# TRACE-LEVEL TOTAL MERCURY IN WATER BY PURGE AND TRAP (DUAL GOLD TRAPS) AND COLD VAPOR ATOMIC FLUORESCENCE DETECTION (CVAFD)

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## 1. SCOPE AND APPLICATION

This method is used for the determination of trace levels of total mercury in water samples. It employs oxidation followed by purge and trap on dual gold traps, and Cold Vapor Atomic Fluorescence Detection (CVAFD). This standard operating procedure (SOP) conforms to EPA Method 1631E and is applicable to the determination of total mercury in surface waters, ground waters, and effluents etc. It is used to analyze water samples logged in for the following tests: W-HG-AF, W-HG-AF-F, and SPLP-HG-AF. The calibration range for this instrument is 0.1 – 30 ng/L. The method detection limit (MDL) is 0.10 ng/L and the practical quantitation limit (PQL) is 0.40 ng/L.


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## 2. SUMMARY OF METHOD

Method 1631 allows for the use of glass containers for sample collection, provided mercury is the only target analyte in the sample. For ambient monitoring projects, the samples are collected and preserved in cleaned and tested 500 mL clear glass bottles purchased from I-Chem (See DEP SOP HG-015 for bottle cleaning procedure). For compliance monitoring projects, the sample bottles do not require cleaning prior to sample collection. The bottles are used for the collection and shipment of samples from the field. They are single use containers which are discarded after use. Upon receipt, the samples are preserved in the lab using hydrochloric acid as a preservative and stored at room temperature in laboratory B110. At least 12 hours before analysis, aliquots of the sample are poured into 125 mL Teflon (FEP) bottles and digested with BrCl at room temperature (all Hg in the 100 mL aliquot is oxidized to $Hg^{2+}$). At the end of the analysis, the Teflon bottles are emptied, rinsed with tap water, and filled with 5 % aqua regia.

The digested samples are then analyzed using a Tekran 2600 mercury analyzer. This instrument employs an autosampler, a gas-liquid phase separator where the mercury in the sample is reduced to Hg (0) by stannous chloride, dual gold amalgamation traps, and an atomic fluorescence detector. The calibration range is 0.1 – 30 ng/L. Only values within this range for digested samples are reported. Samples having concentrations greater than 30 ng/L are diluted to bring their concentrations within range. Calibration standards and blanks are made using in-house de-ionized (DI) water that has been purified with the Solution 2000 Type I reagent Grade Water Purification System.

## 3. APPARATUS AND EQUIPMENT

3.1 Tekran Model 2600 Mercury Analyzers, Serial No. 0001, Software: Tekran-MDS, Version 2.0 with Gilson 223 autosampler.

3.2 Tekran Model 2600 Mercury Analyzers, Serial No. 0154, Software: Tekran-MDS, Version 2.5 with Tekran Model 2621 autosampler.

3.3 125 mL Teflon (FEP) narrow mouth bottles

3.4 500 mL glass I-Chem bottles with Teflon lined caps

3.5 Pipettes:

- 3.5.1 10-100 µL adjustable Eppendorf
- 3.5.2 100 µL and 1000 µL non-adjustable Eppendorf
- 3.5.3 5-10 mL adjustable Finnpipette

3.6 Glass vials (28 x 95 mm, 40 mL) for the Tekran Model 2621 autosampler and Gilson 223 autosampler

3.7 Mettler Toledo New Classic MF top-loading Balance, model MS1602S/03.

3.8 Solution 2000 Type 1 Reagent Grade Water Purification System, model 2035A.

## 4. REAGENTS, STANDARDS, AND SUPPLIES


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**Note**: See DEP SOP MT-069 for standard and reagent documentation, labeling requirements, and expiration dates. Reagents and standards used for sample preparation and analysis must be logged in to the LIMS standard prep tracker to generate a serial number. The label printed from the LIMS standard prep tracker must be placed on the bottle of standard or reagent in the laboratory.

Sample preparation documentation: All standards and reagents used for sample preparation are documented in the LIMS prep worksheet manager.

