



Understanding Mercury

Introduction – Mercury has a history full of fascination and wonder. It is the only metal that is in liquid form at room temperature. The ancient alchemists considered it the original metal and used large quantities of it in their attempts at transmutation. It was used to construct reflecting pools and decorative fountains in the courtyards of kings. In modern times it has been used in thermometers, thermostats, and as parabolic mirrors in telescopes. It was with great disappointment that mankind fully understood the toxicity of such a visually fascinating element. Because of mercury's tendency to accumulate in organisms it can have very long lasting and slow developing negative health effects. Many States now ban products containing mercury from crossing over State lines. The requirements for mercury removal are getting tighter and detection limits are falling.

Approved Methods – Samples can be analyzed for mercury by any of the following methods.

- Manual Cold Vapor Atomic Absorption Spectroscopy (CVAAS)
 - EPA 245.1
 - SM 3112B-2009
- Automated CVAAS – EPA 245.2
- Cold Vapor Atomic Fluorescence Spectroscopy (CVAFS) – EPA 245.7
- Purge and Trap CVAFS – EPA 1631E

Method Summary – For CVAAS an acidified portion of the sample is digested and oxidized at 95°C with permanganate and persulfate solutions. After digestion, excess permanganate is removed via the addition of hydroxylamine hydrochloride. Stannous chloride reduces the mercury to its elemental form. The mercury is then measured via cold vapor atomic absorption.

For CVAFS, the sample is oxidized with a bromine based reagent. Following oxidation, the sample is treated with hydroxylamine hydrochloride and stannous chloride in a similar manner to CVAAS. In the purge and trap method, the mercury is separated from the sample and carried in an inert gas stream, typically argon, to a series of gold traps that help to concentrate the mercury. From there it is introduced into the CVAFS detector. For CVAFS without the purge and trap, the mercury is separated from the sample and carried directly into the detector.

What You Should Know – While proper sampling and storage techniques are important in any analytical process, it is even more important in the case of mercury. With the advent of new sampling and analytical techniques in the mid 1980s, scientists discovered that the previously reported levels of mercury in the environment were biased high, sometimes by as much as three orders of magnitude. It was found that, outside of areas in which mercury was being mined, the highest concentration of the metal was to be found in and around man-made artifacts. Paints, electrical components, lighting fixtures, thermometers, thermostats, and batteries were among the common contributors to ambient contamination. Conditions were often worse in



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the laboratories performing the analyses due to mercury based reagents and equipment with mercury containing parts being even more prevalent. Lack of knowledge as to the true environmental amounts coupled with mercury's volatility made unintentional contamination of the analysis unavoidable. The EPA has published [method 1669](#) to give guidance on trace metal sampling. Strict adherence to these guidelines will minimize the amount of contamination caused by the sampling procedure.

The detection limits that you need will go a long way to determining what method you will use in analyzing for mercury. SM 3112B appears to have the most limited range of the accepted methods with a method calibration range of 1-5µg Hg/L. Method 245.1 has a listed operating range of 0.2-10 µg Hg/L while 245.2 gives a range of 0.2-20 µg Hg/L. Method 245.7 lowers the detection limit down to 5.0 ng Hg/L and gives an upper operating range of 100 ng Hg/L. Method 1631E has the lowest available detection limit of 0.5 ng Hg/L with an upper limit of 100 ng Hg/L. Many of the methods give instructions that the calibration ranges may be extended by appropriate alteration of the sample size. Use of smaller volumes is fairly easy to accomplish to either dilute samples within range or to extend the calibration range, as long as linearity is maintained. It becomes more problematic to use larger sample volumes in an attempt to concentrate the sample and thus lower the detection limits.

