Selecting the Best Technique for Mercury Measurement

A Practical Guide

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**Teledyne Leeman Labs**
110 Lowell Road
Hudson, NH 03051 U.S.A
www.teledyneleemanlabs.com

**Sales Support:** 800-634-9942
**Technical Support:** 800-533-6267
**Main:** 603-886-8400
**Fax:** 603-886-4322
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## About This Guide

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Selecting the Best Technique for Mercury Measurement

ABOUT THIS GUIDE

As governments, scientific communities, environmentalists, medical professionals and the public at large recognize the persistent, bio-accumulative, and toxic nature of mercury, there is increasing demand for better control and monitoring of its release into the environment. The need to better understand how mercury is generated as a global pollutant, as well as determine its transport and fate in our global environment and microecosystems, has necessitated the development of increasingly sensitive analytical techniques for its determination. As these techniques and methodologies become established in the scientific community, a number of regulatory agencies around the world have adopted them and developed analytical methods for their own use.

The global scientific study of the transport and deposition of mercury has resulted in several highly-sensitive mercury analysis techniques, as well as detailed methods based on each technique. Deciding which technique is best suited for your mercury determinations can be difficult to discern. It is our hope that the information in this practical guide will assist you in choosing the mercury analysis technique, as well as the system that will meet your needs and become a sound, long-lasting investment. In this guide we will review:

- Basic principles of mercury analysis
- The application of those analytical principles in the context of both historical and current technologies
- Identifying the mercury analysis technique that will fit your analytical requirements and cost structure
- The primary features and value of the mercury analysis systems offered by Teledyne Leeman Labs

ABOUT TELEDYNE LEEMAN LABS

At Teledyne Leeman Labs we develop instruments that satisfy a variety of mercury analysis needs and provide our customers with a choice of mercury analysis systems that meet their daily analytical requirements. Our customers include laboratories in a variety of fields including Environmental, Academics, Petrochemical, Food, Mining, Agricultural, Nuclear Energy, Pharmaceutical, Nutraceutical, Water and Waste Water. Our mercury analysis systems are based on the mature and time-honored techniques of Cold Vapor Atomic Spectroscopy (CVAS) and gold enrichment (gold trap amalgamation). We then couple these techniques with well-established processes for sample preparation, sample introduction and data collection to create exceptional instruments for mercury determination. Our Hydra II and QuickTrace® mercury product lines are designed to cover a variety of techniques and digest matrices, as well as meet the stringent requirements of US EPA and EN methodologies.
THE BIRTH OF COLD VAPOR ATOMIC ABSORPTION SPECTROSCOPY (CVAAS)

Cold Vapor Atomic Spectroscopy was introduced in 1968 by Hatch and Ott on the heels of the first commercially available atomic absorption spectrometer. In their work they described an attachment for a flame atomic absorption spectrophotometer that enabled the reduction of Hg\(^{2+}\) in a solution to ground-state atoms (Hg\(^0\)). The ground-state mercury atoms were then transported to an optical cell and detector for measurement. Through the combination of these technologies, Cold Vapor Atomic Absorption Spectroscopy (CVAAS) was born. Within a short period CVAAS quickly became the reference technique for mercury determinations with the US EPA adopting the technique for the determination of mercury in water, soil, and fish. Today, CVAAS remains one of the primary techniques for mercury analysis and is the reference method for drinking water monitoring under the Safe Drinking Water Act (SDWA) passed in 1974 and amended in 1986 and 1996.

In many parts of the world, reduction of aqueous samples and mercury determination by CVAAS is still the most commonly used technique. Key characteristics of this approach with late model CVAA systems include:

- Detection limits in the single-digit part per trillion range (ng/L)
- A linear dynamic range of 3 to 4 orders of magnitude
- An abundance of analytical methods designed to determine the mercury concentration in almost any sample matrix

In contrast to early systems, modern CVAAS instruments are more sensitive, automated, smaller, faster and less expensive than generic flame spectrometers with cold vapor attachments. Today’s CVAAS systems provide trace to ultra-trace detection limits of ng/L and are able to analyze samples in approximately one minute. Most systems require very little operator interaction and minimal bench space.

