Mercury concentrations in open-ocean waters: Sampling procedure[1]

Abstract—A PVC sampler was found suitable for collecting seawater samples at depth for Hg determinations. Mercury concentrations averaged 8 ± 3 ng liter^{-1} in surface seawater in the northwest Atlantic Ocean.

A rather broad range for Hg concentrations in seawater (nondetectable to 364 ng liter^{-1}) has recently been reported (Weiss et al. 1972; Topping and Pirie 1972; Carr et al. 1972; Chester et al. 1973; Olafsson 1974). Although this range may reflect the natural variability for the amounts and distribution of Hg in ocean waters, it also suggests that there may be difficulties with the accurate measurement of Hg in seawater.

Low concentrations of Hg may be observed because the analytical procedure does not measure all the chemical fractions of Hg present (Fitzgerald and Lyons 1973). High concentrations may result when interferences such as volatile organics enhance the absorption at the Hg wavelength (253.7 nm) during the usual flameless atomic absorption procedure (Lindstedt 1970; W. F. Fitzgerald et al. 1974). In this study, we used cold-trap preconcentration and measurement of Hg by gas phase atomic absorption spectrophotometry (W. F. Fitzgerald et al. 1974). The direct measurement of Hg in preacidified seawater samples (1.2–1.3% HNO_3 acid) has been defined as "reactive" mercury. Total mercury determinations are carried out on seawater in which the organic matter has been destroyed through photo-oxidation (Armstrong et al. 1966; Fitzgerald 1970). The precision of analysis reported as a coefficient of variation is 30% at 5 ng Hg liter^{-1}, 20% at 10 ng Hg liter^{-1}, and 15% at 25 ng Hg liter^{-1}; the detection limit is 2 ng Hg liter^{-1}.

In addition to analytical difficulties, accurate Hg determinations in seawater will depend significantly on careful sampling at sea and on the sample storage procedure (Coyne and Collins 1972; Newton and Ellis 1974; Feldman 1974). Indeed, these investigations suggest that under nonacidified conditions Hg can be lost rapidly and affect concentrations within a sampler during a hydrocast. Thus, before extensive Hg sampling at depth in the ocean, we devised and tested a sampling procedure.

We are grateful to C. D. Hunt for suggesting the test procedure for the samplers. The sampling program was conducted with the assistance of the captain and crew of the RV *Trident* and our colleagues at the University of Rhode Island.

A recommended procedure for preserving natural water samples for Hg analyses is preacidification (concd HNO_3) to yield a final sample pH of 1 in either glass or polyethylene containers (Coyne and Collins 1972; Carr and Wilkness 1973). We tested a similar preservation procedure with seawater in polyethylene, Pyrex glass, and Teflon containers.

Samples stored in linear polyethylene containers (jerry-cans) showed abnormally high absorption due either to the presence of volatile organic plasticizer material or to polyethylene residue leached by the concentrated HNO_3 and the solution of pH 1. This artifact can be reduced significantly by an ultraviolet photo-oxidative treatment (Armstrong et al. 1966; Fitzgerald 1970) of the water sample before analysis. Wet oxidation/digestion techniques with strong acids, $KMnO_4$, or $KCrO_4$, may also destroy the major fraction of these organic residues. Nevertheless, procedures that use acidified sample storage in polyethylene bottles and gas phase Hg detection may be subject to artificial Hg absorption by organic material.

In our initial open-ocean investigations, time studies over a 2-week period suggested that collection and storage of seawater samples in preacidified Pyrex bottles would be suitable for Hg determinations (Fitzgerald and Hunt 1974). However, in a later coastal water study, unusually large blank values were occasionally observed both for Pyrex containers and glass BOD

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Table 1. A comparison of Hg determinations in surface seawater collections from preacidified Teflon bottles and from 5-liter PVC samplers.

Station No. and Location		S ‰	Temp °C	Hg conc (ng/liter) A* Analyses			A* mean	B+ Analyses			B+ mean
1	40°00.8'N, 66°17.7'W	35.31	14.0	[3]‡	8	8	6	6	7	[10]	8
2	36°35.3'N, 66°03.2'W	36.26	23.8	[6]	4	[6]	5	6	4	[7]	6
3	32°54.4'N, 66°07.0'W	36.57	21.1	13	[9]	8	10	8	10	[11]	10
4	32°03.0'N, 64°52.2'W	36.10	22.5	5	7	13	8	13	7	10	10
Mean and standard deviation of the 24 analyses							8 ± 3				
Blank determinations (stations 2-4)				Below detection limits							

* Preacidified Teflon bottle.
+ Five-liter PVC sampler (General Oceanics, Inc., Miami, Fla.).
‡ Values in brackets represent Hg measurements for seawater stored in separate containers.

bottles. Rather than risk costly open-ocean seawater collections to the unreliable storage in glass we chose to use relatively expensive Teflonware.