Documentation of reagents used for analysis: Hydroxylamine hydrochloride and stannous chloride are added to the samples in the analysis laboratory. Record the serial number of each reagent on the MT-HG-RGNT form. Controlled versions of forms are located on the Division of Environmental Assessment and Restoration (DEAR) intranet site. An Excel copy of the MT-HG-RGNT form can be found on the Chemistry Section's computer network, //FLDEP1/DEAR/Labs/Lab5/Chemistry/InorganicPrep/Mercury/W-HG-AF & W-HG-AF-F. Always make sure the most up-to-date form is used by verifying the version number on the Excel form is the same as the version number on the DEAR intranet site. Print MT-HG-RGNT and include in lab report.

Calibration standards are prepared in the analysis laboratory using standard THG-7 (See 4.5) and digested with BrCl. Hydroxylamine hydrochloride, stannous chloride, and nitric acid are added to the calibration standards. Record the serial number for the $KBrO_3$/KBr solution, the hydrochloric acid, the hydroxylamine hydrochloride solution, the nitric acid, and THG-7 on the MT-HGCAL-STD form. Controlled versions of forms are located on the Division of Environmental Assessment and Restoration (DEAR) intranet site. An Excel copy of the MT-HGCAL-STD form can be found on the Chemistry Section's computer network, //FLDEP1/DEAR/Labs/Lab5/Chemistry/InorganicPrep/Mercury/W-HG-AF & W-HG-AF-F. Always make sure the most up-to-date form is used by verifying the version number on the Excel form is the same as the version number on the DEAR intranet site. The stannous chloride added to the calibration standards is the same as that used to add to the samples. Print MT-HGCAL-STD and include with lab report.

Reagents and standards are stored in the cabinet above the bench separate from the samples.

4.1 Potassium Bromate (0.05 M) / Potassium Bromide (0.1 M) Solution - Add 8.4 g of potassium bromate ($KBrO_3$) and 11.9 g of potassium bromide (KBr) to an acid cleaned 1 L Teflon bottle. Dilute and dissolve both salts with DI water to 1 L. The solution is prepared as needed and is stored at room temperature. The expiration date for this reagent is 1 year from preparation. The solution is purged with nitrogen for at least two hours before use to remove traces of mercury. Bromine monochloride is prepared in situ by adding hydrochloric acid (HCl) and the bromate/bromide solution to the sample.

**Note**: If contamination is suspected, bake $KBrO_3$ at 175 $^oC$ overnight in a glass scintillation vial in a mercury free oven to remove all traces of Hg in the salt. Do the same with KBr in a clean glass vial. Allow the salts to cool prior to solution preparation.

4.2 Stannous Chloride (3 %) - Weigh 60 g of stannous chloride ($SnCl_2 2H_2O$) and place in a 2 L acid cleaned Teflon bottle. Add 100 mL of concentrated HCl and swirl the solution until the salt dissolves completely in the acid. Dilute the


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solution to 2 L. A 2 L stock of stannous chloride solution typically lasts for 1 analytical run. Before every run, the solution is purged with nitrogen for at least two hours before use to remove traces of mercury in the solution. This reagent is prepared fresh daily and is discarded at the end of the same day it was prepared.

4.3 Aqua Regia (5 %) - To a 20 L polyethylene carboy half filled with DI water, slowly add 750 mL of HCl, and 250 mL of $HNO_3$ in the hood. Dilute to the 20 L mark and mix thoroughly. Store at room temperature. The expiration date for this cleaning solution is 1 year from preparation.

4.4 NIST1641D-1-2008 (15.6 µg/L) - See DEP SOP HG-012 for preparation details. This is the second source standard, i.e. obtained from a different source from the standard used to prepare the calibration standards. The expiration date for this standard is 1 year from preparation and it is stored at room temperature.

4.5 THG-**7** Standard (1.0 µg/L) - See DEP SOP HG-012 for preparation details. This intermediate standard is used to prepare the calibration standards. The expiration date for this standard is 60 days from preparation and it is stored at room temperature.

4.6 Calibration Standards - The calibration standards are prepared from intermediate standard, THG-7. The calibration standards are digested with BrCl like regular samples. The expiration date for the calibration standards is 7 days from preparation. See section 7.4 for preparation details.

4.6.1 W-STD1 (0.4 ng/L) - This standard corresponds to the PQL.

4.6.2 W-STD2 (1.0 ng/L)

4.6.3 W-STD3 (2.0 ng/L)

4.6.4 W-STD4 (5.0 ng/L) - Also serves as the ongoing precision and recovery standard (OPR). This standard must be analyzed after calibration, but before analyzing any samples, and again at the end of the analysis.

