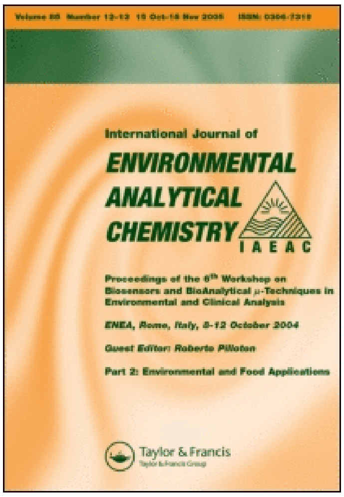

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# Determination of Mercury in Surface Waters Using an Optimized Cold Vapor Spectrophotometric Technique

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# DETERMINATION OF MERCURY IN SURFACE WATERS USING AN OPTIMIZED COLD VAPOR SPECTROPHOTOMETRIC TECHNIQUE

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An analytical method to measure mercury in environmental samples was optimized based upon amalgamation of mercury on gold-coated sand and subsequent ultraviolet absorption measurement of the mercury vapor driven off the sand upon heating. Sample handling and storage methods were employed that were virtually free from mercury loss or contamination. Analytical procedures were tested on standard reference materials obtained from the USEPA and USGS and at concentration levels in the range anticipated for the environmental samples. Stream samples, collected over a seven-month period, were filtered (0.45 $\mu$m) in the field, and the mercury in dissolved and particulate fractions was determined. Dissolved mercury concentrations ranged from 24.1 ng/l to 116.9 ng/l ($N = 120$) while particulate mercury concentrations ranged from 0.2 $\mu$g/g to 33.4 $\mu$g/g ($N = 120$). The method has been found useful for analyzing environmental samples and has been shown to be very sensitive and free of interferences.

KEY WORDS: Mercury analysis, water, suspended sediments, cold vapor.

## INTRODUCTION

Mercury analyses in the natural environment present a great number of difficulties. Poor analytical sensitivity and contamination during the analytical procedure combine to give unreliable Hg concentrations. Several investigators have pointed out the apparent decrease over time in the reported Hg concentrations in some natural waters which they attribute to improved sampling and analytical techniques.[1-3]

Many processes can combine to decrease Hg concentrations during sample storage, mainly adsorption on container walls and volatilization of elemental Hg and Hg compounds.[4] Elemental Hg can be formed via reduction by organic materials in the sample. Baier *et al.*[5] suggested that bacterial conversion of inorganic Hg in water to organic and/or elemental form was another route for the production of volatile Hg forms. Lo and Wai[6] found that $K_2Cr_2O_7$ (0.05% w/v), with its ability to oxidize Hg compounds and destroy bacterial activity, reduces volatile Hg losses on storage.

Pretreatment of sample containers is important in reducing Hg adsorption to container surfaces.[7] Losses vary with container materials and surface-to-volume ratio. Weiss *et al.*[8] found that concentrated $HNO_3$ leaching of borosilicate glass reduces but does not completely eliminate Hg adsorption. Lo and Wai[6] acidified samples with $HNO_3$ to pH 0.5 and observed no Hg losses. Weiss *et al.*[8] demonstrated that small amounts of cysteine will complex Hg and prevent adsorption and volatilization.

In addition to sample contamination and losses, analytical sensitivity must be maximized to detect the low Hg concentrations found in aquatic environments. The removal of interfering compounds, such as volatile organics[9] and water vapor,[10] is necessary to improve signal response. Preconcentration of Hg in samples is also needed to lower the overall detection limit. Working parameters, such as sample volume,[11] carrier gas flow rate,[12] and sample aeration rate must be carefully controlled in order to increase sensitivity.

The aims of the study were to optimize a spectrophotometric method to measure total mercury at concentrations found in natural water systems and to collect reliable analytical data on the concentrations of total mercury in dissolved and particulate stream fractions.

## METHODS

### *Mercury Analysis*

The cold vapor atomic adsorption technique was first developed by Hatch and Ott.[13] In this procedure, Hg is reduced to metallic Hg in an acidic solution using stannous chloride. The Hg is then volatilized by aeration and the vapor absorption measured at 253.7 nm. An additional step, amalgamation of the Hg on gold, was introduced by Joensue[14] to reduce interferences from water vapor, volatile organics, sulfides and $Cl_2$. The amalgam is heated in this procedure, and the Hg vapor is carried into an absorption cell with an inert carrier gas such as $N_2$.