For a majority of CVAAS instruments, a peristaltic pump is typically used to transport sample and stannous chloride into a Gas Liquid Separator (GLS) where a stream of pure, dry gas (typically argon) is introduced to the liquid mixture to release mercury vapor. The mercury in the vapor phase is then carried by the gas through a dryer and into an atomic absorption optical cell. Once in the absorption cell, the elemental mercury will absorb light at 253.7 nm and does so in logarithmic proportion to its actual concentration in the sample. Using this principle the detector, in combination with the software, is able to determine the quantity of mercury present in the sample.

**NOTE**

Beer Lambert’s Law defines the basic relationship between absorbance (A) and concentration (C) as

\[ A \equiv -\log(I/I_0) = abC, \]

Where “I” is the transmitted intensity with analyte present, “I\(_0\)” is the transmitted intensity with no analyte present, “a” is the absorption coefficient of the analyte and “b” is the optical path length.

CVAAS can employ several different mechanisms of conveying the reduced mercury in solution to the gas stream and then onward to the spectrometer. Commercially available approaches include:

- **Bubbling Gas Through the Sample**

  This approach has been used from the introduction of the technique. It is effective, but the turbulent nature of the gas movement is prone to create long-lived bubbles, especially when the sample matrix has a tendency to foam. These bubbles may migrate out of the Gas Liquid Separator (GLS) and interfere with analytical measurements or the proper operation of the instrument. To mitigate the production of bubbles, Teledyne Leeman Labs developed a GLS incorporating a serpentine gas path with our second generation system (the Hydra AA) in which the sharp edges of the path reduced the formation of bubbles. This was a successful approach and is still in use today with the Hydra II\(_{AA}\).
Thin Film Interface

In this design, the sample/reductant mixture is deposited at the top of a glass center post with a frosted surface that effectively increases the reaction surface area. The liquid mix migrates to the bottom of the separator as a thin film while the carrier gas travels upward over the surface of the film. This approach provides a large surface area for the gas/liquid interface and does not introduce turbulence, making bubble formation rare. The thin film interface was originated by and patented by CETAC Technologies in 1998 and is utilized on the Teledyne Leeman Labs QuickTrace® M-7600 CVAA and M-8000 CVAF mercury analyzers.

In-Situ Reduction

In this design, reducing agents are added to the sample cup itself after which the cup is sealed and a carrier gas is introduced directly into the sample container. Claimed advantages to this approach include reduced sample carryover (due to the liquid sample remaining in the sample cup) as well as a lower level of waste generation. Disadvantages include the requirement of a positive seal between the impinger and sample cup for accurate results and a one replicate per sample cup limitation.

Teledyne Leeman Labs Hydra IIAA CVAAS Mercury Analysis System

The Teledyne Leeman Lab’s entry level CVAAS system, the Hydra IIAA is shown in Figure 1. The system is capable of detection limits of < 5.0 ng/L and has a usable range of 5 ng/L - 1 mg/L. By quickly changing the analyzer’s modules it can be converted to a direct analysis combustion (thermal decomposition) mercury analyzer.

How the Hydra IIAA Works

The Hydra IIAA design is based on US EPA method 245.1. The applicable methods typically require sample digestion techniques that produce liquid samples with mercury present in the +2 valence state.

Refer to Figure 2 to trace the processes of the Hydra IIAA CVAAS mercury analyzer. The acidified digested aqueous sample from the autosampler is introduced via the peristaltic pump as Hg^{2+} dissolved in solution (1). Simultaneously, a reducing agent (10% SnCl₂ in 7 – 10% HCl) is introduced via another parallel peristaltic pump channel.