4.6.5 W-STD5 (15 ng/L) - Also serves as the continuing calibration verification (CCV) standard for the analysis. This standard is analyzed after every 10 samples throughout the analysis.

4.6.6 W-STD7 (30 ng/L)

4.7 Hydroxylamine Hydrochloride (10 %) - Weigh 10 g of hydroxylamine hydrochloride and place it in an acid cleaned 125 mL Teflon (FEP) bottle in the hood. Add 90 mL of DI water to the bottle, cap it, and shake vigorously until all the solid has dissolved. Remake the solution when the existing supply is exhausted. Purge the solution using nitrogen for at least one hour before use. The expiration date for this reagent is 1 year from preparation and it is stored at room temperature.

4.8 Industrial Grade 1 argon (99.997 %) is supplied to the instrument from the laboratory's Microbulk argon delivery system. Argon is used as the carrier gas for the mercury vapor from the gas liquid separator to the detector.


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4.9 Industrial Grade 1 nitrogen (99.998 %) is supplied from the laboratory's Microbulk nitrogen delivery system. Nitrogen is used to purge the stannous chloride, potassium bromide/bromate, and hydroxylamine hydrochloride solutions before use.

4.10 Trace Metal Grade Hydrochloric Acid (HCl) - Used in the preservation and digestion of samples. Expiration date is indicated on the bottle by the manufacturer.

## 5. CONTAINER PREPARATION

5.1 All containers used to store reagents are made of Teflon and are cleaned thoroughly with solutions of 5 % aqua regia and DI water before use. All containers are rinsed twice with this acid solution, followed by rinsing with DI water at least six times. All beakers, measuring cylinders, and volumetric flasks are subject to the same cleaning procedure before use.

5.2 Narrow mouth 125 mL Teflon (FEP) bottles with leak proof Tefzel caps are used to digest the preserved samples. The bottles are cleaned with 5 % aqua regia solution before use. Fill the sample Teflon bottles to the brim with this solution, cap them firmly. The bottles are emptied and rinsed thoroughly with DI water, (at least six times) before use. The Tefzel caps are also treated with the same degree of thoroughness as the bottles themselves. Care should be taken to ensure that the threads on the bottles and their caps are washed with acid and DI water.

5.3 At the end of an experiment, any remaining solution in the digestion bottles is transferred into a mercury waste disposal container. The bottles are then rinsed once with DI water and filled to the brim with 5 % aqua regia. They are capped firmly and stored until needed.

5.4 The glass autosampler tubes used during analyses are immersed and stored in 5 % aqua regia solution in a large covered beaker for at least two hours and rinsed with DI water six times prior to use.

## 6. SAMPLE COLLECTION, PRESERVATION AND HANDLING

6.1 For ambient monitoring projects, the water samples are collected using clean techniques in cleaned and tested, double-bagged glass 500 mL bottles with Teflon lined caps. Sampling equipment, such as sampling trains, filters, and peristaltic pump tubing are cleaned and double-bagged in polyethylene bags in a clean room prior to the sampling event (See DEP SOP HG-015 for sampling kit equipment cleaning procedure). Once the samples are collected, the bottles shipped via overnight mail to the laboratory. For compliance monitoring projects, collection using clean techniques may not be necessary. The glass 500 mL bottles are not cleaned and tested for compliance monitoring projects.

6.2 Upon receipt, total mercury samples (in clear glass bottles) are stored in the Mercury Clean Room (B110) on shelves separate from reagents and standards at room temperature and preserved by acidifying them using HCl to a pH below 2. This is accomplished by adding 0.5 mL of concentrated HCl per 100 mL of sample. Since the typical sample has a volume of 500 mL, 2.5 mL of HCl is


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added to each sample. Cap the bottles and shake well. The preservation of the sample should be documented in the sample preservation logbook immediately after preservation. Samples must be preserved with HCl within 48 hours of collection. If samples are received that have exceeded the 48-hour time limit, contact the supervisor and document on the log-in checklist. EPA Method 1631E allows for oxidizing the sample in the sample bottle, which extends the time to preservation to 28 days.

6.3 Precipitation (rainwater) samples will arrive in 1 L fluorinated polyethylene containers. The containers will have varying amount of sample in them, depending on the amount of rainfall collected.

