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# DETERMINATION OF MERCURY IN SEA-WATER USING TIN II REDUCTION AND SYRINGE INJECTION ATOMIC ABSORPTION

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# DETERMINATION OF MERCURY IN SEA-WATER USING TIN II REDUCTION AND SYRINGE INJECTION ATOMIC ABSORPTION

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## INTRODUCTION

The determination of mercury in water by atomic vapour absorption at room temperature involves analytical problems common to many trace analyses - sample preservation, contamination, and environmental concentrations near the detection limit.

Most articles on the subject describe limited studies on one of these specific problems and omit a complete description of the procedure as a whole. Some routines appear to demand an unreasonably high degree of operator care and skill to obtain reproducible results, as well as an imaginative interpretation of curt procedural information.

Such published methods and suggestions have been critically assessed in this laboratory over a two-year period, and incorporated into this procedure which has been optimized for maximum reliability and simplicity under routine analytical conditions. The procedure is based mainly on the techniques described by Harsanyl and others (1973), and Stainton (1971). A particular advantage of this method is the option to strip and concentrate mercury from samples in the field if desired, thus avoiding the need to preserve and transport bulky volumes of sea-water.

Unfortunately some of the published claims for low detection limits and good reliability could not be substantiated. The natural concentrations of mercury in unpolluted sea-water is of the order of 10 $ng.\ell^{-1}$ and this is about the same as the detection limit of this method. Therefore the technique in its present form is only satisfactory for "rough screening" of such low-mercury water.

This method may also be applied to fresh water samples provided salt is added to the water before stripping.

The full description of the method is lengthy and disjointed because of the large amount of detail incorporated. The following summary is included for quick reference.

## SUMMARY OF METHOD

### Outline

A 500 mℓ sample of unfiltered sea-water is collected and treated immediately with $HNO_3$ and $SnCl_2$ solutions. The mercury vapour is stripped off by bubbling nitrogen gas through the sample for 15 minutes and is absorbed into 4 mℓ of acidified $KMnO_4$ solution. The mercury, stabilized and concentrated in the $KMnO_4$ solution, is stored in a screw-capped tube until determined by the syringe injection technique of atomic absorption.

The absolute detection limit is 0.5 $ng.\ell^{-1}$, the practical detection limit about 10 $ng.\ell^{-1}$.

Stripping routine takes 20 minutes per sample; mercury recovery is approx. 90% at 500 $ng.\ell^{-1}$, decreasing as concentration decreases. Coefficient of variation of complete procedure is 40% at 40 $ng.\ell^{-1}$ level.

Injection routine takes 1 minute per sample; mercury recovery is approx. 50% per injection. Coefficient of variation of syringe procedure is 10% at 10 $ng.\ell^{-1}$ level.

### Field preparations (sampling and stripping)

Apparatus Clean. Cover exposed outlets when not in use.
Assemble stripping apparatus, Fig. 1 page 12.
Collect sampling apparatus, page 8.

Reagents (ample for 30 samples and calibrations)

Conc. $HNO_3$ (16M) Purify. Transfer 300-400 mℓ to 500 mℓ flask. Fit 5 mℓ tilt measure and PTFE cap. Exclude light.

$SnCl_2.2H_2O$ (10% m/V in 10% HCl). Transfer 300-400 mℓ to 500 mℓ flask. Fit 5 mℓ tilt measure and PTFE cap.

$KMnO_4$ (0.05% in 5% $HNO_3$ - 0.1g.200 $m\ell^{-1}$). Dissolve preweighed solid in 5% $HNO_3$. Pipette 4 mℓ into each screw-cap tube, one for each sample to be stripped, plus 6 controls spiked with 0, 10 and 20 µℓ of Hg standard in duplicate. Cap. Keep cold.

Hg standard (1.0 µg $Hg.m\ell^{-1}$). Take several glass phials, a file, 10 µℓ and 20 µℓ micropipettes, disposable tips.

### Sampling sequence

1. Collect 500 mℓ of sea-water for each sample.
2. When standards are to be run (minimum of 2 per day and 2 per water type) collect 1½ litres of sea-water;
   add 15 mℓ (3 x 5 mℓ) conc. $HNO_3$ immediately;
   mix;
   keep till stripped (preferably within 2 hours).

### Stripping sequence

1. Add 5 mℓ $HNO_3$ to stripping chamber (if sea-water not already acidified).
2. Add sea-water to mark (500mℓ).

3. Lift absorption tube containing 4 mℓ of $KMnO_4$ solution up under glass frit till surface of solution is almost touching bottom of frit.
4. Add 5 mℓ $SnCl_2$ to stripping chamber.
5. Stopper the unit. Secure with rubber bands.
6. Open second needle valve to start flow of $N_2$ gas (240 $m\ell.min^{-1}$).
7. Immerse frit into the $KMnO_4$. Reverse steps 6, 7 if unskilled.
8. Start timer.
9. Strip for 15 minutes.
10. Lower $KMnO_4$ absorption tube. Recap. Not necessary to store cold.
11. Rinse frit with distilled water (gas still passing through). After every few samples dip frit in $SnCl_2$ to remove brown $MnO_2$; rinse thoroughly with distilled water.
12. Open bottom tap and drain stripping chamber.
13. Remove stopper. Rinse stripping chamber with distilled water.
14. Between samples, turn off $N_2$ stream at second needle-valve.
15. Between sessions, turn off cylinder with key.

Calibration sequence (method of standard additions)

1. Strip one 500 mℓ portion of the 1½ℓ acidified water sample to determine the natural Hg level. (Stripping sequence steps 2-14).
2. Half-fill stripping chamber with another portion of the same acidified sample.
3. Open phial of Hg standard solution.
4. Dispense either 10 µℓ or 20 µℓ.
5. Complete filling the chamber with sample water to 500 mℓ mark.
6. Proceed with stripping sequence steps 3 to 14 or 15.

Laboratory preparations (Hg reduction and injection)

Apparatus — Fig. 2, page 19, 20.

Reagents — $SnSO_4$ (5% m/V plus 1% NaCl, 1% $(HONH_3)_2SO_4$ in 10% $H_2SO_4$).
$(HONH_3)_2SG_4$ crystals.
NaCl crystals.

Injection sequence

1. Add $(HONH_3)_2SO_4$ crystals.
2. Add NaCl crystals.
3. Pass stream of $N_2$ through cuvette.
4. Into syringe draw (a) the 4 mℓ sample,
   (b) a little air,
   (c) 1 mℓ $SnSO_4$,
   (d) air to bring plunger to 20 mℓ mark.

5. Cap the syringe.
6. Shake for about 15 seconds.
7. Disconnect flow of $N_2$.
8. Remove cap of injection port.
9. Remove syringe cap.
10. Inject.
11. Re-cap injection port.
12. Reconnect flow of $N_2$.
13. Peak height is proportional to Hg concentration.

## FIELD REAGENTS AND APPARATUS

### Preparation

Wash all glass and plastic ware. Fill plastic ware with 5-10% HCl and glass ware, especially the screw-capped absorption tubes, with dilute $KMnO_4$ (≈0.5%) in 5-10% $HNO_3$ for several days before use. Clean with dilute acidified $H_2O_2$ solution, or a Sn II solution, rinse and drain. Storage containers should preferably be rinsed and soaked with water characteristic of the sample to be analysed, particularly if polyethylene containers are used (Mahan and Mahan 1977).

#### Notes

1. The Standards Association of Australia recommends an alternative procedure published in AS 2031, Part 1 - 1977. This has not been compared with the above.

2. A whitish deposit, presumably a basic tin chloride, builds up in the stripping chamber after a time. Although the matter was not investigated closely, no adverse change in the characteristics of mercury stripping could be ascribed to the presence of the deposit. It could be loosened to some extent by hot concentrated $HNO_3$, but a really satisfactory means of removal was not found.

### Concentrated nitric acid (16 M)

Use acid as free from mercury as possible (Notes 3, 4). Store in a dark glass or polythene bottle (Note 5). For field use, transfer 300-400 mℓ into a cleaned reagent bottle or conical flask fitted, by means of a ground glass joint, with a 5 mℓ tilt-measure (Note 6). Light can be excluded by wrapping aluminium foil around the container.

#### Notes

3. High purity grades of $HNO_3$, e.g. Merck Cat. No. 452, are satisfactory. All batches should be checked for mercury content before use. Ordinary A.R. grade acid should be redistilled. A little potassium dichromate added to acid to be purified helps to retain any mercury impurity in the still pot.

4. Where the sea-water to be analysed is expected to contain enough mercury to allow a 100 mℓ sample to be used instead of 500 mℓ, there are several advantages in using a diluted acid instead - 20% V/V* - when acidifying samples in the field; more accurate dispensing of a convenient volume, safety, and less risk of contaminating other samples required for nitrate estimation.

