DETERMINATION OF TOTAL MERCURY IN SUSPENDED SOLIDS BY OXIDATION, PURGE AND TRAP, AND COLD VAPOR ATOMIC FLUORESCENCE SPECTROMETRY

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WMRL SUSPENDED SOLIDS SOP

SCOPE AND APPLICATION

This method may be used to determine total mercury in suspended solids samples with a Minimum Reporting Limit of 0.059 ng of Hg per filter.

SUMMARY OF METHOD

Suspended solids are isolated on ashed quartz fiber filters. The filters are transferred from the Teflon petri dishes they are placed in to 125-mL wide mouth Teflon bottles. The filters are oxidized with a 5% BrCl solution to convert all forms of Hg to Hg^{II} oxidation state. The samples are placed into an oven held at 50°C for a minimum of 5 days. Following pre-reduction with hydroxylamine hydrochloride ($NH_2OH*HCl$), the samples are analyzed according to USEPA method 1631 utilizing an automated mercury analysis system.

SAFETY ISSUES

Before beginning any of the procedures involved in this method, each individual must be familiar with the Chemical Hygiene Plan for this lab. Specific safety concerns for each chemical can be found in the Material Safety Data Sheets (MSDS) for that chemical – all of which are located in the laboratory. Two extremely important safety concerns are addressed below.

Chronic mercury exposure may cause kidney damage, muscle tremors, spasms, personality changes, depression, irritability, and nervousness. Due to the toxicological and physical properties of mercury, only highly trained personnel using extremely cautionary procedures should handle high concentration standards. The cautionary measures include use of gloves and high volume fume hoods when preparing standards.

Strong acid solutions are employed in the cleaning of equipment, preparation of reagents, and sample preservation. Proper acid handling techniques should be employed whenever acids are being used. These techniques include the use of acid resistant protective clothing and high volume fume hoods.

SAMPLE PRESERVATIVES AND CONTAINERS

Samples are preserved by freezing as soon after collection as possible in mercury clean Teflon petri dishes and bottles. New Teflon equipment is rinsed with tap water, and cleaned by immersing in 4 N omni pure HCl heated to 65°C for at least 48 hours. Immediately following removal from the bath, the equipment is immersed in fresh reagent grade water and rinsed at least 3 times with reagent grade water. After rinsing, bottles are filled one quarter full with 1% omni pure HCl. Petri dishes as well as the exterior of the bottles are air dried under a mercury-free class 100 laminar flow hood. Dry equipment is assigned a unique identifier barcode then double bagged in new zip-type bags with the unique identifier and date cleaned written on the outer bag. After the initial 48 hour cleaning, only 24 hours is required.

REAGENTS AND STANDARDS

All reagents and/or dry chemicals used to make reagents must be of the highest purity available from the vendor and shown to be low in mercury. Upon receipt at the laboratory, containers will be marked with the date of receipt and stored in the appropriate areas. When reagents are mixed for use in this method, the person who mixes them will initial and date the reagent container.

Reagent Water: Ultra pure reagent grade water containing less than 0.1 ng/L Hg with a resistance greater than 18 MΩ-cm starting from a prepurified source (distilled, reverse osmosis, and others). The water is delivered through a 0.2 µm filter, as obtained from a Millipore Academic water-purification system or equivalent.

Hydrochloric Acid (HCl): EM Science omni pure HCl (containing less than 5 ng/L THg) or equivalent.

Bromine monochloride (BrCl): Dissolve 27.0 g of reagent grade potassium bromide (KBr) in a new 2.5 L bottle of concentrated HCl. Place a Teflon coated stir bar into the bottle and stir for 1 hour or until dissolved. Slowly add 38.0 g reagent grade potassium bromate (KBrO3) to the bottle while stirring. CAUTION: This needs to be done slowly and in a fume hood because large quantities of free halogens are produced. Addition of KBrO3 to the solution should produce a color change from yellow to red to orange. Cap bottle loosely and stir for an additional hour.

Hydroxylamine hydrochloride ($NH_2OH*HCl$): Dissolve 120 g of $NH_2OH*HCl$ in Teflon bottle containing 400 mL of reagent grade water. Add 50 µL $SnCl_2$ to the solution and purge with Hg free N_2 at 300 mL/min for 1 hour. Prepare fresh every 6 months.