6.3.1 Field Blanks - For rainwater field blank samples only, add 350 mL of DI water to the bottle prior to preservation and determining the mass of rainfall collected.

6.3.2 Determining the mass of rainwater collected - After arrival and prior to sample preservation, the mass of rainwater collected must to be determined. This is accomplished by removing the Teflon tape from around the cap of the bottle and weighing the bottle on an analytical balance. Using the Mercury Precipitation – Mass of Sample logbook, document the mass of the bottle plus the collected sample. The field personnel document the tare weight of the bottle on a label placed on the bottle itself. By subtracting the tare weight of the bottle from the mass of the bottle plus sample, the mass of rainfall collected is determined. If a sample is found to have less than 20 g of rainwater (weight of bottle - tare weight of bottle is less than 20 g), then the sample will not be preserved or analyzed and the result for the sample will be reported with an "O" qualifier.

6.3.3 Preservation - The samples should be preserved with HCl in proportion to the mass of the sample (0.5 mL HCL for every 100 g of sample) and corresponding amount of $KBr/KBrO_3$ solution added directly into the bottle to digest the rainwater overnight.

## 7. SAMPLE DIGESTION

7.1 All samples are digested in acid cleaned 125 mL Teflon (FEP) bottles at room temperature for a minimum of 12 hours. Shake the preserved samples (in glass bottle) thoroughly, and transfer 100 ± 0.2 mL (by weight) of each sample to individual 125 mL Teflon bottles and add 2 mL of $KBr/KBrO_3$ solution to each bottle for complete digestion. The samples will turn pale yellow after a few minutes as BrCl is produced in situ. Verify that the pale yellow color remains in the sample. If the yellow color disappears because of consumption by organic matter or sulfides, more BrCl should be added until a permanent yellow color is obtained. Notify supervisor before adding extra BrCl.

**Note**: If additional reagents are used for complete oxidation of samples, the corresponding quality control samples should include additional amounts of reagents. Cap the bottles and shake well. Digest for a minimum of 12 hours.


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7.2 UV photo-oxidation - The recovery of Hg bound within microbial cells may require the additional step of UV photo-oxidation. This step is only required for highly organic samples (possibly effluents). This step is not required for surface or ground water.

7.3 Laboratory Fortified Blank (LFB) - One LFB must be prepared for every 20 sample (or less) batch. LFBs are prepared using sample containers, labware, reagents, and analytical procedures identical to those used to prepare and analyze the samples. This standard is made by diluting the THG-7 standard (section 4.5). Add 0.2 mL of the THG-7 standard to 99.8 mL of DI water and digest as described above in section 7.1.

7.4 Calibration Standards - The calibration standards are prepared by using an Eppendorf pipette to add a specific volume of THG-7 to a glass 500 mL I-Chem bottle containing a measured (by weight) volume of DI water. See Table 1, below, for concentrations and volumes of QC standards.

**Note**: When preparing W-STD1, instead of weighing 199.92 g of water in the I-Chem glass bottle, 200 g of DI water can be added and then pipette out 80 µL of DI water prior to adding the 80 µL of the THG-7 standard. All calibration standards are also subject to the same digestion procedure as described above in section 7.1. A 15.6 ng/L NIST1641D2008-2 standard reference material is also digested. The PQL standard is spiked to have a final concentration of 0.4 ng/L.

7.5 One sample which is not a blank (trip, field, or equipment) is selected at random to prepare duplicate matrix spikes. Prepare three 125 mL Teflon bottles and pipette 50 mL of sample into each one. One will be used to determine the mercury concentration in the sample and the other two will be used for matrix spike duplicates. Matrix spike duplicates are prepared by adding 0.1 mL of the THG-7 standard to the two 50 mL aliquots of the sample. EPA method 1631E requires spike duplicates for a minimum of 10 % of the samples in a batch. Therefore, a second sample is randomly selected in the batch, three aliquots are poured and two of the aliquots are spiked. For rainwater/precipitation samples from the Total Maximum Daily Load (TMDL) project, a 5 ng/L spike is used. Rainwater typically contains much higher levels of mercury – ranging from 5 to 20 ng/L. A summary of the standards, blanks, duplicates, SRMs and matrix spikes is shown below in Table I.