*Percentage concentrations throughout the text are based on dilutions of the normal aqueous or hydrated form of the concentrated acid or salt.

Purified water required for mercury analysis should be distilled from dilute potassium dichromate or alkaline permanganate. Water purified by ion-exchange demineralization may contain mercury if the resin bed is approaching exhaustion or shortly after the latter has been regenerated with caustic soda. It is believed that low mercury acid can also be obtained by bubbling nitrogen through 50% V/V aqueous acid.

5. Polythene is permeable to mercury vapour, and acid stored in polythene bottles will slowly absorb atmospheric mercury through the walls. Store in a closed box if laboratory air is contaminated with mercury. If the acid is not to be used for any other trace metal analyses besides mercury, borosilicate glass storage is best.

6. A plastic dust cap, preferably machined from PTFE, should be fitted over the dispenser spout to keep contaminating dust out and nitrate fumes in.

Tin II chloride solution (10% m/V in 10% HCl)

Put about 40 g of $SnCl_2.2H_2O$ (technical or A.R. grade) into 400 mℓ of about 10% V/V HCl in a cleaned 500 mℓ conical flask with a ground-glass neck. Dissolve by warming and stirring on a hot plate magnetic stirrer unit for ½ to 1 hour (Note 7). Fit a 5 mℓ tilt-measure ready for field dispensing.

Note

7. Add a piece of A.R. granulated tin to prevent oxidation if the solution is to be kept for more than a week. It is unlikely that this solution would be contaminated with mercury, even if a low grade of tin chloride and poor quality water were used, since mercury would be eliminated during the heating necessary to dissolve the salt. However some brands (e.g. Merck tin II chloride G.R., Cat. No. 7815) dissolve completely in cold water. If the solution is suspected of being contaminated, residual mercury may be removed shortly before use by either bringing the solution to the point of boiling and cooling again, or by bubbling high purity nitrogen gas through it for 10 minutes at a rate of 150-250 $m\ell.min^{-1}$.

Potassium permanganate solution (0.05% $KMnO_4$ in 5% $HNO_3$)

Add 10-15 mℓ concentrated $HNO_3$ (Note 8) to 50-100 mℓ of distilled water in a 200 mℓ stoppered graduated cylinder; dilute to 200 mℓ, mix and cool; add and dissolve about 0.1 g AR grade $KMnO_4$ (Note 9). Pipette 4 mℓ aliquots, one for each sample to be stripped plus 6 controls spiked with 0, 10 and 20 µℓ of Hg standard in duplicate (Note 10), into cleaned 15 mℓ borosilicate tubes with teflon-lined screw caps (e.g. Pyrex Cat. No. 9826 15 mm x 125 mm). Replace lids immediately. Keep cool.

Notes

8. Neither the acid strength nor the permanganate strength is very critical. Solutions of acid strength between 2% and 15% absorb mercury vapour effectively. However a concentrated acid solution needs to be matched by a relatively high $KMnO_4$ level to retain effective mercury-absorbing ability, and strong $KMnO_4$ solutions are inherently more

unstable than dilute ones. Also if the acid and/or the $KMnO_4$ is contaminated, high concentrations would contribute a large mercury blank. Low mercury $KMnO_4$ is available (Merck Cat. No. 5084) but it is not essential to use this if other sources are reasonably pure.

9. The solution is unstable especially if warm. It should be made up shortly before use and kept cool. On longer field trips it is often convenient to take one or more pre-weighed portions of $KMnO_4$ and aliquots of 5% $HNO_3$ to mix shortly before use.

10. All of this permanganate solution is normally used for the subsequent mercury determination. Unless the blank value of the solution is high it may be dispensed with sufficient volumetric precision from a tilt-measure.

Standard mercury solution (1.0 µg $Hg.m\ell^{-1}$)

Prepare a stock solution containing 10,000 µg $Hg.m\ell^{-1}$ (= 10,000 ppm) by dissolving 1.354 g of A.R. $HgCl_2$ in 25 mℓ of 20% V/V $HNO_3$ and diluting to 100 mℓ.

Dilute this stock solution 10,000 times into a solution of 5% V/V $HNO_3$ and 0.05% $K_2Cr_2O_7$. Store in glass containers (Note 11).

Note

11. Small glass ampoules are very convenient storage containers. No change in mercury concentration with time has been observed. They can be filled with 2 or 3 mℓ of solution, and kept indefinitely. A separate ampoule is used to prepare each set of standards - filed open immediately before use and afterwards discarded. Screw-capped borosilicate test tubes with teflon liners are also suitable storage vessels which are convenient for field use.

Microlitre pipette(s) and disposable tips

10 µℓ and 20 µℓ sizes are suitable for clean open sea-waters. A selection of larger sizes is more appropriate for other areas.

High purity nitrogen gas (Note 12)

3.2 $m^3$ size gas cylinder ("E" size). The more usual G size is inconveniently large and heavy for field use.

Cylinder head regulator.

Cylinder key.

Two fine in-line metering valves (e.g. Whitey and/or Nupro types).

Adjust the cylinder head regulator in the laboratory to give a gas delivery pressure of 200 kPa, and the first metering valve to deliver about 240 mℓ of nitrogen per minute (Note 13). They may be taped firmly at that setting so that the flow rate cannot be easily changed in the field accidentally. Turn the supply on and off with the second metering valve and the cylinder key only.

Notes

12. Other purge gases, e.g. air, may be satisfactory but have not been tried. But the presence of oxygen for example in the gas stream seems suspect. If the gas supply is suspected of being contaminated with mercury vapour a trap of acid permanganate solution may be put in the train before the stripping unit.

13. This is an optimum figure for our own stripping unit. It optimizes a short and convenient sample stripping time compatible with 100% absorption efficiency by the permanganate solution. The flow rate must be established initially with a soap bubble gauge or other metering device, but with a little experience it can be adjusted visually to produce a prolific supply of small bubbles without causing violent agitation of the sample solution.

Stripping unit (see Figure 1, page 12)

This is a glass chamber, about 330 mm long by 45 mm diameter, blown from borosilicate tubing (Note 14). A graduation mark on the side indicates the fill level for a 500 mℓ sample of water (ignoring the insignificant error of 1% due to $HNO_3$). There is about 100 mℓ "dead space" above the 500 mℓ mark. A large diameter neck, stoppered with a B40 glass or teflon plug, allows quick and easy filling at sea (Note 15). The chamber is drained from a teflon tap at the bottom. The nitrogen gas supply line from the second metering valve is a flexible plastic tube (Note 16). Incoming gas flows through a gas distribution tube with a fritted cylinder, pore size 40-60 μm (e.g. Jobling Cat. No. 3830/04 : porosity 2), which extends as near as practicable to the bottom of the chamber. The outlet tube leading into the permanganate solution is also fitted with a coarse glass frit, pore size 150-250 μm porosity 0 (Note 17). The surfaces of ball and socket connections are lubricated with silicone grease to prevent possible leaks. In addition, 2 clamps are recommended at each ball and socket joint.

Notes

14. If mercury concentrations are high enough (say >100 $ng.\ell^{-1}$), 100 mℓ samples of sea-water may be used and stripped from a smaller chamber (150 mℓ capacity) blown from 25 mm diameter tubing. The top can be sealed with either a B29 stopper or more conveniently, with a plastic screw cap. A large opening is not so essential for introducing the smaller volume. The gas flow rate for this smaller stripper should be adjusted to 120-150 $m\ell.min^{-1}$.

15. A stopper must be lubricated and tied down with rubber bands or spring clips to prevent it from being lifted by the internal gas pressure and leaking. A teflon stopper jammed in a glass neck can be unstuck after cooling the complete head of the unit in icy water for a few moments.

16. Polythene or PVC tubing is quite satisfactory, although nylon pressure tubing is more robust. A ball and socket joint in front of the chamber is not essential but it allows easy cleaning and prevents mechanical strain on the glass unit. The second needle valve could be replaced with a T-form, 3- way teflon stopcock. But while the latter is cheaper it is more vulnerable to breakage and its use results in some wastage of gas.

17. Mercury passing over into the permanganate solution tends to be weakly adsorbed on to the sintered glass or on to $MnO_2$ deposited on the frit. The smaller and coarser the glass frit used, the smaller the error due to this cause. A frit fused into the end of a 5 mm i.d. delivery tube gives little error. Commercially available fritted cylinders such as that recommended for the stripping chamber are too large. On the other hand, the use of a PTFE capillary (Bel-Art Products spaghetti tubing Cat. No. T-21191, i.d. 0.015", wall 0.009"), which would eliminate the problem altogether, was tried, but forcing the gas through the narrow orifice created too large a back pressure and made the system difficult to control. If only a large or a fine frit is available, then it is an essential part of the procedure to dislodge the mercury, otherwise a variable amount - up to 50% of the total - remains behind in the pores of the sintered glass (see FIELD PROCEDURE, Note 21).