Stannous chloride ($SnCl_2$): Add 60 g $SnCl_2$ to 20 mL concentrated HCl in a dark 2.5 L glass bottle by rinsing it out of the weigh boat with reagent water. Allow 30 minutes for the $SnCl_2$ to dissolve. Add reagent water to bring up to 2 L. Purge with Hg free N_2 at 30 mL/min during initial start up and during analysis. Store in refrigerator overnight. Prepare fresh monthly.

Argon (Ar): Grade 5.0 (ultra high purity) that is passed through a gold-coated glass bead trap attached to the outlet of the tank to remove any mercury.

Standards: Upon receipt at the laboratory or on the day of preparation, containers should be labeled with the date received and the initials of the person preparing them. The stock and sub-stock standards should be stored outside of the clean laboratory to prevent contamination of the entire lab.

Stock standard (1000 mg/L): Commercially available Hg standard verified against a NIST standard reference material. All subsequent standards are prepared using the stock standard. Before preparing other standards, ensure the expiration date of the stock standard has not been exceeded.

Substock standard (1000 µg/L): Dispense approximately 50 mL of reagent grade water and 5 mL of BrCl into a 100 mL mercury clean class A volumetric flask. Pipette 100 µL of the stock standard (1000 mg/L) and bring to volume with reagent water. To clean the volumetric flask, fill to approximately 20% total volume with 50% HNO_3, place the ground glass stopper on its side over the opening to prevent pressure buildup, and reflux on a hotplate for 4 hours.

Working standard (1000 ng/L): Dispense approximately 500 mL of reagent grade water and 5 mL of BrCl into a 1 L mercury clean class A volumetric flask. Pipette 1.0 mL of the substock standard (1000 µg/L) and bring to volume with reagent water. Prepare fresh every 6 months.

Analytical Standards: Analytical standards range from 1 ng/L to 40 ng/L, and the standards should span the expected concentrations of the samples to be analyzed. Dispense approximately 500 mL of reagent grade water and 5 mL of BrCl into a 1.0 L Hg clean class A volumetric flask. Pipette a volume of working standard into the flask that yields the desired concentration of the analytical standard and bring to volume with reagent water. For a 1 ng/L analytical standard, 1.0 mL of the working standard would be added. The analytical standard must be compared to the previous analytical standard and agree within ± five percent. Prepare fresh every six months.

Quality control sample (QCS): The quality control sample will be prepared from a Hg source different from that used to prepare the standards routinely used for analysis. The QCS is used during analysis runs to verify statistical control.

Quality control stock standard (10,000 mg/L): Commercially available Hg standard verified against an NIST standard reference material. All subsequent quality control standards and samples are prepared using this stock standard. Before preparing other standards, ensure the expiration date of the stock standard has not been exceeded.

Quality control substock standard (10,000 ng/mL): Dispense approximately 50 mL of reagent grade water and 5 mL of BrCl into a 100 mL mercury clean class A volumetric flask. Pipette 100 µL of the quality control stock standard (10,000 mg/L) and bring to volume with reagent water.

Quality control working standard (1000 ng/L): Dispense approximately 500 mL of reagent grade water and 5 mL of BrCl into a 1.0 L mercury clean class A volumetric flask. Pipette 100 µL of the quality control substock standard (10,000 ng/mL) and bring to volume with reagent water. Prepare fresh every 6 months.

Quality control sample (5 ng/L and 10 ng/L,): Dispense approximately 750 mL of reagent grade water and 5 mL BrCl into a mercury clean 1.0 L class A volumetric flask. Pipette 5 mL (or 10 mL) of quality control working standard (1,000 ng/L) and bring to volume with reagent water. The new QCS must be verified against the previous QCS and agree within ± 5%. A new QCS should be made fresh every month.

QUALITY CONTROL

Each analyst must demonstrate the ability to generate acceptable accuracy and precision with this method. This includes the ability to reproduce standards, produce acceptable relative percent differences between quality control samples and real environmental samples, and produce spike recoveries that meet acceptance criteria.

Blank: A blank is prepared by adding 50 mL of reagent water and 100 µL of NH_2OH*HCl to a 60 mL autosampler vial. Blanks are critical to the reliable determination of Hg at low levels.