**TABLE 1.**
**Summary of Standards and QC Samples**

| Standard | Conc. of Hg in Solution (ng/L) | Volume of DI water or sample in Solution (mL) | Volume of THG-7 (1 µg/L) Hg Stock |
|---|---|---|---|
| W-STD7 | 30 | 194 | 6.0 mL |
| W-STD5 | 15 | 197 | 3.0 mL |
| W-STD4 | 5.0 | 199 | 1.0 mL |
| W-STD3 | 2.0 | 199.6 | 400 µL |


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| Standard | Conc. of Hg in Solution (ng/L) | Volume of DI water or sample in Solution (mL) | Volume of THG-7 (1 µg/L) Hg Stock |
|---|---|---|---|
| W-STD2 | 1.0 | 199.8 | 200 µL |
| W-STD1 | 0.40 | 199.92 | 80 µL |
| QC Sample | ----- | 100 | |
| Matrix Spike (Surface water) | 2.0 | 100 | 200 µL |
| Matrix Spike (rainwater) | 5.0 | 100 | 500 µL |
| DI PQL | 0.40 | 199.92 | 80 µL |
| NIST1641D2008-2 | 15.6 | 199.8 | 200 µL NIST 1641D-1-2008 Stock |
| LFB | 2.0 | 99.8 | 200 µL |

7.6 Method Blank and Continuing Calibration Blank (CCB) - Method blanks are used to demonstrate that the analytical system is free from contamination. Method blanks are prepared and analyzed using sample containers, labware, reagents, and analytical procedures identical to those used to prepare and analyze the samples. Prepare 5 100 mL aliquots of the method blank in five 125 mL Teflon bottles. Five method blanks (digested DI water blanks) are analyzed with every batch of samples. These blanks contain the same amount of digestion reagents as regular samples. The concentration of Hg in the method blank is subtracted from the concentration of Hg in the sample. The method blank Hg concentration must be below 0.5 ng/L prior to blank subtraction. The method blank is equivalent to the system blank and the reagent blank in EPA method 1631E. This digested blank also serves as the CCB and is analyzed after every 10 samples.

7.7 Just prior to the analysis of a batch of samples, add 100 µL of 10 % hydroxylamine hydrochloride solution to each 100 mL of digested sample in the FEP bottles. The reagent is a mild reducing agent, and serves to reduce excess BrCl in the samples. Hydroxylamine should also be added to all the standards, blanks, QC samples, and to any solution containing BrCl prior to analysis. The pale yellow color of the sample will disappear with the addition of the hydroxylamine. Swirl the bottle gently.

## 8. SETTING UP THE TEKRAN 2600

8.1 Check the argon regulator to ensure the argon supply pressure to the instrument is 30 psi. The argon supply should be left open, supplying argon to the instruments 24 hours a day.

8.2 Prepare 2 L of the 3 % solution of stannous chloride according to section 4.2.

8.3 Check the volume of the rinse solution, DI water. There should be at least 20 L of rinse solution in the appropriately labeled 25 L reservoir bottle.


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8.4 Purge the stannous chloride solution of any potential mercury contamination for at least 1 hour using nitrogen.

8.5 If necessary, the soda lime inside the drying tube should be replaced.

8.6 If necessary, adjust the flow meter for the detector line (Argon) to 70 mL/min and the flow meter for the phase separator line to 450 mL/min.

8.7 Set-up the peristaltic pump. The grey-grey tubing is used for stannous chloride, blue-blue tubing for the sample, and purple-purple and blue-blue tubing are used for waste.

8.8 Set up the rinse water pump. Make sure that all pump tubing is securely connected at both ends of the tube.

## 9. INSTRUMENT PARAMETERS

Table 2 shows the settings for the method parameters that are used to measure Hg concentrations between 0.10 and 30 ng/L on a Tekran 2600 Mercury analyzer. The instrument control parameters which define a method are stored in a method file. The instrument and its fluorescence detector are left on 24 hours a day.