Sampling-collecting equipment

Surface water: The following simple equipment is suitable for small vessels:

2 x 500 mℓ plastic (polycarbonate preferably) measuring cylinders fitted with plugs to exclude dust. If not commercially available the plugs may be turned out of perspex. Alternatively the ends of the cylinders (and other exposed apparatus) may be covered with a sealing film, e.g. Parafilm, when not in use.

A steel rod long enough to allow the operator to reach the water. Clamp one of the cylinders to one end.

Polythene bottles encircled with a mark to indicate the 1½ litre level.

Perhaps a filter funnel or a similar means of transferring the sample to the stripping unit without spillage on a tossing vessel.

Sub-surface water: Standard-type, preferably non-metallic sampling bottles and associated gear.

Miscellaneous apparatus

Frame to support the stripping unit. Specially constructed or retort stand and 4 bossheads and 4 clamps.

Rope, cylinder cradles, G-clamps or nails to secure the gas cylinder and stripping unit frame.

Test tube rack to house permanganate tubes.

Wash bottle full of distilled water.

Container for collecting stripped sample water (acidic!) and washings, and/or drainage tube for leading the wastes directly over the side of the vessel.

Interval timer.

## FIELD PROCEDURE

For surface samples, collect a measuring cylinder full of water from near the bow, or from another position uncontaminated by the ship. Deeper samples must be taken with a sampling bottle. Transfer the sample to a polythene bottle when standards are to be run (Note 18), or otherwise transfer it to the second measuring cylinder (or unclamp the first one). Adjust the volume to 500 mℓ by shaking out the excess.

Turn on the nitrogen gas at the cylinder, but with the flow to the stripper turned off at the second metering valve. Clamp a tube of permanganate in place with the glass frit of the gassing tube above but close to the surface of the absorbant solution (Note 19).

Dispense 5 mℓ of $HNO_3$ (Note 18). Pour the sample into the stripping chamber. Dispense 5 mℓ of $SnCl_2$. Immediately replace the stopper and secure with rubber bands or springs.

Open the second needle valve to start the flow of gas. Then lift the permanganate tube to immerse the glass frit to a position close to the bottom of the solution (Note 19).

Start the interval timer and continue bubbling for 15 minutes (Note 20).

At the end of this stripping period remove the tube of permanganate absorbant (Note 21), replace its cap and keep it for the mercury determination later. It does not matter if $MnO_2$ precipitates from solution at this stage, so the tube does not have to be stored cold. Drain and rinse the stripping chamber with distilled water ready for the next sample. Rinse the permanganate frit with distilled water. After every few samples dip frit in $SnCl_2$ to remove brown $MnO_2$; rinse thoroughly with distilled water. Turn off the $N_2$ gas flow at the second needle-valve after the unit has been rinsed and made ready for the next sample - the gas pressure forces moisture out of the sintered glass frits which would otherwise contaminate and change the volume of following samples. Turn off the gas with the cylinder key between working sessions.

The first sample taken on every working day should be done in duplicate (Note 22).

### Notes

18. If there is any delay of more than 5 minutes between collection and stripping of samples, the $HNO_3$ should be added immediately to bring the water to 1% acid concentration, and the $SnCl_2$ added later at the time of stripping. HCl could be substituted for $HNO_3$ in this step but it could not be used to acidify the $KMnO_4$ solution since permanganate oxidizes HCl to $Cl_2$ and is itself reduced to $MnO_2$.

    A marking-pen ring which completely encircles the polythene bottle at the 1½ litre level, allows the volume to be more easily and precisely estimated on a swaying ship.

    Glass bottles are claimed to be more easily cleaned (Bothner and Robertson, 1975) and there may be advantages in using, for example, Winchester bottles (2½ℓ) for this reason if mechanical protection is arranged.

19. When the flow of $N_2$ provides a back pressure in the gassing tube, $KMnO_4$ solution does not penetrate through the sintered glass into the gassing tube. Thus there is less chance of $MnO_2$ precipitating in the pores of the frit, adsorbing Hg and contributing to erratic and falsely low results. This problem is more serious if the working environment is warm to hot.

    The first gas to come through the gassing tube is air displaced from within the line itself, and there are 3 or 4 seconds available after turning on the $N_2$ to immerse the tube before any mercury reaches this point. However, if this sequence cannot be managed quickly the tube may be immersed first and particular care taken when rinsing afterwards (see Note 21).

20. Practically all the extractable mercury appears to be stripped off in 10 minutes, after which the amount plateaus off at a fixed fraction of the total mercury in the water sample depending on the initial concentration. Fifteen minutes ensures that all extractable mercury is collected even if abnormally slow stripping conditions occur, and it does not have to be timed as precisely as would a 10 minute interval. However, at low mercury concentrations ($<50\ \mu g.\ell^{-1}$) stripping efficiency is noticeably erratic anyway and it is best to be as precise as possible with respect to gas flow rate and timing.

21. If erratic results are obtained from replicate determinations, it may be due to mercury being adsorbed on the glass frit of the gassing tube - perhaps coprecipitating with $MnO_2$ - as mentioned in Notes 17 and 19. If so include the following procedure:

    At the end of the stripping interval, leave the carrier gas stream on and the permanganate tube in place, open the tap at the bottom of the stripping chamber and let out a few mℓ of sea-water. This action causes the permanganate solution to suck back a few centimetres into the gassing tube. When the tap is turned off the nitrogen gas stream forces the solution forward through the sintered glass. Repeat this flushing action several times (6 seems enough) before removing the tube of $KMnO_4$ absorbant. The solution left in the pores of the glass frit should not be rinsed into the permanganate solution because it would change the volume of the latter by an arbitrary amount. Rinsing the frit is not necessary if experimental conditions are replicated carefully for every sample. The concentration in the pores of the frit is the same after the flushing procedure as in the bulk 4mℓ of absorbant. After this tube of permanganate with absorbed mercury has been removed and capped, the gassing tube is washed clean of equilibrated permanganate by similarly flushing with distilled water until the purple colour is removed. Occasional washing with dilute $SnCl_2$ removes accumulated brown stain of $MnO_2$.

22. Two samples should be taken from the first station on each work day. The first sample to be processed through the sampling, stripping, and especially the laboratory apparatus, is likely to give erratic mercury concentration results. After the first sample has flushed out the system, there are rarely any further stability problems for the remainder of a given work session.