Standards: A standard curve is created by analyzing a series of analytical standards (1, 2, 5, 10, 20, and 40 ng/L). By plotting response vs. concentration, a correlation coefficient is calculated. The standard curve must have a correlation coefficient greater than or equal to 0.995. All sample concentrations must fall within the calibration curve. If the sample concentration exceeds the upper limit of the standard curve, the sample must be diluted and reanalyzed. If the correlation coefficient fails to meet the above criteria, then an additional set of standards must be analyzed to rule out operator error. If the second set of standards fails, the analyst must isolate and correct the problem before continuing analysis.

Quality control sample: The quality control sample or QCS must be made from a mercury source different from that used for calibration standards. Each QCS must be analyzed prior to sample analysis. A 5 ng/L and 10 ng/L QCS is also analyzed after every rack of samples and at the end of the day. The recovery of the QCS must be between 90 and 110% (4.5 and 5.5 ng/L or 9.0 and 11.0 ng/L) of the expected value. If either of the initial QCS or any QCS analyzed prior to or subsequent to a batch of samples fails to meet the acceptance criteria, an additional QCS must be run. If the second QCS still does not meet acceptance criteria, the instrument is recalibrated and the QCS is analyzed until statistical control has been reestablished. After control has been reestablished, all samples analyzed since the last acceptable QCS measurement are reanalyzed. If insufficient sample volume remains to reanalyze the samples, they must be flagged appropriately.

Method Blanks: For every ten samples, a method blank must be processed. A minimum of 3 method blanks must be processed for a preparation batch. The preparation batch is all the samples that were prepared that day. A method blank includes an ashed QFF, 95 mL of reagent grade water, and 5 mL of BrCl. The method blank is used to correct for background levels of Hg found in reagents. All method blanks should have a mass of less than 0.20 ng. If a method blank has a mass greater than 0.20 ng, the batch will be evaluated and flagged.

Certified Reference Materials (CRM): A CRM that best represents the sample matrix is selected, processed, and analyzed every ten samples. The recovery of the CRM must be between 80 and 120% of the expected value. If a CRM falls outside the acceptable criteria, the batch needs to be evaluated and flagged.

Matrix Spike: A matrix spike is prepared by adding a known mass of Hg standard to an environmental sample. A matrix spike must be analyzed in every rack of samples. Therefore, the unspiked aliquot of the spiked sample in the second rack was analyzed in the first rack, for the third rack in the second, etc. Percent recovery for a matrix spike must fall between 85 and 115%. The percent recovery is calculated as follows:

$$\% \text{ Recovery} = ((|C_s - C_{us}|) / D) / ((M / V) / 1000) \times 100$$

C_s = Concentration of unspiked sample
C_{us} = Concentration of spiked sample
D = Dilution factor (sample aliquot volume in mL/50)
M = Mass of spike
V = Total volume of sample (mL)

If the percent recovery falls beyond the range of 90 and 110%, the environmental sample should be re-spiked, volume permitting, and another environmental sample should be spiked, to rule out any matrix interference. If the percent recoveries for the new spikes fall beyond the range of 90 and 110%, the sample set represented by the spiked samples are flagged.

Batch Detection Limit (BDL): A BDL is determined from the method blanks. The BDL is a function of the Hg detected in the reagents.

$$\mathbf{BDL = \sigma * 3}$$

BDL = Batch Detection Limit
σ = Standard deviation from the mass of Hg detected in method blanks

If the BDL exceeds 0.059 ng, the run will be evaluated and the samples may be flagged.

PROCEDURE

The samples are handled using ultra clean sampling techniques. During analysis, it is important to be aware of possible interferences from free halogens, water vapor, and Argon gas. The presence of free halogens will destroy the gold trap resulting in low mercury values. Free halogens can be removed with the addition of a soda lime trap directly upstream of the gold trap during separation. If water vapor collects on the trap during the purging step, a false peak will result during analysis. The addition of soda lime directly upstream of the gold trap will remove water vapor. The fluorescent intensity of the detector is strongly dependent on the inertness of the Argon gas. The amalgamation step virtually eliminates quenching due to impurities in the Argon gas, but it is the analyst's responsibility to ensure high purity inert Argon is used and the analytical train is leak free.