A diagram of the gold sand amalgamation gas flow system used in this study is given in Figure 1. Nitrogen gas flow is adjusted by rotometer $A_1$ and diverted by stopcocks $F_1$ and $F_2$ through a clean-up step (traps C and E) before entering sample reaction vessel G. Stannous chloride and Hg containing sample are injected into the reaction vessel through a septum located at the top and aerated to reduce Hg and remove it from solution. The $N_2$ with Hg vapor flows across gold column I where Hg is collected and concentrated while other volatile interfering compounds are diverted out of the system by stopcocks $K_1$ and $K_2$. The Au column is maintained at a temperature of 100 °C to prevent condensation of $H_2O$ vapor. After sample aeration, flow is directed around the reaction vessel and across the Au column for one minute to insure complete removal of $H_2O$ vapor while the optical cell is by-passed. This drying step is necessary to prevent $H_2O$ vapor from entering the optical cell while it is connected to the gas train.

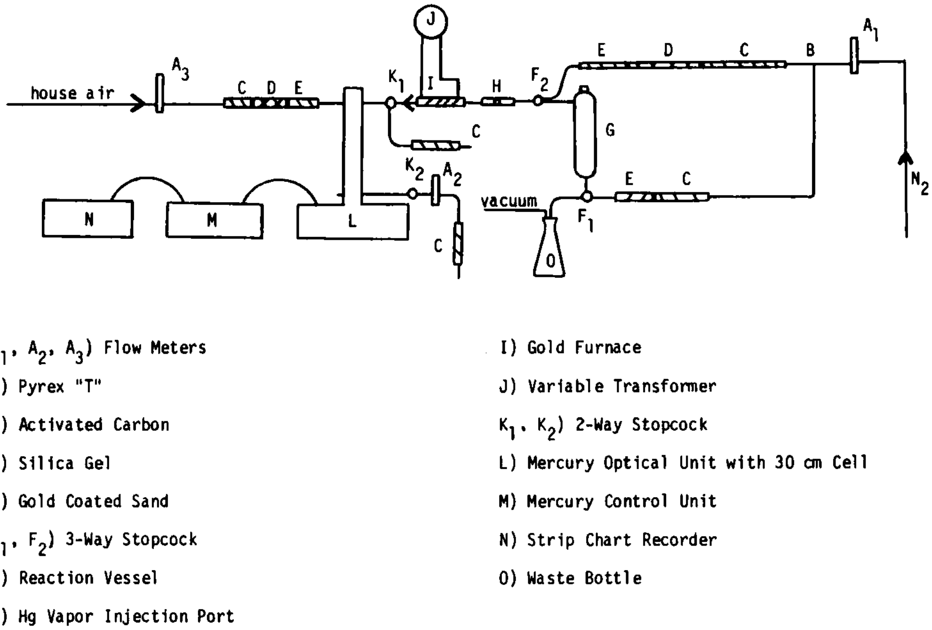

**Figure 1** Gold amalgamation/cold vapor apparatus.

Traps C, D and E remove interfering compounds and Hg from the $N_2$ before passing across the Au column.

The optical cell is connected to the gas train by stopcocks $K_1$ and $K_2$, and flow is readjusted by rotometer $A_2$. The Au column is heated with high resistance wire connected to variable transformer J to remove the amalgamated Hg which is then swept into the optical cell. Peak height is noted on strip chart recorder N. The aerated sample is removed from the reaction vessel to waste bottle O by stopcock $F_1$. Mercury vapor calibration injections were made through septa H to insure reproducibility throughout the analysis. The reference side of the system used house air which was cleaned up in the same manner as the $N_2$.

Absorption measurements were made using a dual absorption cell mercury monitor. All tubing that might come in contact with Hg vapor was 6 mm i.d. quartz or Vycor. Joints were sealed with heat-shrinkable teflon tubing. The reaction vessel in which samples were placed was borosilicate glass and had a screw cap top and a 3-way teflon stopcock bottom. The sample injection port at the top of the reaction vessel was capped with a teflon/silicone septum. A rubber septum was placed over the teflon/silicone septum to insure a good seal. A bakelite cap with a hole drilled in the center held the septa securely. The Hg vapor injection port, placed downstream of the reaction vessel, was made from a pyrex tee capped with a rubber sleeve stopper.

Nitrogen was used as the carrier gas for all experiments. A filter train of activated carbon, silica gel and gold-coated sand prevented the introduction of organic vapors, water and mercury vapor into the system while the optical cell was connected to the gas train. Three-way teflon stopcocks allowed the reaction vessel to be by-passed during Hg measurements to prevent water vapor in the vessel from entering the absorption cell.