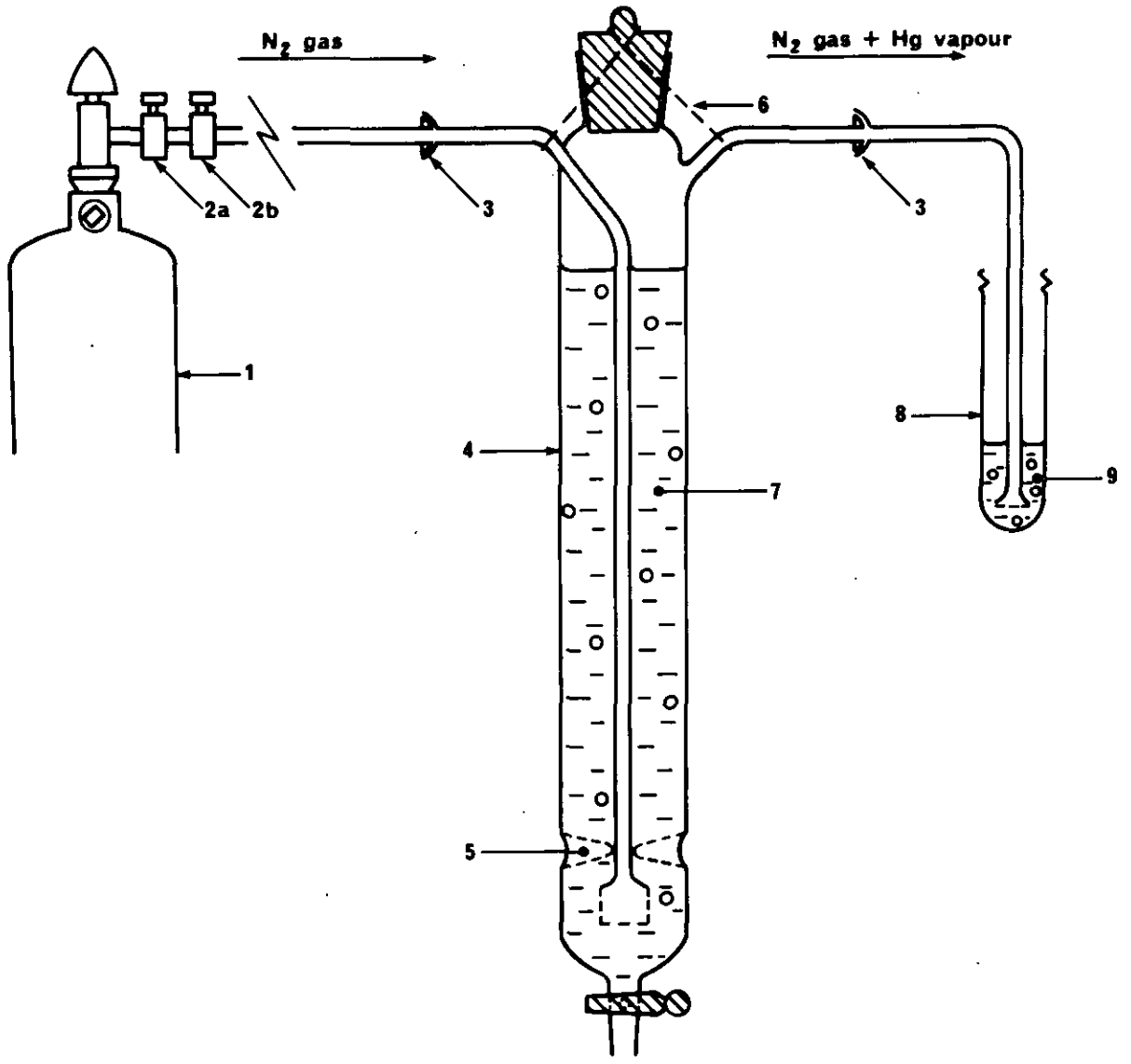


Fig. 1. Apparatus for Stripping and Concentrating Mercury.

1. High purity nitrogen gas.
2a. First fine metering valve.
2b. Second fine metering valve.
3. Ball and socket joints.
4. Sample stripping chamber.
5. Glass bracing spider.
6. Rubber bands.
7. Acidified seawater plus tin II chloride reductant.
8. Screw-cap tube.
9. Acidified permanganate absorbant solution.

## CALIBRATION PROCEDURES

### Standard mercury recovery test from the stripping sequence

Transfer 500 mℓ of acidified sample water from the 1½ litres in the polythene bottle into the stripping chamber and strip off the contained mercury in the routine manner.

Transfer another 200-300 mℓ into the chamber.

Dispense 10 µℓ, or an appropriate multiple, of 1.0 $\mu g.m\ell^{-1}$ mercury standard solution. 10 µℓ contains 10 ng of mercury. Complete filling the chamber with sample water to 500 mℓ mark (Note 24).

Proceed with the stripping routine.

Repeat the procedure with a second, larger spike of mercury standard.

Notes

23. A minimum of 2 mercury recovery tests should be carried out every working session. This usually means at least 2 every operating day. Where it is known or suspected that significantly different water types have been sampled - e.g. significant differences in the range of mercury concentration, salinity, turbidity or temperature - two or more recovery tests should be performed on each type.

24. Spiking the water before all sample water has been added ensures reasonably good mixing of mercury standard throughout the chamber. If the standard were dispensed last it would be concentrated in the surface layer or even on the inside glass wall of the chamber above the 500 mℓ mark. $SnCl_2$ solution added in these circumstances would come into immediate contact with a relatively concentrated zone of mercury and result in rapid evolution of mercury vapour which would be lost before the stopper or the permanganate absorbant tube was in place.

### Blanks and Controls

Sample acid: The mercury blank for the $HNO_3$ used is most reliably estimated from knowing the stripping efficiency (mercury recovery from the stripping operation) combined with the incremental mercury signal from two or more injections of acidified permanganate solutions at different acid concentrations, e.g. 5% and 15%.

Note

25. At some risk in interpreting the absorbance readings, the mercury blank may be obtained by stripping 2 lots of 500 mℓ aliquots of the same sea-water containing different additions of $HNO_3$, say 5 mℓ and 25 mℓ. Any increment of mercury may be due to the extra 20 mℓ of acid. On the other hand the more acidic, non-standard conditions may release a more refractory fraction of mercury from the sample water which would be impossible to distinguish from mercury in the acid. The magnitude of this problem has not been studied.

Tin II chloride: The blank of this solution is negligible (see Note 7).

Potassium permanganate: Prepare a duplicate set of 3 control tubes for each day's work and each batch of reagents.

Into 4 mℓ aliquots of acidified permanganate solution dispense 0 (blank), 10 and 20 µℓ of the 1.0 $\mu g.m\ell^{-1}$ mercury standard (equivalent to 0, 20 and 40 ng of mercury per litre of sample).

Notes

26. Standards should cover the range of mercury concentrations expected in samples. Different spikes from the above may be chosen if more appropriate.

27. The control tubes should be subjected to the same storage and aging conditions as the permanganate tubes used for the samples. Therefore prepare them at the same time as the sample tubes. If dispensed before a field trip, take the controls along too, even though they will not be used - to encounter the same environmental conditions as the sample tubes.

LABORATORY REAGENTS AND APPARATUS

Tin II sulphate solution (5% m/V in 1% NaCl, 1% $(HONH_3)_2SO_4$ and 10% $H_2SO_4$)

Dissolve 5.0 g $SnSO_4$ (technical grade or better) and 1.0 g each of NaCl and $(HOHN_3)_2SO_4$ in 100 mℓ of 10% V/V $H_2SO_4$.

Notes

28. This reagent may be prepared without the $(HONH_3)_2SO_4$ which is added as a preservative. Instead it may be stored like the $SnCl_2$ solution, by adding granulated tin and similarly purified by sparging with nitrogen (see Note 7). However only a low level of mercury is likely, which may be tolerable and would report with the permanganate reagent blank.

29. The presence of sodium chloride in the tin reagent mixture stabilizes the mercury equilibrium in the syringe. When sodium chloride is absent there must be no delay injecting the vapour after shaking, otherwise erratic and lower absorption values are obtained. Without salt present there is an inverse relationship between absorbance peak height and the time delay between the completion of shaking and injection (see Table 4).

    Another function of sodium chloride, although not important in water analysis, is that it prevents frothing in the syringe when shaking digested or hydrolyzed samples which contain relatively high concentrations of calcium or organic residues, fish tissues for example.

Hydroxylammonium sulphate, $(HONH_3)_2SO_4$

A.R. grade crystals are required.

Alternative names are hydroxylamine hydrogen sulphate, $(HONH_2)_2.H_2SO_4$, or "hydroxylamine sulphate".

Sodium chloride, NaCl

A.R. grade crystals normally contain negligible mercury.

Standard mercury solution (1.0 µg $Hg.m\ell^{-1}$) and micropipettes

See under FIELD REAGENTS AND APPARATUS, page 5.

All-glass syringe

20 mℓ capacity chamber ("Kampa" interchangeable)

Teflon capillary cut to 120 cm long and plastic connection to the glass nipple (e.g. luer connection Kel F 24 TF44233).

Syringe cap (e.g. glass beads in plastic tubing).

Magnesium perchlorate, $MgClO_4$, drying tube

Length of glass tubing, about 6 mm diam. x 60 mm long, filled with fine granulated $MgClO_4$, optionally plugged at either end with glass wool. Change frequently, preferably every working day for careful work.

Note

30. The use of a $MgClO_4$ drying tube to remove water mist in the carrier gas before it enters the absorption cell has been criticised for reducing the height of the absorption peaks, impeding the flow of carrier gas as it becomes exhausted, and increasing the time of analysis by requiring frequent changing (Christmann and Ingle 1976). A preheating chamber was substituted. This comprised a length of glass tubing held at 110°C to vaporize the water mist. This system was claimed to be superior. No mention was made of possible gas expansion problems with the changes in temperature. While we have not compared the relative merits of the two systems, we have found the $MgClO_4$ system quite satisfactory.

Atomic absorption spectrophotometer

Including mercury lamp, mercury vapour cuvette (Note 31), and a supply of high purity nitrogen gas.

Note

31. The volume of the absorption cuvette must be large enough to retain all the mercury vapour from each sample in the light path at the same time. This method was tailored for a cuvette of 29 mℓ capacity and 170 mm light path length - the standard Varian accessory.

## LABORATORY PROCEDURE

The entire 4 mℓ of each mercury-absorbed-in-permanganate solution (samples, standards and controls) is used for an atomic vapour absorption determination of the mercury concentration.

Maintain a slow flow (100-150 mℓ. $min^{-1}$) of high purity nitrogen through the drying tube and absorption cuvette before using the instrument for sample determinations. It is more important to have a *constant* flow rate than to know the exact flow rate.

Before analysis add a few crystals of hydroxylammonium sulphate to each sample in its screw cap tube (Note 32), recap and rock the tube gently until the solution is clear. This redissolves any precipitated $MnO_2$ and the mercury adsorbed on it. Vigorous shaking extracts mercury from the liquid into the vapour phase and must be avoided. Add a few crystals of sodium chloride (10-30 mg) and similarly dissolve gently (Note 33).