Detector carrier gas flow rate: 70 mL/min
Phase Separator flow rate: 450 mL/min
Pressure at the Detector purge inlet: 25 psi

**TABLE 2.**
**Tekran 2600 Method Parameters**

| | Comment | Value | Start | Duration | Notes | End |
|---|---|---|---|---|---|---|
| 1 | MFC | 80.0 ml/min | 2 | 600 | MFC:80 ml/min for 600 sec | 602 |
| 2 | Pump | 42.0% | 3 | 600 | PUMP: ON for 600 sec | 603 |
| 3 | V3:gas | ON | 3 | 630 | V3: gas ON for 630 sec | 633 |
| 4 | V4:WashPmp | ON | 4 | 600 | WashPmp: ON for 600 sec | 604 |
| 5 | V1:Vent | ON | 5 | 140 | V1: Vent A | 145 |
| 6 | A/S Up | 5 | 6 | 0 | A/S UP | 6 |
| 7 | A/S Move | -2 | 8 | 2 | A/S Move to sample tube | 10 |
| 8 | Opt2:Beep | ON | 11 | 2 | Opto-2:Signal Position Change | 13 |
| 9 | A/S Down | 5 | 12 | 0 | A/S Down 5 Speed | 12 |
| 10 | Pump | 52.0% | 12 | 23 | Pump 52.0% for 18 sec | 35 |
| 11 | AD12 Scan | 0 | 20 | 5 | AD12 Scan & Store | 25 |
| 12 | Pump | 42.0% | 29 | 574 | Pump 42.0% for 574 sec | 603 |
| 13 | V2:Load-A | ON | 45 | 70 | V2:Load ON for 70 sec | 115 |
| 14 | A/S Up | 5 | 115 | 2 | A/S UP | 117 |


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| | Comment | Value | Start | Duration | Notes | End |
|---|---|---|---|---|---|---|
| 15 | A/S Move | -1 | 117 | 3 | A/S Move to Rinse Tube | 120 |
| 16 | Opt2:Beep | ON | 120 | 1 | Opto-2:ON for 1 sec | 121 |
| 17 | A/S Down | 5 | 121 | 4 | A/S Down | 125 |
| 18 | Heater-A | 100.0% | 135 | 32 | Heat A 100% | 167 |
| 19 | A/S Up | 5 | 137 | 2 | A/S UP | 139 |
| 20 | A/S Move | 0 | 139 | 3 | A/S Move to Wash Stn | 142 |
| 21 | Opt2:Beep | ON | 142 | 1 | Opto-2:ON for 1 sec | 143 |
| 22 | A/S Down | 5 | 143 | 4 | A/S Down | 147 |
| 23 | Fan-A | ON | 167 | 40 | Fan A ON | 207 |
| 24 | Heater-B | 100.0% | 185 | 35 | Heat B 100% for 32 sec | 220 |
| 25 | Heater-A | 0.0% | 186 | 80 | Heater-A: 0% for 80 sec | 266 |
| 26 | Ad24 Start | 0 | 195 | 50 | AD24 Start: 50 lines | 245 |
| 27 | Heater-B | 0.0% | 245 | 50 | Heater-B: 0.0% for 50 sec | 295 |
| 28 | Fan-B | ON | 245 | 50 | Fan-B:ON for 40 sec | 295 |
| 29 | Done | 0 | 246 | 0 | Done | 246 |

## 10. STARTING A RUN

10.1 Start the Tekran 2600 program and go to the menu “worksheet” followed by “run” and “new”.

10.2 Fill in the worksheet with the samples and QC to be analyzed. A suggested sequence is shown below:

CLEAN
CLEAN
MBLK
MDL
W-BLK1
W-BLK2
W-BLK3
W-BLK4
W-BLK5
5 CALIBRATION STANDARDS
CCV (W-STD5)
RINSE
CCB
ICV (W-STD4)
ICB (CCB)
W-PQL


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NIST1641D2008-2
SAMPLE
SAMPLE_SP1
SAMPLE_SP2
LFB_1
SAMPLE 1
SAMPLE 2
SAMPLE 3, etc.
CCV (W-STD5)
RINSE
CCB

End of run sequence:

CCV (W-STD5)
RINSE
CCB
ICV (W-STD4)
ICB (CCB)

10.3 Every 10 samples a continuing calibration verification (CCV, W-STD5) should be run to ensure that the system is still in calibration and to check for baseline drift. This check standard should be followed by a rinse. The rinse solution consists of 5 % aqua regia in DI water. This is followed by a CCB.