Sea sand (20–30 mesh) was given a very thin gold coating by vapor deposition of Au wire (0.032 mm dia.). A Vacuum Evaporator was used to evaporate gold onto the sand. This procedure did not coat the entire sand particle, but it was estimated that approximately 75% of the particle became coated by repeating the deposition five times after shaking the sand.

The tube holding the Au-plated sand was made of 100 mm x 6 mm i.d. Vycor and was wound with 3 metres of Nichrome wire (8.43 ohms/m) for heating. A 40 mm length of Au-coated sand held in place with quartz wool was used to collect and concentrate the Hg vapor. A variable transformer controlled heating. The temperature inside the collection furnace was calibrated using a thermocouple which in turn was calibrated against the boiling points of $H_2O$ (100 °C) and $Na_2CO_3$ (851 °C). Flow meters were calibrated with a soap bubble meter. A strip chart recorder set to a 10 mV range and a chart speed of 5 mm/minute was used to record absorption.

Mercury-saturated air was used for calibration and was prepared by allowing a small amount of elemental Hg (1 ml) to equilibrate with air in a closed pyrex test tube. The tube was fitted with a rubber sleeve stopper for syringe extraction and immersed in a constant temperature water bath at $51\,°C \pm 0.1\,°C$. The concentration of Hg-saturated air was calculated from the ideal gas law. Known volumes of Hg vapor were withdrawn using a gas-tight constant rate syringe. Mercury injections into the gas train were made either into the reaction vessel for standard curve determinations or through the pyrex tee septum for calibration during analyses.

### *Standard Curves*

Standard curves were initially prepared with both vapor phase and aqueous Hg standards. Aqueous Hg standards were prepared from a stock solution (0.1354 g $HgCl_2$ + 10 ml concentrated $HNO_3$ diluted to 100 ml with deionized water) by serially diluting to obtain a working standard range between 1–20 ng Hg. Aqueous standards were analyzed in triplicate, and at least five different concentrations were run.

Vapor phase standard curves were prepared by aerating 10 ml $SnCl_2$ and 50 ml deionized water in the reaction vessel for ten minutes to remove any traces of Hg in the vessel and system. The Au column was heated to release Hg. A precise volume of Hg vapor was withdrawn from the calibration tube and injected into the reaction vessel through the septa located at the top. Aeration was carried out for one minute. The Au column was heated and peak height recorded. Other volumes of Hg vapor were injected into the same $SnCl_2$/water solution to establish the curve. Every point was analyzed in triplicate.

There was good agreement between the two methods for establishing a standard curve (Figure 2). Mercury concentrations in the aqueous samples gave slightly greater responses than vapor samples, probably because of trace Hg contamina-

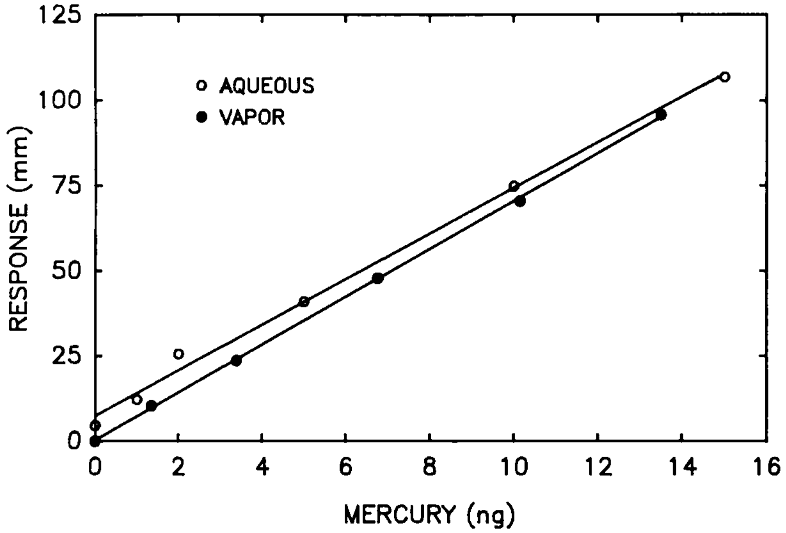

**Figure 2** Standard curves for vapor phase and aqueous Hg standards.

tion from glassware and from handling during dilutions. Aqueous Hg standards, both stock and working solutions, showed variability and instability with sources of error resulting from weighing solid $HgCl_2$ and from contamination of labware used in the preparation of the standards. The average coefficient of variation for all aqueous standards was 5.9% while that of vapor standards was 2.2%. In general, variability increased with decreasing Hg concentration for aqueous standards. Vapor standards involve less processing and proved to be superior to aqueous standards with respect to convenience, precision and accuracy.