Draw into the 20 mℓ capacity syringe, in succession: the 4 mℓ sample aliquot (Figure 2a); enough air - 0.5 to 1.5 mℓ - to bring the plunger back to the 5 or 6 mℓ mark; 1.0 mℓ of tin II sulphate reducing solution and finally, with the syringe held vertically upwards, more air - about 14 mℓ - to bring the plunger back to the 20 mℓ mark on the syringe barrel (Note 34). Holding the plunger steady, replace the teflon capillary with a cap - e.g. a plastic tube with a glass bead or two inside (Figure 2b).

Shake the syringe and contents with a vigorous sideways, or "castanet-like" action of the wrist for 10-20 seconds. Divert the nitrogen gas flow to exhaust through the 3-way tap. Remove the bead-tube cap and the cap of the injection port. Insert the syringe. Slowly inject the gas volume (15 mℓ) containing the mercury vapour through the drying tube into the absorption cuvette until the solution level reaches point A in Figure 2c (Note 29).

Finally, remove the syringe carefully, to retain the 5 mℓ sample solution intact, replace cap on injection port, and redirect the slow flow of nitrogen through the cell. This flushes the mercury vapour remaining in the drying tube space into the path of the absorption light beam. The peak absorbance, produced before mercury starts to be removed from the far end of the cuvette, is taken as the sample signal (Figure 3).

The partition of mercury between the aqueous and vapour phases is such that only about 50% of the total is in the vapour phase and therefore injected into the spectrophotometer. Repeat the injection routine on the mercury depleted sample retained in the syringe. Draw in a fresh 15 mℓ of air into the syringe on top of the partly exhausted sample and re-partition the residual mercury by shaking. Inject as before (after the baseline reading has returned to zero). This peak height should be 50% of the first one.

The arithmetic sum of the two absorbance peaks is a more precise estimator of the mercury concentration than the first peak alone (Note 35).

### Notes

32. The addition of hydroxylammonium sulphate is not necessary if the $KMnO_4$ has not decomposed to form $MnO_2$, such as when the analysis is done within a few hours of collection and the solution has been

kept at less than 10°C in a cold room or refrigerator. Even so, omission of this step is probably risky at very low mercury concentrations.

33. Sodium chloride stabilizes the mercury in solution after the permanganate has been reduced. No losses of mercury are subsequently incurred, whether the remainder of the procedure is carried out immediately or several hours later.

34. After a little experience there is no difficulty in drawing up the whole 4 mℓ sample volume through the syringe capillary.

    It is essential to maintain a constant gas:liquid volume ratio for each suite of samples and standards. For example, if it were decided to use a 2 mℓ sample instead of 4 mℓ - perhaps because the mercury concentration were offscale - and to keep the same volume of the other reagents, then the gas:liquid ratio would change from 3:1 to 5:1 and the peak absorbance signal would not be 50% of the original, in proportion to the lesser amount of mercury being measured, but more like 60%.

35. The injection routine may be repeated on the same sample as many times as desired. Each peak height is usually 50% of the one before down to the detection limit. However, some anomalous patterns of sequential peak heights have been obtained which so far remain unexplained.

    Because of increasing total time per sample (30-40 seconds per injection), and decreasing precision as peaks approach the detection limit, there is little advantage in extending beyond 2 or 3 replicate injections.

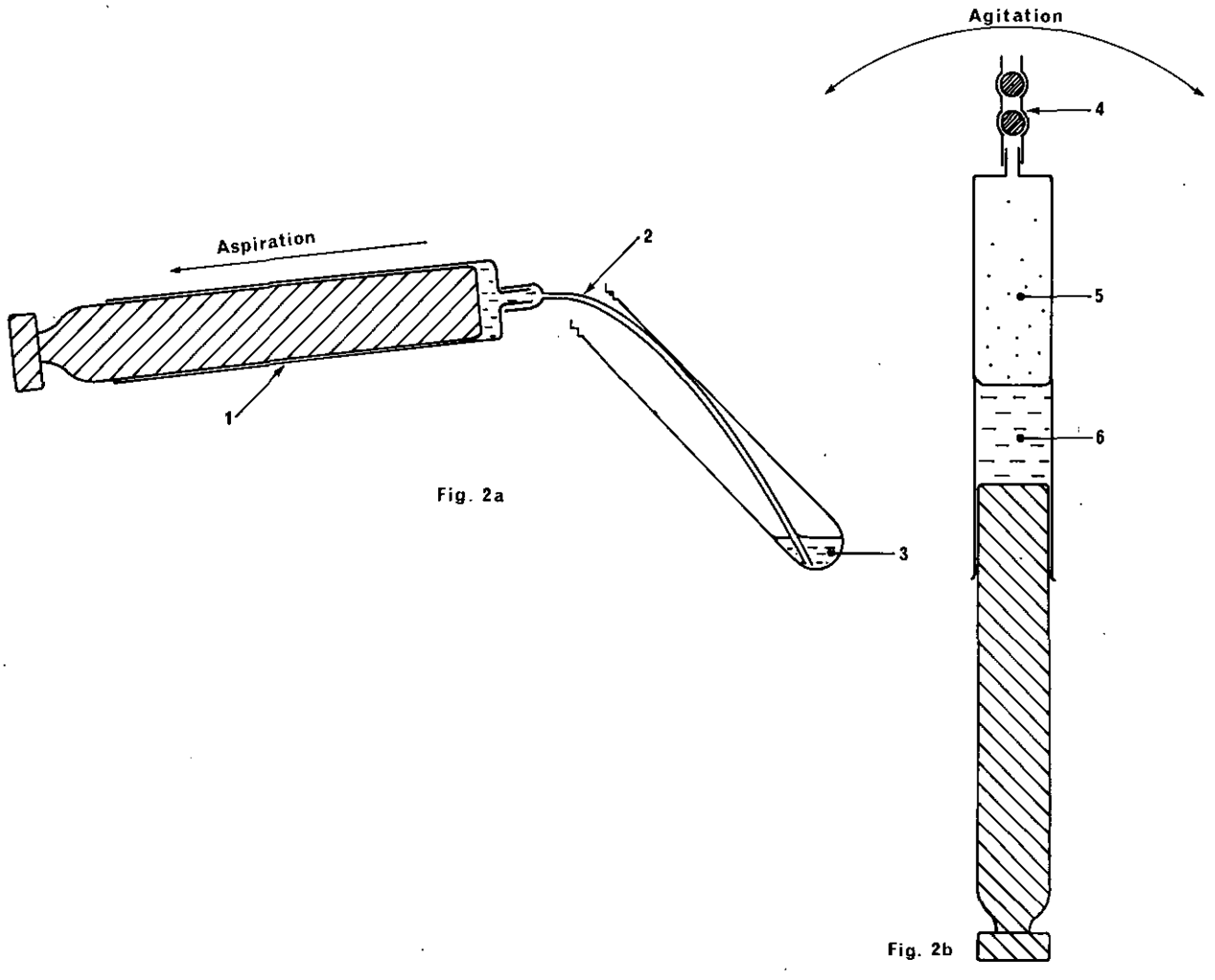


Fig. 2. Reduction and Injection of Mercury.

1. All-glass syringe.
2. Teflon capillary.
3. Mercury-in-permanganate sample.
4. Bead cap.
5. Mercury vapour (in air).
6. Mercury-in-permanganate sample + tin II reducing reagent.
7. Three-way tap.
8. Magnesium perchlorate moisture trap.
9. Mercury lamp.
10. Absorption cuvette.
11. Atomic absorption detector.
12. Injection port plug.