NOTE

The reducing solution typically used is stannous chloride (10% w/v) in 10% hydrochloric acid although a sodium or potassium borohydride solution will also work. While a reducing solution of SnSO₄ in sulfuric acid is called out in EPA methods 245.1 and 7470, it is not recommended to obtain the best analytical results.
The sample and reagent streams join at the mixing tee (2) and immediately enter the mixing tube (3) where the stannous chloride (Sn$^{2+}$) reduces Hg$^{2+}$ in solution to Hg$^{0}$ while the mixture is en route to the Gas Liquid Separator (GLS). At this stage, the analyte is present as a finely dispersed emulsion of liquid (metallic) Hg$^{0}$ micro-droplets, in excess SnCl$_2$ solution medium. The reducing solution converts the mercuric ions to free mercury Hg$^{0}$. The solution and Hg$^{0}$ enter a Gas Liquid Separator (GLS) where a carrier gas is bubbled through the solution to extract the mercury vapor (4). The liquid stream is pumped to waste and the gaseous stream containing Hg$^{0}$ vapor is dried in the Nafion$^\text{®}$ dryer (5) and then directed to the Cold Vapor Atomic Absorption Spectrometer (CVAAS) (6). In the spectrometer, the gas is directed through two 5” high-sensitivity (for low concentrations) optical cells, but can be reconfigured to route the flow through an optional 1” low-sensitivity (for high concentrations) optical cell. The light from the Hg Lamp travels through the cells using a system of reflective mirrors. The signal rises to a near steady-state condition. The signal is then measured by the AA Detector (7) for the integration time and repeated for the programmed number of repeats.

NOTE

The normal configuration in the Hydra II$^{\text{Â}}$AA spectrometer uses two 5” optical cells in series providing a 10” optical path that yields a very sensitive response with typical detection limits of < 5.0 ng/L. For higher levels of Hg concentration the user may elect to route the gas through an additional 1” optical cell. This yields a linear response for 10x the levels that the 10” optical path provides.

The majority of the water, containing excess reducing agent, acid, any non-participating “spectator ions,” and reaction by-products is finally drained out the bottom of the GLS and is pumped to waste. Waste gases exiting the system are chemically scrubbed with an activated carbon mercury trap or exhausted out of the lab at the end of the process.

Figure 2  Teledyne Leeman Labs Hydra II$^{\text{Â}}$AA Process Diagram

Teledyne Leeman Labs QuickTrace$^\text{®}$ M-7600 CVAA Mercury Analysis System

Teledyne Leeman Lab’s second level CVAAS system, the QuickTrace$^\text{®}$ M-7600 CVAA mercury analyzer, is shown in Figure 3. The dual-beam system is capable of ultra-trace detection limits of < 0.5 ng/L.

Figure 3  Teledyne Leeman Labs QuickTrace$^\text{®}$ M-7600 CVAA Mercury Analyzer
How the QuickTrace® M-7600 Works

The QuickTrace® M-7600 CVAA mercury analyzer design is based on the US EPA method 245.1, but provides the additional ability to analyze samples in the trace range of less than 1 ng/L. The applicable methods typically require sample digestion techniques that produce liquid samples with mercury present in the +2 valence state.