Vapor standard curves were used for all Hg determinations. Vapor standard curves were prepared before each set of analyses by a series of injections into the reaction vessel as described above. A calibration was carried out before each analysis within a set by injecting Hg vapor into the system through the pyrex tee injection port. The response was compared to that of five identical injections made before sample analyses had begun to determine whether instrument response had deteriorated. Injections during the analysis fell within this range or the system cleanup procedure was repeated until the value did fall within the range. Mercury levels recorded from injections into the tee injection port were typically 5–10% greater than corresponding Hg levels recorded from injections into the reaction vessel.

### *Optimization of System Parameters*

Largest peak heights were obtained at low $N_2$ gas flow (Figure 3). Very low flows cannot be used, however, because of sensitivity to small variations in flow. At the other extreme, high flow rates disrupt plug flow and lead to smaller peak heights. A flow rate of 100 ml/minute was found to be a good compromise. The flow meter

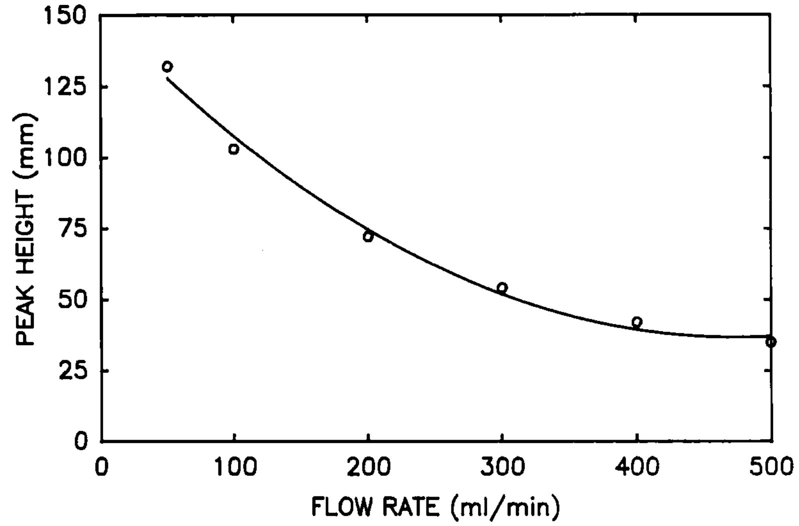

Figure 3 Effect of carrier gas flow rate on Hg peak height.

positioned at the exit port of the optical cell controlled carrier gas flow precisely at 100 ml/minute to give 1% coefficient of variation in peak height at a mean Hg level of 1 ng.

The effect of Au column temperature on peak height was examined at a constant carrier gas flow rate of 100 ml/minute. Heating at temperatures below 300 °C resulted in incomplete recovery of Hg from the column. Response increased rapidly between 300 °C and 500 °C and leveled off about 600 °C. Heating above 600 °C did not improve signal height but instead led to a second peak. The broad shape of the second peak suggests the presence of materials other than Hg which desorb slowly. The peak is believed to be due to non-volatile organic compounds that coat the gold and vaporize at the higher temperatures.

The aeration rate of the sample in the reaction vessel must be high to facilitate proper mixing with the reducing agent (Figure 4). Slow rates (750 ml/minute) do not remove all of the mercury from solution, and rates above 1250 ml/minute cause turbulence which ejects droplets out of the reaction vessel and interferes with the Hg analysis. An aeration rate of 1000 ml/minutes prevents excess sample turbulence yet removes the maximum amount of Hg vapor from the solution.

### *Precision and Accuracy*

The accuracy of the procedure was evaluated by analyzing USEPA water pollution quality control samples and USGS standard reference materials (Table 1). The precision of the method was evaluated from five replicate analyses of both dissolved and particulate fractions of a single sample. These replicates showed a coefficient of variation of 6.4% at a mean Hg level of 49.6 ng/l for the dissolved fraction and 14.4% at a mean level of 70.4 ng/l for the particulate fraction.