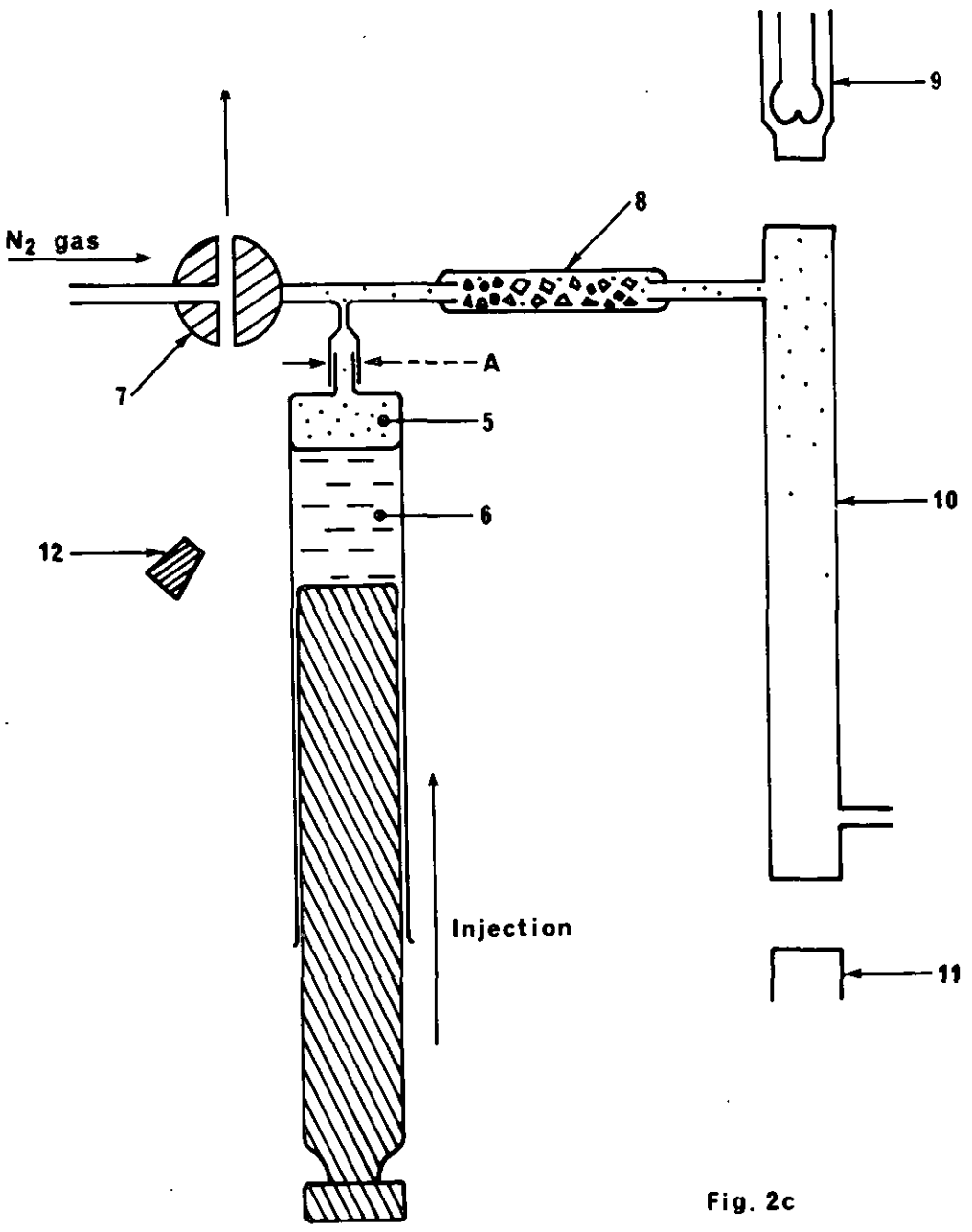


Fig. 2c

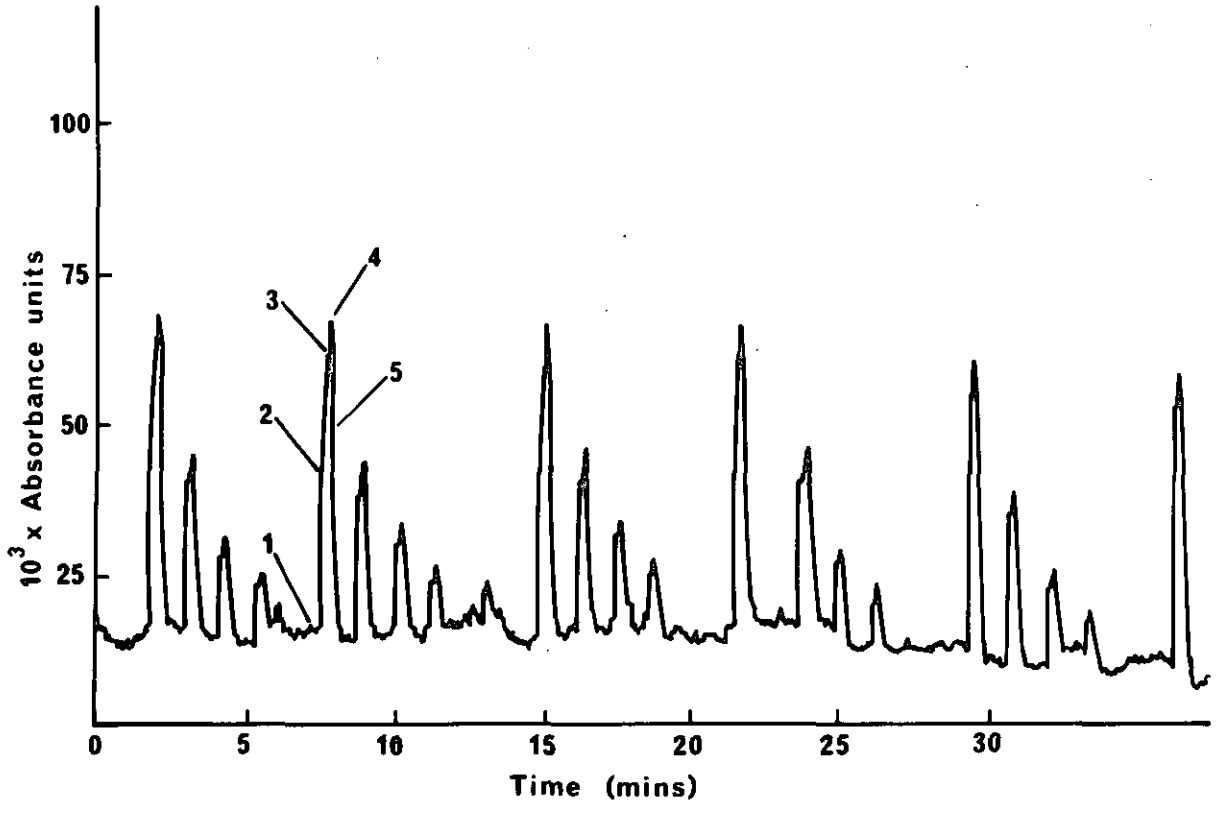


Fig. 3. Actual Recorder Trace of Mercury Absorbance Peaks of Trials 1 to 5, Table 3. (Scale x 1)

1. Base line.
2. Mercury entering absorption cuvette during injection.
3. Plateau absorbance before nitrogen gas stream is reconnected.
4. Peak absorbance when all mercury is in the light path.
5. Mercury being flushed from cuvette by nitrogen.

# DISCUSSION

## Detection Limit

For a Varian-Techtron AA6 instrument with cuvette absorption length of 170 mm, the absolute detection limit is of the order of 0.5 ng Hg - usually between 0.2 and 0.8 ng depending on stripping efficiency. This amount of mercury gives a combined read-out signal change (the sum of two successive peaks) of 0.002 absorbance units as calculated from

$$\frac{\text{change in } (\text{peak}_1 + \text{peak}_2)}{\text{standard addition of Hg}} \text{ when the}$$

instrumental drift is < 0.001 absorbance units.

Using values from Tables 2 and 3

$\sum_{1}^{2} a = 0.0157$ for a 5 ng Hg addition

$\sum_{1}^{2} a = 0.0630$ for a 20 ng Hg addition

therefore (0.0630-0.0157) absorbance units = 15 ng Hg

$$\therefore \text{ 0.002 absorbance units} = \frac{15 \times 0.002}{(0.0630-0.0157)}$$

$$= 0.6 \text{ ng Hg, which is}$$

the detection limit in this instance.

If the standard spike of mercury is greater than 50 ng (equivalent to 100 ng $Hg.\ell^{-1}$ for 500 mℓ samples) then consistent values for the detection limit are obtained. If the spike is of the order of 2-10 ng Hg then the values are more scattered indicating that the detection limit calculated from large spikes is more apparent than real. In short one cannot detect a real spike of 0.5 ng in practice at low concentration levels, as is evident from the scatter of values particularly in Table 1.

A common explanation for this is that the stripping efficiency - recovery of mercury - depends on the percentage of labile mercury available in the sample and this depends to some extent upon wall effects and the amount and type of other, especially organic, matter present. Presumably the spike can be immobilized too, but the effect of this is not noticeable when the spike is very much larger than the "binding" capacity of the solution. Hence the improvement in reproducibility for large standard additions and consequently the very low apparent detection limits calculated from such trials.

Whatever the reason for erratic reproducibility at low concentrations there is the practical corollary that there is no particular advantage in having undetectable blank readings for the laboratory reagents provided the readings are consistent and small - no more than about 50% of the minimum value expected from the samples -; a detectable blank can be an advantage both as an absorbant for extraneous binding substances in solution and as a "marker" above the electronic background drift.

The background electronic drift ("noise") can usually be maintained $\leqslant 0.001$ absorbance units if the instrument is kept on at all times except for the lamp which needs a half hour warm up period only. An exception is when high atmospheric humidity causes water droplets to condense on the external quartz surfaces of the absorption cuvette.

Partition Equilibrium Constant

The method depends on removing mercury from the liquid to the vapour phase. Reproducibility is critically dependent on maintaining those factors constant which affect the partitioning of free mercury between the liquid and gaseous phases.