Working with detection limits in the parts per trillion range, protecting these samples from contamination cannot be over emphasized. The greatest difficulty in low-level mercury analysis is preventing the samples from becoming contaminated. Extreme caution must be used throughout the preparation, collection and analysis procedures to avoid contamination. It is very important that the laboratory air be low in both particulate and gaseous Hg. The mercury in the air can be reduced with the use of gold-coated cloth at the intakes of the laminar flow hoods. Pump head tubing should be changed at least every 15 days of operation. As the pump head tubing ages, significant instrument drift can occur and the pump head tubing should be changed.

The following labware is required for sample preparation and analysis:

- Laboratory oven capable of maintaining 50°C ± 5°C.
- Pneumatic fixed-volume and variable pipettes in the range of 5 µL to 10 mL
- Analytical balance capable of measuring to the nearest 0.1 g for use during analysis.
- Analytical balance capable of measuring to the nearest 0.1 mg for processing CRM.

Sample Preparation

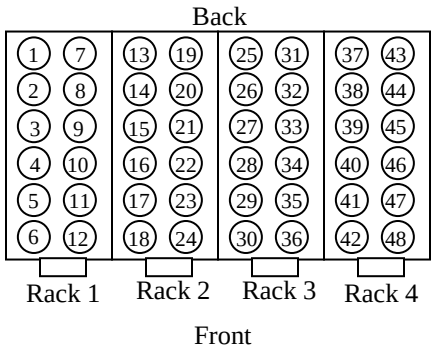
An Excel spreadsheet is created to track which filter is transferred into which 125-mL bottle. The bottle IDs for the method blanks are recorded and the bottle ID and mass of CRMs are also noted in this spreadsheet.

Remove filters from freezer to thaw while beginning the sample setup. Discard the storage acid in a 125-mL wide mouth Teflon bottle and rinse three times with reagent water. One bottle needs to be rinsed for each filter to be processed. Extra bottles need to be rinsed for method blanks and CRMs. A method blank and CRM are processed for every 10 filters with an additional blank and CRM analyzed at the beginning and end of the entire sample setup. A minimum of 3 method blanks need to be processed, therefore, a minimum of 30 samples must be setup.

Using Hg clean Teflon forceps, transfer the filter from the petri dish into a 125-mL wide mouth Teflon bottle. Rinse forceps with reagent water between filters. Place the extra barcode for the petri dish onto the 125-mL bottle. Next, using a 50-mL repipettor containing reagent grade water, fill the plunger with 50-mL. Dispense a small amount of water into the petri dish to remove any particulate matter that may remain in the petri dish. The water used to rinse the petri dish is added to the 125-mL bottle. Finish dispensing the remaining volume into the bottle. After all the bottles have received 50 mL of water, add an additional 45-mL of water to all bottles, bringing the total volume of water to 95-mL. Under a fume hood, add 5-mL of BrCl to each bottle. Cap the bottles tightly, and double bag. Place the bottles in a 50°C oven for a minimum of 5 days to fully oxidize the samples. The samples are then ready for analysis.

Instrumentation and Equipment

Analysis is performed using the Model 2630 automatic sample changer from Tekran (Toronto, ON) which holds 4 racks of 12 60-mL autosampler vials and contains a rinse station. The detector is a commercially available Model 2600 CVAFS mercury detector from Tekran equipped with a mass flow controller capable of measuring 30 mL/min and an auxiliary flow meter capable of measuring 300 mL/min. Gas flow is controlled by a regulator capable of supplying 30 psi of pressure. Below is a diagram of the autosampler racks containing vials and their numbered positions.



The Model 2610 peristaltic pump from Tekran flushes the rinse station and pumps sample, reagents, and rinse water to the phase separator. The pump also removes waste from the phase separator and overflow from the rinse station. The gold coated glass bead trap is constructed of a 7-mm outside diameter (O.D.) quartz tube, 10 cm long and with a constriction 3 cm from the outlet end. A quartz plug is placed into the inlet end, about 0.7 g (filling about 3.5 cm in the tube) of gold coated glass beads are added, and the inlet end is plugged with another piece of quartz wool. After the traps are packed, another constriction is added at the inlet end. Female fittings for gold traps are made from small pieces of 6-mm inside diameter (I.D.) monobarb Teflon tubing.

The soda lime trap is supplied with the Tekran Model 2600 CVAFS mercury detector. The trap is filled with 4-8 mesh soda lime. The soda lime trap captures moisture and free halogens that are generated by purging the sample. The soda lime trap removes these constituents before they can reach the gold trap. Moisture will create interferences with the Hg detector and free halogens will destroy the gold trap.

