Florida Department of Environmental Protection

Analysis of Total Mercury by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry

Bureau of Laboratories
Michael Thompson, *Chemistry Section*

Mercury Analysis Methods

EPA Method 1631E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry. MDL = 0.1 ng/L

EPA Method 245.7: Mercury in Water by Cold Vapor Atomic Fluorescence Spectrometry. MDL ~ 1.0 ng/L

EPA Method 245.1: Determination of Mercury in Water by Cold Vapor Atomic Absorption Spectrometry. MDL = 120 ng/L.

Overview of Performing Method 1631E

- Cleaning sampling supplies and transporting supplies to the field.
- Field sample collection.
- Transporting samples back to the laboratory.
- Laboratory receiving, preservation, and storage.
- Sample preparation.
- Sample analysis.
- Reporting results.

Preparations for Field Sampling

Glass bottles for sample collection

- Cleaned
- Tested
- Labeled

Sample Trains

- Cleaned
- Tracked

Deionized Water

- PETG bottle, 2 L

Preservation and Holding Time

Method 1631 Requirements

- Samples are preserved by adding either 5 mL/L of HCl or 5 mL/L of bromine monochloride (BrCl).
- Samples must either be preserved or analyzed within 48 hours of collection.
- Preserved samples are stable for up to 90 days from the date of collection.
- Refrigeration is not necessary.

Sample Preparation

- A 100 mL aliquot of the thoroughly shaken and preserved sample is transferred to a 125 mL Teflon bottle.
- 2 mL of a potassium bromide / potassium bromate (KBr / $KBrO_3$) solution is added to each 100 mL aliquot of sample.
- The sample will turn pale yellow after a few minutes as bromine monochloride ($BrCl$) is produced in situ.
- The $BrCl$ oxidizes all mercury in the sample to the Hg^{2+} state.

Sample Analysis

- After oxidation of mercury to Hg^{2+} using BrCl, excess BrCl is destroyed with hydroxylamine hydrochloride ($NH_2OH \cdot HCl$).
- 100 µL of 10% $NH_2OH \cdot HCl$ is added to each 100 mL aliquot of sample.
- The sample is now ready for analysis with the Tekran 2600 Automated Analysis System.
- 30 mL of sample analyzed.