The distribution (or partition) equilibrium constant

$$K = \frac{\text{conc'n of Hg in vapour phase}}{\text{conc'n of Hg in liquid phase}}$$

$$= \frac{(\text{mass Hg in gas phase, } m_g)/(\text{volume of gas, } V_g)}{(\text{mass Hg in liquid phase, } m_\ell)/(\text{volume of liquid, } V_\ell)}$$

$$= \frac{m_g . V_\ell}{m_\ell . V_g} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \text{I}$$

Let $a_1$ = absorbance reading after first equilibration of liquid phase with air

Let $a_2$ = absorbance reading after second equilibration of same liquid phase with similar volume of air

Now $a_1 \propto m_{g_1}$

and $a_2 \propto m_{g_2}$

$$\therefore \frac{a_1}{a_2} = \frac{m_{g_1}}{m_{g_2}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \text{II}$$

$$\text{also } m_{\ell_1} = m_{g_2} + m_{\ell_2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \text{III}$$

$$\therefore K = \frac{m_{g_1} . V_{\ell_1}}{m_{\ell_1} . V_{g_1}} = \frac{m_{g_2} . V_{\ell_2}}{m_{\ell_2} . V_{g_2}}$$

If $\frac{V_\ell}{V_g}$ is constant, $\frac{m_{g_1}}{m_{\ell_1}} = \frac{m_{g_2}}{m_{\ell_2}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \text{IV}$

$$= \frac{m_{\ell_1} - m_{\ell_2}}{m_{\ell_2}} \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{ (from III)}$$

$$= \frac{m_{\ell_1}}{m_{\ell_2}} - 1$$

$$= \frac{a_1}{a_2} - 1 \quad \ldots\ldots\ldots\ldots\ldots \text{ (from IV And II)}$$

$$= \frac{a_1 - a_2}{a_2}$$

$$\therefore K = \frac{a_1 - a_2}{a_2} \cdot \frac{V_\ell}{V_g}$$

Hence the peak heights $a_1$ and $a_2$ are affected by K and by the gas:liquid ratio. Two sets of gas:liquid equilibria are involved, one at the nitrogen stripping stage, another at the syringe injection stage. Therefore it is most essential to maintain bubbling rates, syringe air volumes etc., constant for each set of determinations. One of the reasons for not recommending a manifold system to distribute gas from one nitrogen cylinder to several stripping chambers, is the difficulty in controlling fluctuations in pressure within the remainder of the system, and therefore the gas flow rate to other units, when one unit is being serviced. It is felt that for optimum control each unit should have its own gas supply. Since it becomes awkward to operate more than two stripping units at the same time a large number of separate gas cylinders is not required.

Other parameters which affect K are temperature, pressure, and salting-out effects. Also, in general, equilibrium "constants" are only constant over a limited range of concentrations.

Pressure, Temperature and Salting-out Effects

The pressure effect is minimized in the first "equilibration" in the stripping chamber by preventing a high back pressure from building up, which would happen for example if a single capillary orifice were used for gas distribution into the permanganate solution. In the syringe equilibration the plunger should not be inadvertently compressed while agitating the gas liquid mixture.

Koirtyohann and Khalil (1976) showed that K increased with increasing temperature - as would be expected from common sense considerations - but that the effect was small over the range 0-30°C for the static conditions of the syringe technique. The temperature effect may be more pronounced in a dynamic system in which the absorbance peak height depends on the *rate* of mercury evolution, rather than the quantity evolved (Clifton 1975). It may partly contribute to the poor reproducibility of the stripping stage of the method in some trials.

Koirtyohann and Khalil derived an expression for K equivalent to that above, and obtained an experimental value of 0.4 and also, from solubility data for mercury in the literature, a calculated value of 0.36 to substantiate their work.

Their experimental technique was not described in detail. In some respects it was similar to our own system, although one significant difference was their injection of a gas volume (30 mℓ) into an absorption cuvette which could only accept one third of it (9.4 $cm^3$) at a time. The mercury concentrations used were not stated clearly.

We failed to get consistent experimental values for K. They varied widely, as much as from 0.10 to 0.55 between different sets of samples, and over a narrower range, e.g. from 0.46 to 0.55, between consecutive injections from the liquid phase of the one sample.

Although K is sensitive to small changes in the relative peak heights of a pair of equilibria being compared, particularly at low absolute concentrations, a precise explanation for the scatter of K values cannot be found at this stage. But three general observations can be made. First, K is not significantly higher when NaCl is present as one of the syringe reagents. That is, no salting-out effect is evident which favours a higher equilibrium proportion of mercury in the vapour phase. Second, since the proportion of mercury in the vapour injected from each equilibration is erratic it follows that total precision increases as the number of successive injections increases. If the fraction of mercury is low for a first injection, it leaves the fraction of mercury remaining in the liquid phase relatively high which results in relatively high second and subsequent peaks from following equilibrations. If portioning is continued down to the detection limit (usually 5 to 9 injections) and all peaks summed, then all mercury originally in the syringe is measured and the problem of injecting a constant fraction of each sample and the standards is eliminated. Third, K is frequently, but not always, found to be low for the first injection compared with later equilibrations on the same sample, especially if the mercury concentration is high, suggesting that it is difficult to obtain good partitioning into the gas phase from concentrated solutions under the conditions of this method. On the other hand the values of K appear to decrease as mercury concentration decreases, although the evidence is confusing. This drop off in the values of K implies that the last traces of mercury are difficult to extract from solution - an observation mentioned elsewhere in the discussion (pages 22, 26).

Such trends are indicated in the most precise data quoted, here, the mean peak values from Table 3.

$K_{1,2} = \frac{40.2 - 22.8}{22.8} \cdot \frac{5}{15} = 0.26$. Similarly $K_{2,3} = 0.29$, and

$K_{3,4} = 0.23$

Tables 1, 2 and 3 illustrate the increase in reproducibility obtained by including the second equilibration peak. Such improvement does not necessarily continue for further equilibrations especially if the peaks approach the detection limit.

These data were produced from water containing low concentrations of mercury and without sodium chloride crystals added after the hydroxylammonium sulphate or included in the tin sulphate reagent. Equilibrated samples were injected immediately - within 5 to 10 seconds - after agitation to avoid the time delay effect shown in Table 4.

The coefficient of variation of the complete procedure is 40% ($\sum_{1}^{2}a$, Table 1) at the 40 ng.$\ell^{-1}$ level, while the coefficient of variation of the syringe procedure alone is only 10% ($\sum_{1}^{2}a$, Table 2) at the 10 ng.$\ell^{-1}$ level. Of this 10% about 6% ($\sum_{1}^{2}a$, Table 2 - $\sum_{1}^{2}a$, Table 3) can be attributed to errors in dispensing the small volume of standard additions and perhaps in the cleaniness of the tubes.

Thus the stripping procedure contributes by far the greater part of the total uncertainty in the method for determining mercury in water. Mercury determinations on biological tissues and on minerals which, after a digestion step, need to utilize the syringe procedure only, can be of a very high precision indeed.

Absorption Efficiency and Stripping Efficiency

Because a potassium dichromate solution acidified with nitric acid is an excellent preservative for mercury in sea-water (Feldman 1974, Lo and Wai 1975) tests were carried out in which mercury was stripped from spiked (500-2000 $ng.\ell^{-1}$ level) samples of sea-water into an absorbant of acidified dichromate solution. It absorbed only 70% of the mercury under the same conditions that acidified permanganate solutions absorbed 100%. $K_2Cr_2O_7$ has a lower oxidation potential than $KMnO_4$ and this is presumably the reason why it fails to trap all mercury vapour passed through it. It was deduced that the acidified permanganate solution absorbed 100% of the mercury vapour passing into it, since three permanganate traps were placed in series after the stripping unit, and no mercury was found to pass over into the second or third tubes.

While conditions can be fairly easily controlled to ensure that all mercury vapour released in the stripping unit is absorbed by permanganate solution - "100% absorption efficiency" - getting the mercury released in the first place can be a problem.

Repeated experiments show that at the 5 ng $Hg.\ell^{-1}$ level the stripping efficiency can be quite variable between different sets of samples and as low as 20%. As the mercury concentration rises the stripping efficiency and its reliability quickly increase to a fairly constant 93% at the 500 ng $Hg.\ell^{-1}$ level and higher.

The $V_\ell:V_g$ ratio at the syringe equilibrium is 5 mℓ:15 mℓ, i.e. 1:3, and results in 50% of the total mercury present being in the vapour phase. If the same situation is assumed to apply at the stripping "equilibrium". then 50% of the mercury in a 500 mℓ sample would be removed for every 1500 mℓ of nitrogen bubbled through. At a gas flow rate of 240 $m\ell.min^{-1}$, 3600 mℓ bubbles through the stripper in 15 minutes, and a crude theoretical stripping efficiency of 80% can be calculated: 50% from the first 1500 mℓ, plus 25% for the next 1500 mℓ, plus 5% from the remaining 600 mℓ. By similar reasoning the theoretical stripping efficiency for a 100 mℓ sample, sparged with nitrogen at 150 $m\ell.min^{-1}$ for 15 minutes, is >99%.