10.4 Click on the "start" icon to start the run.

## 11. COMPLETING AN ANALYSIS

11.1 The analyst should perform blank correction on the instrument output for regular samples, CCV standards, and QC samples. For all samples, the blank correction can be determined with the following formula:

$$\text{Blank Correction} = \frac{\text{Average of 5 Digestion Blanks}}{\text{Mean Calibration Factor}}$$

11.2 The blank correction value must be lower than 0.5 ng/L. This "blank level" mercury in the blanks comes from a combination of sources including the digestion reagents (hydrochloric acid, bromide, bromate and hydroxylamine hydrochloride), the detector background (dark current) signal, and the DI water used to prepare the blanks. Thorough purging of the reagents with nitrogen usually results in very low reagent contribution (< 0.1 ng/L) to the blank.

11.3 To calculate the blank-corrected concentration of a sample from the instrument output, divide the output by the mean calibration factor and then subtract the blank correction value, as shown in the formula below. The blank correction is performed on **all** the samples in the analysis including QC samples, and is calculated as follows:


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$$\text{Blank Corrected Concentration} = \frac{\text{Instrument Output}}{\text{Mean Calibration Factor}} - \text{Blank Correction}$$

11.4 The relative standard deviation (RSD) of the calibration factors for all calibration points must be less than 15 % where,

$$\text{RSD} = \frac{\text{Standard Deviation of Calibration Factors}}{\text{Mean Calibration Factor}} \times 100$$

11.5 The calibration factor for any point < 0.5 ng/L (W-STD1) must be within 25 % of the average calibration factor for all points.

$$\text{Percentage} = \frac{(\text{Calibration Factor of W-STD1}) - (\text{Mean Calibration Factor})}{\text{Mean Calibration Factor}} \times 100$$

11.6 To check the MDL for the run multiply the standard deviation of the blanks by the corresponding '**t**' value, where '**t**' is the value of the Student's t test. For five, the '**t**' value is 3.747 for a 99 % confidence interval. This product, which checks the MDL for the analytical run, must be below 0.10 ng/L.

**Note**: This MDL check requirement is only needed for samples from the South Florida Water Management District (SFWMD).

11.7 It is the responsibility of the analyst to ensure that QC limits are not exceeded in the course of the analysis and that appropriate actions are taken. Record all calculated blank-corrected recoveries in the analysis program sheet. Any changes in the sample sequence should also be recorded here, as well as any instrument problems encountered and action taken.

11.8 After the run is completed, print the data and "export file" to Tek Data. The file should be stored in the directory "Tek_Data". The naming of the data file should follow the following convention, YYYYafMMDDw1-A. For example, 2016af0210w1-A indicates that the file contains data from the first analytical run on water samples (w1) conducted on February 10, 2016. The "af" stands for atomic fluorescence and thereby identifies the instrument used for the analysis. This nomenclature identifies the day the data file is generated, the matrix analyzed, and the instrument used to analyze the sample. Since this method applies to waters only, the letter 'w' is used as the identifier. If more than one run is conducted in any given day, then the numbers 1, 2 … may be used to number successive runs in the day. The –A or –C refers to which instrument the samples were analyzed on. Tekran A has the serial number 001. Tekran C has the serial number 0154. Check to make sure the file is saved correctly before exiting the program. Then, the worksheet needs to be saved as an Excel and text file. The


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Excel and text file are saved to \\FLDEP1\DEAR\Labs\Lab3\Chem_Data\Inorganic\Mercury\Tekran with the same naming format, YYYYafMMDDw1_A.

## 12. SHUTTING DOWN THE TEKRAN 2600

12.1 Disconnect the pump tubing from the stannous chloride. Rinse out the stannous chloride line for about 5-10 minutes by connecting it to DI water. Also make sure that the phase separator is thoroughly rinsed in the process. Make sure that the rinse water is continuously pumped away from the bottom of the phase separator, so as to prevent a buildup of water in the separator.

12.2 After rinsing out all the lines for about 5-10 minutes, switch the pumps off and release the pump tubing from the peristaltic pump rollers and the rinse pump.

## 13. QUALITY CONTROL

Quality Control Limits for this method are listed below in Table 3.