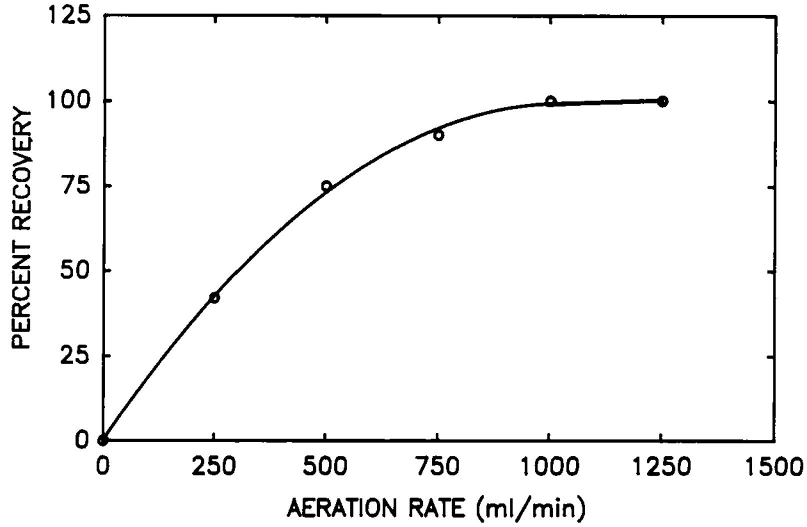

**Figure 4** Effect of aeration rate in reaction vessel on Hg percent recovery.

**Table 1** Analysis of reference samples

| *Sample* | *Certified mean* | *Standard deviation* | *Present work* | *Standard deviation* | *Number of samples analyzed* |
|---|---|---|---|---|---|
| USGS-COQ 1 | 55.2 ng/g | 0.55 | 55.1 ng/g | 0.94 | 12 |
| EPA-trace metal sample, WP 475 no. 1 (undiluted, 1 ml sample size) | 2.8 μg/l | 0.71 | 3.05 μg/l | 0.40 | 8 |
| EPA-trace metal sample WP 475 no. 1 (diluted 1:20, 50 ml, sample size) | 158 ng/l | — | 158 ng/l | 0.58 | 3 |

The limit of detection was defined as a signal that gave twice the blank value and was estimated to be 20 ng/l for a 50 ml sample size. The absolute limit of detection for each analysis was 0.5 ng Hg. One-day and five-day storage experiments were conducted to determine the reliability of the preservation technique. Mercury concentrations changed less than 1.2% over 5 days.

## *Sampling and Sample Storage*

Six streams and rivers located in central North Carolina were selected for sampling. Five of the streams receive municipal wastewater effluent and one stream, used as a control, receives no known discharges. Streams were sampled over a seven month period on dates which included both low and high stream flows. The mean annual flow was estimated for each site using a relationship developed for North Carolina streams from 25 years of data collection. Flows greater than the stream mean were classified as high flow, while those less than or equal to the stream mean were classified as low flow. Samples were collected at stream flow extremes to accentuate differences in mercury concentrations due to flow. Each site was sampled ten times, five at low stream flow and five at high stream flow. Mean differences between high and low stream flows were determined to be statistically different ($\alpha = 0.05$) for each stream. Samples were filtered at the time of collection to avoid changes in equilibrium between dissolved and particulate Hg concentrations.

Review of the literature suggested a pretreatment procedure for sample bottles. Borosilicate storage bottles (125 ml) were leached in a cleaning solution of concentrated $HNO_3$:$K_2Cr_2O_7$ 10% (w/v): cysteine 0.15% (w/v) (0.5:0.4:0.1) for at least 48 hours to remove any mercury, rinsed five times with deionized–distilled water and capped with a teflon/silicone septum. Three reagents ($HNO_3$, $K_2Cr_2O_7$ and cysteine) were added to all dissolved-fraction sample bottles to preserve the samples. One ml of concentrated $HNO_3$ (Ultrex) was added to the sample bottles using an oxford pipet whose tip had been soaked for five days in the cleaning solution and rinsed with deionized–distilled water. One ml of $K_2Cr_2O_7$ (10% w/v) and 1 ml of cysteine (0.15% w/v) were added using a glass syringe that had been acid leached and rinsed and whose tip had been heated to 600 °C.

Stream samples were collected for transfer in pretreated bottles that were rinsed with deionized–distilled water five times and twice with stream water. Samples were immediately filtered through 47 mm diameter membrane filters (0.45 $\mu$m) at the stream site directly into the pretreated storage bottles containing the three preservation reagents.

Filters were soaked in the cleaning solution which was diluted 1:10 with deionized–distilled water for 48 hours, rinsed and then stored in deionized–distilled water until needed. The glass filter funnel was modified by connecting the vacuum funnel end of a fritted disk filter assembly to the bottom of the funnel using an o-ring seal. A screw cap with a 13 mm hole drilled into the center was attached inside the ground glass joint of the vacuum funnel with silicon sealant so that filtrate ran directly into the storage bottles. The particulate samples on the filters were transferred to labeled Wheaton bottles using polyethylene tweezers and PVC gloves that had been soaked in diluted cleaning solution and in deionized–distilled water. All samples were sealed with a teflon/silicone septum under a bakelite cap and stored on ice for transport back to the laboratory. Field blanks were prepared by filtering deionized–distilled water, using the same method as samples, at a minimum of three sites each sampling trip. Sample blanks for the dissolved fraction showed coefficients of variation that ranged from 5.1% to 14.0% throughout the sampling period. Particulate sample blanks showed coefficients of variation that ranged from 13.9% to 21.4%.

