Pretreatment of Polyolefin Bottles with Chloroform and Aqua Regia Vapor to Prevent Losses from Stored Trace Mercury(II) Solutions

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Pretreatment of polyolefin bottles by leaching the interior with $CHCl_3$ followed by exposure to the vapors of aqua regia (CAR) is superior to chemical preservatives in reducing Hg losses from 1 ppb Hg(II) solutions stored in polyolefin bottles. This treatment has been evaluated using 4 plastic compositions and 3 types of water samples chosen to represent a range of biological activity. Losses after 15 days storage are approximately 10%, independent of the composition of the container plastic or the characteristics of the water sample. Both steps of the CAR treatment are necessary for full effectiveness, suggesting that both additive removal and creation of a biocidal, oxidizing environment are important.

Loss of mercury during sample storage prior to analysis remains a serious potential source of error in the determination of traces of mercury in natural water samples. When polyolefin bottles are used for sample storage, chemical preservatives added to samples at the time of collection are of limited effectiveness. Further, the magnitude of these losses can depend strongly on the composition of the plastic container and the nature of the water sample, thus biasing the results. However, with respect to weight, cost, and durability, polyolefin bottles are extremely attractive for collecting, transporting, and storing the large numbers of samples necessary for environmental studies. Clearly, there is a need for a more effective technique for preventing the loss of mercury from natural water samples stored in polyolefin bottles. This paper reports a pretreatment with chloroform and aqua regia (CAR) which meets this need. The CAR treatment is inexpensive, suitable for routine use, and substantially more effective than existing chemical preservatives or pretreatments (*1, 2*) in preventing mercury loss from natural and distilled water.

Loss of mercury from solution can occur by reduction of Hg(II) to fugitive species such as the metal, or by binding of mercury to the container, and trace constituents of either the water or the plastic container may be causative agents. Earlier workers have established the ability of traces of dissolved organic matter (*3*) and of certain microorganisms (*4–7*) to reduce Hg(II) and have suggested these as causes of mercury loss (*8–11*), but they have not implicated trace constituents of polyolefin plastics as causes of mercury loss. Among the moieties in polyolefin plastics which can cause mercury loss are amino, thiol, sulfide, and phenolic groups of protective additives as well as active sites on the polymer matrix such as hydrocarbon radicals and carbonyl groups (*12–20*). The CAR treatment is designed to prevent the trace constituents of both the water sample and the container surface from removing mercury from the solution. Leaching the interior of the container with $CHCl_3$ removes soluble additives from the surface, and exposing the cleaned surface to aqua regia vapor deactivates active sites on the polymer matrix by chlorination and/or oxidation. The release of Cl_2 and $CHCl_3$ from the plastic also prevents chemical or biological reduction of mercury on storage. In addition to being a good solvent (*21*), $CHCl_3$ reacts with radicals and double bonds (*22, 23*) and is an effective biocide (*9, 24*). Aqua regia vapor is mainly Cl_2, which not only reacts with free radicals and double bonds, but is also a persistent biocide and oxidizing agent.

EXPERIMENTAL

New 500-mL polyolefin bottles rinsed with distilled water were used throughout. Borosilicate glass flasks for oxidation of samples were pretreated at 550 °C for 16 h. Chemicals and solvents were reagent grade and mercury was removed, when possible, from inorganic reagents by reduction with $SnCl_2$ and purging with N_2. Test Hg(II) solutions were prepared by addition to water samples in test bottles of an aliquot of 100 ppb Hg(II) prepared within 2 h by dilution of 1000 ppm Hg(II). After capping, test bottles were disturbed as little as possible during storage but, prior to sampling, solutions were swirled to suspend particulate matter.

The mercury concentration of water samples was determined using the steady-state Hatch–Ott method (*25*). To liberate Hg from organic matter, samples were pretreated in the following manner. Each 50-mL aliquot was transferred to a flask containing 1 mL of 4 M NaCl–2% w/v $K_2Cr_2O_7$ in 1% HNO_3, and 2.5 mL of concentrated HNO_3 was added. The flask was sealed with Parafilm and held at 3 °C for 24 h, after which 1 mL of 5% w/v $K_2S_2O_8$ was added; the flask was resealed and held at 3 °C for 12 h. After thermal equilibration at 25 °C in a water bath, mercury was determined in the usual manner. Results obtained using this pretreatment did not differ significantly from those obtained using the pretreatment of El-Awady et al. (*26*).

The identity of the polymer in the polyolefin bottles was determined as described earlier (*27*). Levels of unsaturation were determined by the IR method of de Kock and Hol (*28*) and the method of Lomonte, as modified by de Kock and Hol (*28, 29*). After extraction of 50 g of diced plastic with $CHCl_3$ for 72 h and removal of the solvent under N_2, additives were separated by TLC as described by Crompton (*21*). Potassium iodoplatinate was used to visualize dialkylthiodipropionates (*30*), and separated components were removed for IR and UV examination by extraction into CH_2Cl_2.

The levels of additives on the interior surface of bottles were estimated by extraction of capped bottles for 5 min using 10 mL of $CHCl_3$. The cap was isolated from the $CHCl_3$ with Al foil and additive levels were estimated by UV absorbance measurement of the extract.

Levels of humic acid were estimated gravimetrically using 0.45-μm cellulose acetate filter disks. After prefiltration to remove particulate matter, several liters of water were acidified to pH 1 with HCl, allowed to stand for 12 h, and filtered, and the insolubility of the humic acid residue in absolute alcohol was verified visually. The pH and alkalinity of MC water and the characteristics of PC water were determined by standard methods (*31*) and the remaining characteristics of MC water were supplied by the NYS Department of Health (*32*).

CAR Treatment. The bottle is filled with $CHCl_3$, capped tightly, allowed to stand for 72 h, and the $CHCl_3$ is removed. A 20-mL beaker with 15 mL of fresh aqua regia is placed in the cap which was open end up, and the bottle is screwed loosely into the cap. After exposure of 12 h for CPE plastic and 18 h for PP and LPE plastics, the AR is removed, the cap tightened, and the bottle

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