**TABLE 3.**
**Tekran 2600 Method QC Limits**

| CALIBRATION CURVE | **CF R**SD < 15 % and W-STD1 within 25 % of average CF | | |
|---|---|---|---|
| MDL check for SFWMD = SD (5 blanks) * 3.747 | 0.10 ng/L or less | | |
| | | | |
| | **LEVEL** | **RECOVERY** | **RPD** |
| PQL (W-STD1) | 0.40 ng/L | 70 % - 130 % | |
| ICV (W-STD4) | 5 ng/L | 85 % - 115 % | |
| NIST1641D2008-2 | 15.6 ng/L | 85 % - 115 % | |
| DUP. SAMPLE | | | ≤ 20 % |
| DUP. SPIKE (Surface water) | 2.00 ng/L | 80 % - 120 % | ≤ 20 % |
| DUP. SPIKE (Rain water) | 5.00 ng/L | 80 % - 120 % | ≤ 20 % |
| LFB | 2.0 ng/L | 80 % - 120 % | |
| CCV (W-STD5) | 15 ng/L | 85 % - 115 % | |

## 14. INTERFERENCES

14.1 Potential negative interferences for this method include oxygen and water vapor. Oxygen quenches the fluorescence signal, while the presence of water vapor scatters the analyte's fluorescence, thus reducing the signal reaching the detector. Oxygen is largely eliminated from the system by the use of argon, and by using an oxygen trap to capture trace quantities of the gas. The soda-lime trap eliminates moisture in the carrier stream before it reaches the gold traps.


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14.2 Compounds which fluoresce at the same wavelength as mercury constitute a positive interference for this method. Aromatic hydrocarbons are serious interferences, since these compounds fluoresce strongly at 254 nm. Again this interference is eliminated by the use of ultra-pure carrier gas and by the use of a hydrocarbon trap in the argon and nitrogen gas streams.

## 15. CORRECTIVE ACTIONS FOR COMMON PROBLEMS

Corrective actions for common QC failures are listed in Table 4 below. The instrument also requires routine maintenance such as changing the soda lime every other day, and changing the pump tubing on a regular basis.

**TABLE 4.**

**Corrective Actions**

| Problem | Corrective Action |
|---|---|
| Calibration standard's response factor below expected value. | Check the detector lamp and its alignment. |
| Calibration acceptance parameters (see section 11.4 and 11.5) not met. | Remake the standards and recalibrate the instrument. |
| Failure of instrument blank. | Check vials for contamination and the detector for drift. Change soda-lime, and clean the phase separator. If these measures fail to fix the problem, change the pump tubing. |
| Failure of CCV. | Check the detector for drift. |
| Failure of external SRM (NIST1641D2008-2), PQL, matrix spikes, or replicate RPD. | Re-digest the samples and repeat the analysis. |

## 16. SAFETY/HAZARDOUS WASTE MANAGEMENT

16.1 Review the Laboratory Health and Safety Plan located on the Division of Environmental Assessment's intranet site.

16.2 Refer to DEP SOP HG-013 for correct waste disposal procedures.

16.3 Always wear safety glasses or protective eyewear while working in the lab. Powder free nitrile gloves should be worn while handling chemicals. Concentrated acids should be handled in a ventilated hood. Since this method is conducted in a clean room, appropriate clean room garb, including a *Tyvek* coat, *Tyvek* shoe covers, and a hair net should be worn at all times.

## 17. REFERENCES

17.1 Tekran 2600 instrument manual

17.2 EPA Method 1631, Rev. E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry, (Aug, 2002)



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17.3 DEP SOP HG-012, Mercury Group Standards Preparation Procedures

17.4 DEP SOP HG-013, Mercury Waste Disposal

17.5 DEP SOP MT-069, Metals Standard and Reagent Preparation Procedure

17.6 Health and Safety Plan, located on the Division of Environmental Assessment and Restoration intranet site.

17.7 DEP SOP HG-015, Preparation of Sampling Kits for the Collection of Trace Level Mercury Water Sample.

17.8 Solution 2000 Type I Reagent Grade Water Purification System Operating Manual.

## Appendix of Significant Changes

| | |
|---|---|
| 12/02/2008 | Changes have been made in Sections 7 and 11. Other minor revisions to the text were made for format and clarity. |
| 07/02/2009 | Updated calibration requirements to EPA method 1631E.<br>Added storage temperature and holding times for reagents, stock standards, and working standards.<br>Added sample digestion temperature and sample storage temperature. |
| 07/20/2010 | Added method calibration requirements to section 11.<br>Added Appendix A |
| 07/07/2011 | Removed references to the use of an instrument blank. |


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