### *Sample Treatment for Mercury Analysis*

One ml of $KMnO_4$ (10% w/v) was added through the teflon/silicone septum to all

**Table 2** Purification of reagents

| *Reagent* | *Purification method* | *Typical post-purification Hg concentration (ng/l)* |
|---|---|---|
| $H_2SO_4$ (conc.) | Add 50 ml $SnCl_2$ (10% w/v) to 2 litres of reagent, aerate for 5 hours with air scrubbed with activated carbon | 32 |
| $KMnO_4$ (6%) | Boil solution, allow it to cool and filter through pyrex wool before each use | 60 |
| $NH_2OH$-HCl (20%) | Add 25 mg of $SnCl_2$ and aerate for 2 hours with air scrubbed with activated carbon | 10 |
| $SnCl_2$ (10%) | Aerate for 2 hours with air scrubbed with activated carbon | 10 |
| $HNO_3$ (Ultrex) | None | 100 |
| $K_2Cr_2O_7$ (10%) | None | 80 |
| Cysteine | None | 20 |
| Water | Deionized–distilled | 10 |
| $K_2S_2O_8$ (5%) | None | 40 |

filtrates and to blanks immediately upon return to the laboratory from the field. The samples were then stored at 4 °C and analyzed within 24 hours of collection. The $KMnO_4$ was added to digest organic Hg species.

The particulate samples on the filters were stored at 4 °C for 24–48 hours before digestion. The digestion procedure, adapted from the technique developed by Agemian and Chau,[15] consisted of adding 15 ml of a concentrated $H_2SO_4$:$HNO_3$ (2:1) mixture directly to the storage bottles and heating at 60 °C for two hours in a water bath. After cooling, additional oxidants, 10 ml $KMnO_4$ 10% (w/v) and 5 ml $K_2S_2O_8$ 5% (w/v), were injected through the septum using a syringe. Persulfate oxidation, in addition to permanganate, insures that organo-Hg compounds are oxidized to mercuric ion. All samples were stored overnight at 4 °C. Samples were diluted with deionized–distilled water to 125 ml the following day and $NH_2OH$-HCl (20% w/v) was added until the sample color was a faint pink, indicating complete reduction of excess oxidant.

The chemicals used in wet chemical digestion are the major contributors to Hg contamination subsequent to sample collection. Reagent contamination was minimized using procedures outlined in Table 2. All materials that contacted the samples were soaked in the cleaning solution and rinsed with deionized–distilled water. Reagent contamination was typically less than 1 ng Hg with these procedures.

## RESULTS AND DISCUSSION

Total dissolved mercury concentrations varied with both sampling site and flow.

**Table 3** Means and ranges of dissolved Hg concentrations at high and low stream flow

| *Stream* | *Low flow dates (ng/l) (N = 5)* | *High flow dates (ng/l) (N = 5)* | *All dates (ng/l) (N = 10)* |
|---|---|---|---|
| Control | 39.9<br>(34.9–47.4) | 34.3<br>(24.1–41.3) | 37.1<br>(24.1–47.4) |
| A-2 | 62.1<br>(51.6–68.4) | 47.5<br>(42.1–51.9) | 54.8<br>(42.1–68.4) |
| B-1 | 87.5<br>(66.1–105.3) | 49.4<br>(43.8–53.3) | 68.5<br>(43.8–105.3) |
| C-2 | 78.4<br>(60.5–116.9) | 61.3<br>(41.6–85.1) | 69.9<br>(41.6–116.9) |
| D-1 | 72.4<br>(55.7–102.7) | 55.9<br>(34.1–71.5) | 64.2<br>(34.1–102.7) |
| E-1 | 64.1<br>(56.4–72.2) | 43.6<br>(28.4–60.0) | 53.9<br>(28.4–72.2) |