Seawater samples for Hg analysis were collected and preserved in acid-cleaned Teflon (FEP) bottles (0.5 to 2 liter) preacidified with high purity concentrated nitric acid ($Hg < 0.2$ ng ml^{-1}) to yield a 1.2–1.3% acid seawater solution. Local coastal water having an average measured reactive Hg concentration of 6 ± 2 ng $liter^{-1}$ maintained this concentration for 3 weeks. Samples were tested following storage at room temperature for 80 s, 21 min, 1.5 and 4 h, 2.2, 12, 13, and 20 days. The blank determinations for the Teflon containers are, in general, below our detection limits.

As a continuous check on the effectiveness of this storage procedure, open-ocean seawater collections, including the samples reported here, are preserved in two separate Teflon containers. No attempt is made to analyze these samples sequentially and a 2–4 week separation is common between determinations. Within the analytical precision of the cold-trap method no change in the natural seawater concentrations of reactive Hg occurs between the time of collection and analyses (3–8 weeks later).

During RV *Trident* cruise 152 (8–19 May 1974), we took both surface seawater samples and collections for vertical Hg profiles (to 750 m) at four stations between Narragansett, R. I., and Bermuda (locations in Table 1).

We used the following experimental design to test both the effectiveness of a widely used 5-liter PVC sampler (General Oceanics) (Teflon-coated stainless steel closing spring) and the sample handling for the determination of Hg in open-ocean seawater. Before a sampling cast began, surface collections were carefully made from a rubber workboat some 0.8–1.5 km away from the *Trident*. The workboat was driven by a small electric motor, allowing samples to be taken off the bow while underway. At stations 1–3, two surface samples were collected by hand (using polyethylene gloves) in 500-ml Teflon bottles preacidified as noted with concentrated HNO_3 to yield a 1.2–1.3% acid seawater solution. In addition to these samples, surface seawater was also collected in a 5-liter PVC sampler. The Teflon bottles and the sampler were stored before and after collection in a polyethylene bag to prevent contact with the rubber workboat and the ship. At station 4, sampling operations were the same, except that one 2-liter Teflon bottle was used.

The hydrocast began immediately after our return to the ship. The first bottle on the hydrowire was the closed PVC sampler containing the surface water collection. This bottle went down closed with the surface sample to 1,000 m followed by four additional open and cocked samplers set for various depths to 750 m. The cast was conducted in the usual fashion, with samples from each bottle transferred to preacidified Teflon storage containers for Hg determinations on shore. The surface seawater remained in the sampler under test for about 1 h. At each station, a different PVC sampler was used.

At stations 2–4, preacidified 500-ml or 2-liter (station 4) Teflon bottles were carried through the entire surface sample collection procedure as blanks. The bottles were opened in the workboat for an interval comparable to the time needed to collect a surface sample. Distilled deionized water was added to them on return to the *Trident*. In each case, the blank determination was below our detection limits (2 ng Hg liter^{-1}).

Our results are summarized in Table 1. Within the analytical precision limits, the Hg concentrations in the surface seawater collected in Teflon are not significantly different from those in the same water after 1 h in the PVC sampler subjected to the hydrocast procedure and sample transfer usually used. A "Student's" t-test at each station showed that the differences in the mean values of Hg for the Teflon bottles and PVC samplers had a greater than 0.20 probability of resulting from chance alone, assuming that the two measurements actually had the same mean value. Thus, the differences between the means are not significant and we can conclude that no adsorption losses of Hg occur. There is also no evidence of significant volatile organic contamination during the hydrocast or by sample manipulations aboard ship. The Hg concentrations at other depths show little variation from the surface values, suggesting that the open samplers are not contaminated or affected significantly by the hydrocast procedure.

It appears that Teflon storage is acceptable and the PVC sampler with Teflon-coated stainless steel closing spring can be used satisfactorily for Hg collections at depth. These 24 analyses of surface waters between 40°N and 32°N at ~66°W yield a mean concentration of 8 ng Hg liter^{-1} with a standard deviation of ±3 (*see Table 1*). The differences in Hg concentrations between stations appear mainly to reflect the analytical precision limits. The mean values between stations 2 and 3, however, may really be different.

These values in Table 1 agree with the open-ocean results of Leatherland et al. (1971) who found a range of Hg concentrations between <3–20 ng liter^{-1} with a mean of 13 in the northeast Atlantic. In previous investigations of the amounts and distribution of Hg in the surface waters of this region of the northwest Atlantic Ocean, we found a mean total Hg concentration of 7 ng liter^{-1} and a range between 6 to 11 (Fitzgerald and Hunt 1974). We also found no significant differences between the Hg concentrations measured directly in preacidified open-ocean seawater ("reactive" Hg) and the total Hg determination in the "organic-free" photo-oxidized samples. In the present investigation, no significant difference was observed between the reactive Hg determination and the total Hg measurement carried out with about a third of the samples.

These data for Hg differ significantly however from those of R. A. Fitzgerald et al. (1974), who report an average concentration of 129 ng Hg liter^{-1} for surface samples in this area of the Sargasso Sea.

Such discrepancies between observers show clearly that methods of sample handling and analysis have not been standardized. The problems associated with the accurate measurement of Pb in seawater have been carefully documented in a recent report (Meeting Rep. 1974). The recommendations from that report concerned with analytical methods, laboratory technique, and sampling can be usefully applied to Hg and other trace constituents in seawater.

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