The rinse station is supplied by a 5-L Teflon carboy filled with reagent water and acidified to 1% with HCl.

The $SnCl_2$ solution is placed into a dark 2.5-L glass bottle and slowly purged with N_2 throughout analysis.

Initial Start-up, Calibration, and Sample Analysis

Turn on the Argon gas in the sample preparation room across the hall from the lab. Check volume for $SnCl_2$ reservoir and fill if needed. Fill rinse water reservoir with fresh reagent water acidified to 1% with HCl. Place the rinse water line into the rinse water reservoir and the $SnCl_2$ and purge gas lines in the $SnCl_2$ reservoir. Verify the baseline reading on the detector is between 0.010 and 0.015. If the baseline is out of that range, adjust by turning the offset knob. Verify that the Argon mass flow controller switch is set on remote setting. Adjust the flow meter for gas phase separator to 300 mL/min. Adjust the flow meter for the auxiliary gas flow so that the $SnCl_2$ slowly bubbles (~100 mL/min). Connect the cassettes for the pump head tubing to the pump. Place the pump in local mode to adjusting the tensions for the lines. First, set the tension on the pump head tubing for the $SnCl_2$ to achieve steady flow. Then set the tension on the pump head tubes for the sample probe, the rinse water station, and the waste lines to one click looser than the $SnCl_2$. Leave the pump in local mode while rinsing the system at the beginning of the day, but before starting analysis, change the pump switch to remote.

Pack the soda lime trap with fresh soda lime and verify that the edge of the soda lime trap is free from debris to ensure a complete seal between the glass tube and the gasket inside the cap. Condition the soda lime and rinse system with reagent water for 20 minutes.

LimsLink software: LimsLink is the supporting software of the Tekran Model 2600 system. To run, open the software and click on the *run* button. Select the Single Dip method and press the *new* button. Enter date of analysis, description of sample set, and analyst initials. Configure the autosampler by pressing the *A/S config* button. Select sampler model # 223. For the first four sample rack locations, set the rack ID to 112. Leave the fifth sample rack location blank, and click OK. Next, press the *wash station* button to move autosampler arm to the wash station. Go to *Options* → *Expansion 2*. This will import the template that includes the calibration curve and the initial QCS into the LimsLink spreadsheet.

To set up a standard curve, add 100 μL of NH_2OH*HCl to the first 7 autosampler vials. Add reagent water to vial #1, then add approximately 50 mL of 1 ng/L, 2 ng/L, 5 ng/L, 10 ng/L, 20 ng/L, 40 ng/L analytical standards to the next 6 vials. These vials will occupy positions 1 through 7 in the first rack. For the Quality Control Standards (QCS), add 100 μL NH_2OH*HCl to autosampler vials #8 and #9 and approximately 50 mL of 5 ng/L and 10 ng/L QCS. Fill two autosampler vials with 10% aqua regia for rinse between samples. These vials will be located in positions 11 and 12. Fill one autosampler vial with reagent water to rinse the system at the beginning of the curve before the blank. This vial will be located in position 10.

Using the LimsLink program, configure the run by pressing the *Configure Run* button. Select the range of samples to be analyzed, select that you wish to run the clean program, and press *Ok*. Press the *Start Run* button.

After statistical control has been established for the system, sample analysis can begin. Add 100 μL of NH_2OH*HCl to 12 autosampler vials. Add approximately 50 mL of sample to each of the 12 vials. The excess BrCl in the sample needs to be reduced to avoid destruction of the gold coated glass bead traps by the presence of free halogens. The 100 μL of NH_2OH*HCl added to the vials should be sufficient for this to occur. The yellow color will disappear, indicating the reduction of the BrCl. Only neutralize samples in vials immediately prior to analysis. Samples should not be stored neutralized. The sample vials will occupy positions 13 – 24 in rack 2. In the LimsLink spreadsheet, enter the bottle ID for the samples under the Sample ID column. In the Sample Tube column, enter the corresponding vial position occupied by that sample. Under the Rinse Tube column, alternate entering 11 and 12, which correspond to the 10% Aqua Regia rinse vials in rack 1.