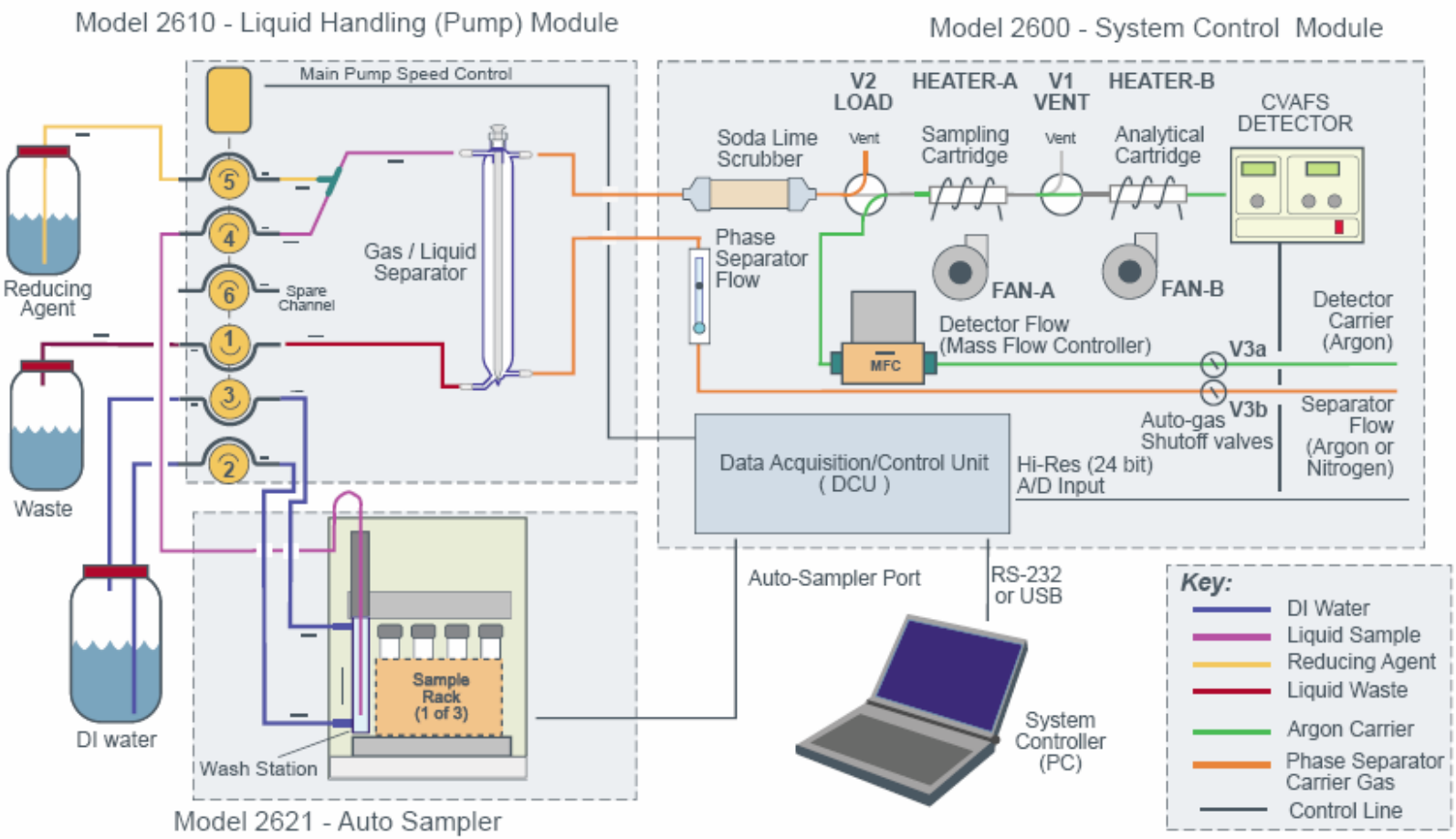
Tekran 2600 Instrument Components

- Auto Sampler
- Six Channel Peristaltic Pump
- Phase Separator
- Dual Gold Traps
- Atomic Fluorescence Detector

Sample Analysis

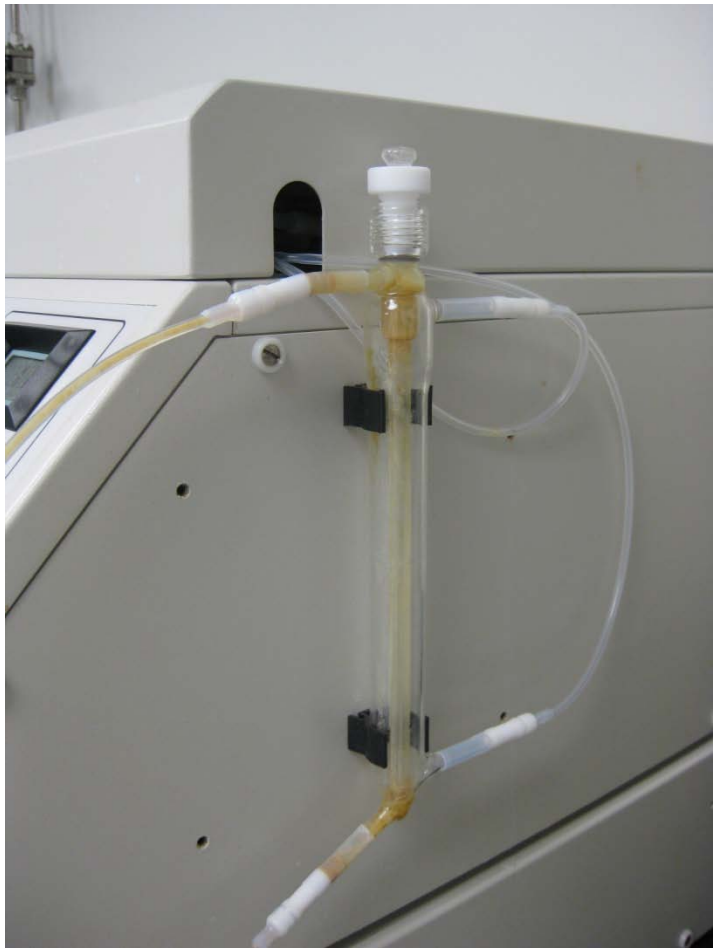
Oxidation	Bromine monochloride (BrCl)	Hg^{2+} (liq.)
Reduction	Stannous Chloride ($SnCl_2$)	Hg^0 (liq.)
Purge	Gas / Liquid Separation	Hg^0 (gas)
Trap	Gold Traps	Hg^0 (gas)
Desorption	Heat Gold Trap	Hg^0 (gas)
Detection	Atomic Fluorescence	λ = 253.7 nm