**Table 4** Mercury concentrations found in previous studies

| *Dissolved mean Hg (ng/l)* | *Dissolved Hg-range (ng/l)* | *Particulate mean Hg (μg/g)* | *Particulate Hg-range (μg/g)* | *Reference* |
|---|---|---|---|---|
| 62.2 | 34.1 – 116.9 | 5.4 | 0.2–33.4 | Present work (polluted) |
| 37.1 | 24.1–47.4 | 4.2 | 0.2–12.0 | Present work (background) |
| 47.5 | 5–130 | — | — | 17 (polluted) |
| 19 | 10–30 | — | — | 17 (background) |
| 90 | — | — | — | 18 (polluted) |
| 36 | — | 8.1 | — | 18 (background) |
| 38 | — | 0.44 | — | 19 (polluted) |
| 6 | — | 1.8 | — | 20 (background) |
| 8 | — | 0.4 | — | 21 (background) |
| 50 | — | 7.6 | — | 21 (polluted) |
| — | — | — | 1.3–14.0 | 22 (background) |

Values ranged from 24.1 ng/l to 116.9 ng/l (Table 3). Control site mean concentrations were lower than all other sites at both low and high stream flows. All mean high flow dissolved mercury concentrations were lower than mean low flow concentrations, indicating a dilution effect due to the storm water. Total dissolved mercury concentrations found in streams receiving municipal effluent are in agreement with values reported in the literature (Table 4). Background levels found in the effluent free stream are in agreement with some background studies but are considerably higher than other studies. The observed differences can be attributed to the differences in geochemistry of the watersheds and the differences in the amount of dissolved organic matter in the water.

Total particulate mercury concentrations ranged from 29.6 ng/l to 135.3 ng/l (Table 5). The control site had significantly ($\alpha = 0.05$) lower concentrations than any other site at low stream flows but was lower only for two of the five dates at

**Table 5** Means and ranges of Hg concentrations due to the solid fraction at high and low stream flows

| *Stream* | *Low flow dates (ng/l) (N = 5)* | *High flow dates (ng/l) (N = 5)* | *All dates (ng/l) (N = 10)* |
|---|---|---|---|
| Control | 43.5<br>(35.0–47.3) | 48.5<br>(29.6–56.7) | 46.0<br>(29.6–56.7) |
| A-2 | 60.5<br>(55.0–67.4) | 86.3<br>(70.3–135.3) | 73.4<br>(55.0–135.3) |
| B-1 | 73.4<br>(62.2–94.8) | 69.3<br>(60.7–90.2) | 71.4<br>(60.7–94.8) |
| C-2 | 94.1<br>(72.3–107.1) | 94.7<br>(83.0–108.9) | 94.4<br>(72.3–108.9) |
| D-1 | 71.9<br>(51.9–89.1) | 60.1<br>(46.2–77.0) | 66.0<br>(46.2–89.1) |
| E-1 | 82.2<br>(71.6–97.0) | 61.9<br>(44.7–73.1) | 72.1<br>(44.7–97.0) |

**Table 6** Means and ranges of particulate associated Hg per unit weight

| *Stream* | *Low flow (μg Hg/g SS) (N = 5)* | *High flow (μg Hg/g SS) (N = 5)* | *Both flows (μg Hg/g SS) (N = 10)* |
|---|---|---|---|
| Control | 8.8<br>(5.5–12.0) | 1.4<br>(0.2–2.3) | 5.1<br>(0.2–12.0) |
| A-2 | 8.7<br>(3.5–20.8) | 0.9<br>(0.4–2.1) | 4.8<br>(0.4–20.8) |
| B-1 | 24.6<br>(5.0–33.4) | 2.0<br>(0.4–2.5) | 13.3<br>(0.4–33.4) |
| C-2 | 3.4<br>(1.7–5.4) | 1.5<br>(0.4–2.5) | 2.4<br>(0.4–5.4) |
| D-1 | 6.0<br>(2.8–12.8) | 0.6<br>(0.5–0.8) | 3.3<br>(0.5–12.8) |
| E-1 | 4.7<br>(3.2–6.1) | 1.0<br>(0.2–1.5) | 2.9<br>(0.2–6.1) |

high flow. The mean particulate concentrations for five of the six streams were not significantly different at high *vs* low flow. On the other hand, one stream had a significantly ($\alpha = 0.05$) higher mean concentration at high flow than low flow. This was due to the large quantity of suspended solids collected during high flow events.

Particulate Hg values were influenced by the amount of suspended material in the water column during the sampling period. In order to better evaluate the data, particulate-associated mercury was normalized on a suspended sediment weight basis. Total mercury concentrations ranged from 0.2 μg/g to 33.4 μg/g (Table 6). High flow total Hg concentrations were significantly ($\alpha = 0.05$) lower than low flow Hg concentrations on a normalized sediment weight basis. Mercury concentration differences may be due to the changing particle size distribution at the two flows.