Configure the autosampler by pressing the *Configure Run* button. Select the range of samples to be analyzed and press *Ok*. Press *Start Run*. Samples must be bracketed by a 5 ng/L and 10 ng/L QCS. QCS can be refilled in vials 8 and 9 in rack 1. After the first set of samples is complete and it has been verified that the QCS meet criteria, repeat sample setup above. Samples can be placed in racks 2, 3, or 4.

Shut Down

After the last sample has been analyzed the following steps must be performed to shut down the instrument for the next analysis. Remove the rinse water and $SnCl_2$ lines from the reservoirs and place them in a vial filled with 1.0 M KOH. Set the pump speed to *Local*. Rinse system with KOH, reagent water, 10% aqua regia, and 1% HCl solution in that order. Run the peristaltic pump until the rinse water station on the autosampler is empty and the lines are dry. Turn off the peristaltic pump and release the pump head tubing cassettes. Turn off needle valves for the purge flow and the phase separator flow. If you are the last analyst using the Argon purge gas, turn off the valve across the hall in the sample preparation room.

MAINTENANCE

The instrument maintenance guidelines are outlined in the Tekran 2600 manual. The pump head tubing should be changed every 15 days of operation.

CALCULATIONS

Raw peak areas are entered into a Microsoft EXCEL spreadsheet during analysis to calculate mercury concentrations and to ensure acceptance criteria are being met. The following equations are used to calculate environmental and QCS total mercury concentrations.

CONCENTRATION OF ENVIRONMENTAL SAMPLE

Concentration of sample

$$\mathbf{C_{ng/L} = PA/S},$$

where
$C_{ng/L}$ = concentration of sample
PA = peak area
S = slope of calibration line

Mass of Hg in method blank

$$\mathbf{M_{FB} = C_{ng/L} * V_B},$$

where
M_{FB} = mass in method blank
$C_{ng/L}$ = concentration of sample
V_B = volume of sample originally in bottle

Mass of Hg on filter

$$\mathbf{M_F = (C_{ng/L} * V_B) - M_{FB\text{-}AVE}},$$

where
M_F = mass of Hg on filter
$C_{ng/L}$ = concentration of sample
V_B = volume of sample originally in bottle
$M_{FB\text{-}AVE}$ = average mass in all method blanks

ng/L concentration

$\mathbf{C_{ng/L} = M_F/V_F}$,
where
$C_{ng/L}$ = concentration of sample in ng/L
M_F = mass of Hg on filter
V_F = volume of water that passed through filter

CONCENTRATION OF CRM

Concentration in sample
$\mathbf{C_{ng/L} = PA/S}$,
where
$C_{ng/L}$ = concentration of sample
PA = peak area
S = slope of calibration line

Mass of Hg in bottle

$\mathbf{M_B = (C_{ng/L} * V_B) – M_{FB\text{-}AVE}}$,
where
M_B = mass of Hg in bottle
$C_{ng/L}$ = concentration of sample
V_B = volume of sample originally in bottle
$M_{FB\text{-}AVE}$ = average mass in all method blanks

ng/g concentration

$\mathbf{C_{ng/g} = M_B/M_C}$,
where
$C_{ng/g}$ = concentration of CRM in ng/g
M_B = mass of Hg in bottle
M_C = mass of CRM added to bottle

CONCENTRATION OF QCS

Concentration of sample
$\mathbf{C_{ng/L} = (PA_S – PA_B) / S}$
where
$C_{ng/L}$ = concentration in ng/L
PA_S = peak area of sample, in PA units
PA_B = peak area of blank, in PA units
S =Slope, in ng/L/PA units

DATA VALIDATION AND EVALUATION

After the data has been entered into the Microsoft EXCEL spreadsheet, someone other than the analyst must verify that no values have been incorrectly entered in the spreadsheet that calculates the final concentrations using the same basic formulas above. The QC officer carefully evaluates the data to ensure all data quality objectives have been met for the run.

Reporting

Reporting units for total mercury are in ng/L as Hg. Concentrations will be reported to three significant figures. After the data has been verified it may be transferred to the customer via e-mail or hard copy, and uploaded into the database.

Archiving

All raw data produced in the laboratory is archived. All electronic data is archived on the lab computer dedicated to analysis on the Tekran 2600, which is backed up daily.

REFERENCES

Method source:

U.S. Environmental Protection Agency. 2002. Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, Cold Vapor Atomic Fluorescence Spectrometry. EPA-821-R-02-019. Office of Water. 36 p.