Tekran 2600 Flow Diagram



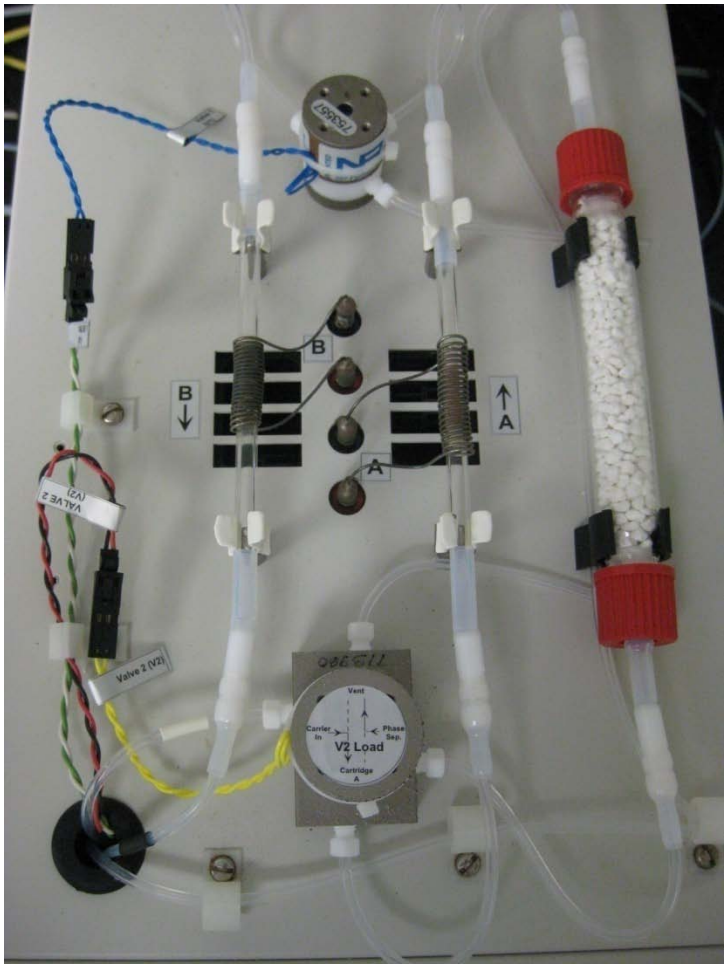
Phase Separation

- The sample is mixed in-line with stannous chloride ($SnCl_2$) to reduce all Hg^{2+} to Hg^0.
- The Hg^0 is stripped from the aqueous phase with a phase separator.



Sample Analysis

- After gas / liquid separation, Hg^0 is swept through a soda lime dryer with the carrier gas, argon, and then trapped on the first gold trap.
- The gold trap is then heated, releasing the Hg^0 and the carrier gas sweeps it to the analytical gold trap.
- The second gold trap is heated to release the Hg^0 and the carrier gas sweeps it to the cuvette.



Atomic Fluorescence Detection

- Elemental mercury atoms in the argon carrier gas stream are excited by a source of ultraviolet radiation. The atoms fluoresce as they return to the ground state. Both the excitation and fluorescence occur at wavelength 253.7 nm.
- A low pressure mercury vapor lamp produces the ultraviolet radiation at 253.7 nm.
- A photomultiplier tube (PMT) views the fluorescence through a interference filter at a right angle to the incident light.
- The intensity of the fluorescence is directly proportional to the amount of elemental mercury present.

Calibration Requirements

- Calibration Factors
- Five point calibration
- The relative standard deviation of the calibration factors for all calibration points must be less than 15%.
- The calibration factor for any point < 0.5 ng/L must be within 25% of the average calibration factor for all points.

$$\text{Calibration Factor} = \frac{\text{Instrument Output}}{\text{Concentration of Calibration Standard } \left(\frac{\text{ng}}{\text{L}}\right)}$$

$$\text{Sample Result} = \frac{\text{Instrument Output}}{\text{Mean Calibration Factor}} - \text{Blank Correction}$$

Quality Control

- Sample batch defined as a set of samples oxidized with the same reagents and analyzed during the same analytical run.
- Up to 20 samples in one batch.
- Five method blanks.
- One laboratory fortified blank.
- One standard prepared at the limit of quantitation.
- One certified reference standard: NIST1641d.
- Matrix spike duplicates at a frequency of 10%.
- Continuous calibration verification standard and blank analyzed every 10 samples.

Blank Subtraction

- EPA Method 1631E allows blank subtraction using the method blank or a field blank associated with the samples.

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

- The mean result for the 5 method blanks must be < 0.5 ng/L with a standard deviation < 0.1 ng/L.

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

Summary

EPA Method 1631E provides the lowest detection limit for mercury in water by implementing dual gold traps and atomic fluorescence spectrometry.

Michael Thompson

Florida Department of Environmental Protection

michael.thompson@dep.state.fl.us