Your detection limits will also dictate the preservation and holding time that is required for your sample. According to footnote 17 in Table II of 40 CFR part 136, "Samples collected for the determination of trace level mercury (<100 ng/L) using EPA Method 1631 must be collected in tightly-capped fluoropolymer or glass bottles and preserved with BrCl or HCl solution within 48 hours of sample collection. The time to preservation may be extended to 28 days if a sample is oxidized in the sample bottle. A sample that has been collected for determination of total or dissolved trace level mercury must be analyzed within 90 days of sample collection." Samples that are collected for methods intended for greater than trace level are to be preserved in HNO₃ to a pH of less than 2 and have a holding time of 28 days.

The reagents used in mercury analysis, particularly low level mercury, are especially hazardous to work with. Be sure to pay special attention to all safety issues and ensure proper PPE is in place at all times. The mercury standards in and of themselves can be dangerous, while the BrCl, hydroxylamine hydrochloride, and stannous chloride all give off noxious fumes that can severely irritate the respiratory tract.



Method Procedure

Note – This is not intended to be a standalone method and does not address all safety or quality control aspects that may be required. Please consult your local regulations to comply with all requirements. This method will only address the preparation of the sample for analysis.

CVAAS

1. Collect your sample in an appropriate size [polyethylene, fluoropolymer, or glass vessel](#). For reduced volume methods a 250 mL size container is generally sufficient to allow for spikes or duplicates and have enough left over for reanalysis if necessary.
2. Preserve the sample with the [appropriate amount of nitric acid](#) to a pH less than 2.0. This may be done after transport to the lab.
3. Allow the sample to sit for a minimum of 16 hours after preserving and verify that the pH is below 2.0. If the pH is not below 2.0 add additional nitric acid and wait an additional 16 hours to recheck the pH. Repeat as needed.
4. Adjust the [HotBlock](#) temperature to give a sample temperature of 95°C.
5. Add 20 mL of well mixed sample to the [SC475](#) digestion vessel. NOTE – If using the larger [SC490](#) vessels double the given sample and reagent volumes.
6. Add 1.0 mL [concentrated H₂SO₄](#) and 0.5 mL [concentrated HNO₃](#).
7. Add 3.0 mL of [potassium permanganate solution](#) to the sample and allow to sit for 15 minutes. If the purple color does not remain after 15 minutes add additional portions until the color remains for 15 minutes.
8. Add 1.6 mL of [potassium persulfate solution](#) to the sample.
9. Cover the sample (if required) with a [disposable watch glass](#) or [reflux cap](#).
10. Allow samples to digest at 95°C for 2 hours.
11. After 2 hours remove samples from the HotBlock and allow to cool to room temperature.
12. Add 1.2 mL of sodium chloride hydroxylammonium chloride to the sample.
13. Follow the instructions given by your instrument manufacturer for calibration and analysis of the samples.

CVAFS

1. Following the procedure outlined in [EPA 1669](#), collect your samples in fluoropolymer or [glass containers](#) that have been rigorously cleaned. The caps must be fluoropolymer lined and seal tightly. Don't forget [field blanks](#) or [trip blanks](#) if they are required for your project.
2. Preserve the samples with 5 mL/L [12 N HCl](#) or 5 mL/L [BrCl solution](#).
3. If sample was preserved with HCl or if the amount of BrCl was not sufficient (yellow color did not remain for 12 hours) add additional BrCl solution to the samples. (See EPA 1631 section 11.1 for detailed instructions on



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the amount of BrCl solution to add and how to deal with difficult matrices.) Allow the samples to digest at room temperature for a minimum of 12 hours.

4. Follow the instructions given by your instrument manufacturer for calibration and analysis of the samples.
5. [Stannous chloride](#) and [hydroxylamine hydrochloride](#) are available for use in preparing solutions for the sample analysis.

See the [1631 Low Level Hg](#) page for a full list of reagents and supplies for your mercury analysis needs. As always, with either method, don't forget your [calibration standard](#).

We all like things that make life easier. Was this document helpful? Or do you...disagree with something?

Have something to add? Contact me at DavidS@envexp.com to let me know what you think.