However such simply determined figures have not been closely reproduced in practice, indicating that other factors also have a significant effect on stripping efficiency especially at low mercury levels. The problems of achieving a reliable stripping efficiency at low mercury concentrations remains unresolved.

It cannot be assumed that a stripping efficiency derived from the use of standard additions of ionic mercury - which is easily recoverable - is necessarily the same as the stripping efficiency of mercury originally in the sample and which is associated with unknown and possibly more stable chemical species.

Whether more mercury would be released from sea-water subjected to an organic oxidation step was not investigated. The execution of an oxidation step introduces more uncertainty due to contamination possibilities, especially in routine work. Filtration likewise increases the chances of inadvertent contamination. However Fitzgerald and Lyons (1975), working in the 5-15 $ng.\ell^{-1}$ range, found no significant differences between "reactive" mercury concentrations measured directly in pre-acidified open-ocean sea-water and "total" mercury determinations in "organic-free" photo-oxidized samples. This finding may not be true of polluted water or of water otherwise high in organic matter.

## Effect of Sodium Chloride

Sodium chloride is included as a reagent in most similar analytical procedures for mercury determination described in the literature, usually without critically examining the reasons for doing so. Its role is poorly understood. Some articles speculate about the volatility and stability of bonds between mercury and chlorine ions.

We found that 2-3% sodium chloride added to distilled water samples spiked with 1000 ng. $Hg.\ell^{-1}$ increased the stripping efficiency from 68% to 93%. Hence the salinity of sea-water appears ideal for highly efficient stripping, but that fresh and brackish water samples would need some sodium chloride added (3% m/V). No tests were actually conducted on natural fresh water samples.

The role of sodium chloride in increasing the apparent stripping efficiency of mercury from water samples (increase in mercury volatility), contrasts with the stabilizing effect of chloride ions at the syringe equilibration stage when it prevents the loss of mercury (decrease in mercury volatility). The latter effect is confirmed by the finding of Koirtyohann and Khalil (1976) that when chloride ions are absent, mercury is released into the gas phase from acidified samples in the syringe in the complete absence of the reducing agents. They state an absorbance signal about 20% as large as that observed in the presence of the reducing agents. We have found the figure could be higher, up to 40%. If standard mercury additions were easily lost from acidified water samples before chloride ions were added or before the stripping procedure was started, it would register as a decrease in stripping efficiency, preventable by chloride ions and therefore consistent with the effect of chloride at the syringe stage. This point has not been investigated.

Table 1

Reproducibility test of complete stripping and syringe procedures

12 x 500 mℓ aliquots taken from a bulk sample of unfiltered, acidified sea-water and carried through the complete procedure.

| Trial | $10^3$ x Absorbant Peak Heights | | | | | |
|---|---|---|---|---|---|---|
| | $a_1$ | $a_2$ | $a_3$ | $a_4$ | $\sum_1^2 a$ | $\sum_1^4 a$ |
| 1 | 42* | 28 | 19 | 4 | 70 | 93 |
| 2 | 26 | 17 | 10 | 6 | 43 | 59 |
| 3 | 22 | 15 | 11 | 10 | 37 | 58 |
| 4 | 11 | 10 | 9 | 9 | 21 | 39 |
| 5 | 14 | 13 | 12 | 11 | 47 | 50 |
| 6 | 12 | 8 | 8 | 6 | 20 | 34 |
| 7 | 9 | 11 | 11 | 11 | 20 | 42 |
| 8 | 25 | 20 | 18 | 15 | 45 | 78 |
| 9 | 19 | 14 | 13 | 13 | 33 | 59 |
| 10 | 28 | 21 | 18 | 16 | 49 | 83 |
| 11 | 18 | 17 | 14 | 13 | 35 | 62 |
| 12 | 12 | 13 | 12 | 12 | 25 | 49 |
| mean, $\bar{x}$ | 19.38 | 15.58 | 12.92 | 10.50 | 37.08 | 58.83 |
| std.dev., s | 9.46 | 5.50 | 3.65 | 3.71 | 14.87 | 18.08 |
| coeff. of var'n, $\frac{100s}{\bar{x}}$ | 48% | 35% | 28% | 35% | 40% | 31% |

*chart recorder sensitivity used for all tables
= 2mV per 10 inches (full chart paper width)

Table 2

Reproducibility test of complete syringe procedure

A single solution of acidified permanganate prepared; 4 mℓ aliquots dispensed into 10 separate tubes; each individually spiked with 5 ng of mercury and reduced with hydroxylammonium sulphate crystals; each 4 mℓ withdrawn into syringe, equilibrated and injected 4 times.

| | $10^3$ x Absorbant Peak Heights | | | | | |
|---|---|---|---|---|---|---|
| Trial | $a_1$ | $a_2$ | $a_3$ | $a_4$ | $\sum_1^2 a$ | $\sum_1^4 a$ |
| 1 | 6 | 7 | 7 | 5 | 13 | 25 |
| 2 | 8 | 6 | 6 | 3 | 14 | 23 |
| 3 | 11 | 8 | 7 | 5 | 19 | 31 |
| 4 | 10 | 7 | 6 | 3 | 17 | 26 |
| 5 | 9 | 7 | 4 | 2 | 16 | 22 |
| 6 | 9 | 7 | 5 | 3 | 16 | 24 |
| 7 | 9 | 7 | 5 | 4 | 16 | 25 |
| 8 | 7 | 8 | 6 | 4 | 15 | 25 |
| 9 | 10 | 6 | 5 | 3 | 16 | 24 |
| 10 | 9 | 6 | 4 | 4 | 15 | 23 |
| mean, $\bar{x}$ | 8.80 | 6.90 | 5.50 | 3.60 | 15.70 | 24.80 |
| std.dev., s | 1.48 | 0.74 | 1.08 | 0.97 | 1.64 | 2.49 |
| coeff. of var'n, $\frac{100s}{\bar{x}}$ | 17% | 11% | 20% | 27% | 10% | 10% |

Table 3

Reproducibility test of injection routine only

50 mℓ of acidified permanganate solution prepared, spiked with 250 ng of mercury (= 20 ng.4mℓ$^{-1}$) and reduced with hydroxylammonium sulphate crystals; 4 mℓ aliquots withdrawn into syringe, each equilibrated and injected 4 times.

$10^3$ x Absorbant Peak Heights

| Trial | $a_1$ | $a_2$ | $a_3$ | $a_4$ | $\sum_1^2 a$ | $\sum_1^4 a$ |
|---|---|---|---|---|---|---|
| 1 | 42 | 23 | 13 | 7 | 65 | 85 |
| 2 | 42 | 24 | 13 | 7 | 66 | 86 |
| 3 | 42 | 23 | 12 | 7 | 65 | 84 |
| 4 | 41 | 23 | 12 | 8 | 64 | 84 |
| 5 | 39 | 23 | 12 | 5 | 62 | 79 |
| 6 | 40 | 23 | 13 | 9 | 63 | 85 |
| 7 | 39 | 24 | 13 | 8 | 63 | 84 |
| 8 | 42 | 21 | 10 | 7 | 63 | 80 |
| 9 | 38 | 22 | 12 | 6 | 60 | 78 |
| 10 | 37 | 22 | 11 | 7 | 59 | 74 |
| mean, $\bar{x}$ | 40.20 | 22.80 | 12.10 | 7.10 | 63.0 | 81.90 |
| std.dev., s | 1.87 | 0.92 | 0.99 | 1.10 | 2.21 | 3.93 |
| coeff.of var'n, $\frac{100s}{\bar{x}}$ | 5% | 4% | 8% | 15% | 4% | 5% |

Table 4

Effect of time delay when sodium chloride absent from tin sulphate reagent mixture

Three 4 mℓ aliquots taken from the same mercury-in-permanganate solution (20 ng Hg.4mℓ$^{-1}$). Each equilibrated and injected 3 times. First aliquot injected immediately after completing shaking (minimum delay possible is 5-10 seconds). Aliquots 2 and 3 retained in syringe without agitating for periods indicated between shaking and injecting.

| Aliquot No. | Time Delay | $10^3$x Absorbant Peak Heights | | |
|---|---|---|---|---|
| | | $a_1$ | $a_2$ | $a_3$ |
| 1 | 5-10 secs. | 40 | 23 | 12 |
| 2 | 25-30 secs. | 34 | 22 | 10 |
| 3 | 55-60 secs. | 26 | 14 | 10 |

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