palframan	†
Dr AT Palin	until June 1975*
Dr SJ Patterson	*
Mr LR Pittwell	*‡
Dr JL Portmann	after June 1975*
Mr LD Purdie	after June 1975*
Dr L Ranson	after February 1975†
Mr BD Ravenscroft	after June 1975*
Prof JP Riley	*†‡
Mr R Sinar	*
Mr PAH Sperring	until January 1976*
Mr BT Whitham	after June 1975*
Mr AL Wilson	*†‡
Dr R Wood	after June 1975*

*main committee member**

working group member†

special panel‡

HER MAJESTY'S STATIONERY OFFICE

Government Bookshops

49 High Holborn, London WC1V 6HB
13a Castle Street, Edinburgh EH2 3AR
41 The Hayes, Cardiff CF1 1JW
Brazennose Street, Manchester M60 8AS
Southey House, Wine Street, Bristol BS1 2BQ
258 Broad Street, Birmingham B1 2HE
80 Chichester Street, Belfast BT1 4JY

Government publications are also available through booksellers

ISBN 0 11 751326 1