Smaller, more buoyant particles are expected to predominate particle loads which occur at low flow. At high flows, larger particles, which become resuspended, predominate. The surface area-to-volume ratio is higher for smaller particles and results in a greater amount of mercury adsorbed for a given weight of suspended material.[16] The larger particles tend to dilute the Hg concentration on a unit weight basis. Although the normalized Hg concentration on particulates at high flow is much lower than low flow conditions, the total mass of Hg transported during high flow events can be great when suspended sediment concentrations are high. Mercury concentrations are in agreement with some values reported in the literature but differ from other values (Table 4). Differences may be due to the size and organic content of the particles collected on the filter and the proximity of the sample site to discharge outfall.

## CONCLUSIONS

The analysis of mercury presents a number of problems which can be overcome if proper care is given to sample handling, storage and analytical procedures. An analytical method was optimized for the analysis of total Hg at concentrations found in aquatic environments. A technique which utilizes chemical reduction, aeration, preconcentration, and thermal release of Hg was used to separate and measure total Hg in water and suspended sediment samples. System parameters such as aeration rate, thermal desorption temperature, and carrier gas flow rate were evaluated to improve sensitivity and avoid interferences. In addition, sample handling and storage techniques were refined to minimize sample contamination and loss.

Total mercury concentrations, measured in aquatic samples, varied with both site location and streamflow. The highest total mercury concentration was 195 ng/l and the lowest was 54 ng/l. Mean total Hg concentrations decreased in both dissolved and particulate fractions with increasing stream flow indicating a dilution effect. High-flow dissolved Hg concentrations were diluted with storm water, while particulate Hg concentrations were diluted with less contaminated sediments which were transported into streams during storm events or were resuspended during such events.

The technique used demonstrates that reliable analytical data on the concentrations of mercury in solution and associated with suspended solids can be determined. The method is very sensitive and free of interferences.

### *References*

1. R. A. N. McLean, M. O. Farkas and D. M. Findlay. In: *Polluted Rain* (T. Toribara, M. Miller and P. Morrow, Eds.) (Plenum Press, New York, 1980), pp. 151–173.
2. W. F. Fitzgerald. In: *The Biochemistry of Mercury in the Environment* (J. Nriagu, Ed.) (Elsevier/North-Holland Press, New York, 1979), pp. 161–173.
3. H. V. Weiss, K. Bertine, M. Koide and E. D. Goldberg, *Geochem. Cosmochim. Acta* **39**, 1 (1975).
4. C. Feldman, *Anal. Chem.* **46**, 99 (1974).

5. R. W. Baier, L. Woznowich and L. Petrie, *Anal. Chem.* **47,** 2464 (1975).
6. J. M. Lo and C. M. Wai, *Anal. Chem.* **47,** 1869 (1975).
7. G. E. Batley and D. Gardner, *Wat. Res.* **11,** 745 (1977).
8. H. V. Weiss, W. H. Shipman and M. A. Guttman, *Anal. Chem. Acta* **81,** 211 (1976).
9. J. V. O'Gorman, N. H. Surh and P. L. Walker, *Appl. Spectrosc.* **26,** 44 (1972).
10. J. W. Wimberley, *Anal. Chim. Acta* **76,** 337 (1975).
11. S. R. Koirtyohann and M. Khalil, *Anal. Chem.* **130,** 136 (1976).
12. J. E. Hawley and J. D. Ingle, *Anal. Chem.* **47,** 719 (1975).
13. W. R. Hatch and W. L. Ott, *Anal. Chem.* **40,** 2085 (1968).
14. O. I. Joensue, *Appl. Spectrosc.* **25,** 526 (1971).
15. H. Agemian and S. Y. Chau, *Analyst* (*London*) **101,** 91 (1976).
16. K. G. Robinson and M. S. Shuman, *Lake and Reservoir Management* **4,** 147 (1988).
17. T. A. Jackson, J. W. Parks, P. D. Jones, R. N. Waychik, J. A. Sutton and J. D. Hollinger, *Hydrobiol.* **92,** 473 (1982).
18. R. E. Cranston and D. E. Buckley, *Environ. Sci. Technol.* **6,** 274 (1972).
19. D. R. Miller and Q. N. LaHam, *Environ. Res.* **19,** 231 (1979).
20. J. D. Smith, R. A. Nicholson and P. J. Moore, *Nature* (*London*) **232,** 393 (1971).
21. R. Turner and S. E. Lindberg, *Environ. Sci. Technol.* **12,** 918 (1978).
22. A. R. Abernathy and P. M. Cumbre, *Bull. Environ. Contamin. Toxicol.* **17,** 595 (1977).