Refer to Figure 4 to trace the processes of the M-7600 mercury analyzer. The carrier gas (Ar or N₂) enters the reference cell of the spectrometer (1) to facilitate measurement of the incident radiant power (P₀) at 253.7 nm, and then continues on to the Gas Liquid Separator (GLS). Meanwhile, an acidified digested aqueous sample is introduced, via the peristaltic pump as Hg²⁺ dissolved in solution (2). Simultaneously, a reducing agent (10% SnCl₂ in 7% HCl) is introduced via a parallel peristaltic pump channel. The sample and reagent (SnCl₂) streams join at the mixing tee (3), and immediately enter the liquid mixing tube (4). Stannous chloride (Sn²⁺) reduces Hg²⁺ in solution to Hg⁰ while the mixture is en route to the GLS. At this stage the analyte is present as a finely dispersed emulsion of liquid (metallic) Hg⁰ micro-droplets, in excess SnCl₂ solution. The finely dispersed Hg⁰/SnCl₂ emulsion is introduced into the top of the GLS (5). The Hg⁰/SnCl₂ emulsion flows over the frosted GLS center post in a relatively thin film, covering the entire post from top to bottom. The carrier gas from the reference cell of the spectrometer simultaneously enters the bottom of the GLS tangentially and swirls around the wetted center post and then continues upwards toward the GLS gas exhaust port. Elemental mercury Hg⁰ droplets in the thin emulsion film quickly evaporate into the gas vortex surrounding the post. The carrier gas stream then efficiently sweeps the Hg⁰ vapor (along with some evaporated water) upward and out of the GLS gas exhaust. The gas is then dried by the Nafion® dryer (6) and conveyed onward to the sample cell in the spectrometer (7) for an absorbency measurement by the AA Detector (8). Ultimately, the gas stream exits the sample cell and is exhausted to a solid KMnO₄ trap where Hg⁰ is absorbed and clean carrier gas passes to the lab atmosphere. The majority of the water, containing excess reducing agent, acid, any non-participating "spectator ions," and reaction by-products is finally drained out the bottom of the GLS and is pumped to waste.

Figure 4  Teledyne Leeman Labs QuickTrace® M-7600 Process Diagram
COLD VAPOR ATOMIC FLUORESCENCE SPECTROSCOPY (CVAFS)

In contrast to most CVAAS systems, the desirable characteristics of CVAFS-based mercury analyzers include:

1. Ultra-trace ng/L detection limits
2. A much wider dynamic range than CVAAS
3. Typically 4 orders of magnitude for CVAFS versus 3 to 4 for CVAAS
4. Typically available in two configurations:
   - Stand-alone atomic fluorescence detection
   - Atomic fluorescence detection coupled with a gold enrichment (commonly referred to as gold amalgamation) system to pre-concentrate the mercury prior to detection.

The detection limits for fluorescence without pre-concentration on a gold coated substrate is typically less than 0.2 ng/L, whereas employing gold amalgamation can be as low as 0.01 ng/L. The US EPA has promulgated methods for each of these approaches. Method 245.7 is for use without gold amalgamation and Method 1631 is with gold amalgamation. These methods were developed to satisfy the need for quantitation at the National Recommended Water Quality Criteria for mercury. These criteria are published pursuant to Section 304(a) of the Clean Water Act (CWA) and provide guidance for states to use in adopting water quality standards which ensure that ambient waters are safe for fish, and subsequently, that fish are safe for consumption. Additional information on this subject is available at [http://water.epa.gov/scitech/swguidance/standards/current/index.cfm](http://water.epa.gov/scitech/swguidance/standards/current/index.cfm).

CVAFS instruments typically utilize a peristaltic pump to introduce sample and a stannous chloride reducing agent along with a stream of pure, dry argon gas to a Gas Liquid Separator (GLS) where it releases mercury vapor.

**NOTE**

Nitrogen, oxygen and compressed air are not appropriate for atomic fluorescence since the gases exist naturally as diatomic molecules. Nitrogen suppresses the fluorescence signal by a factor of approximately 10, while oxygen suppresses it by 30-fold.

The process to this point is similar, if not identical, to that of CVAAS although chemical preparation prior to analysis may be quite different. The mercury vapor is then transported by the carrier gas through a dryer to an inert switching valve where it is either directed to a gold trap for pre-concentration prior to introduction to the fluorescence detector or directly to the detector by-passing the gold trap altogether. The drying stage is quite important in atomic fluorescence as water vapor and other molecular species can interfere with the measurement. Once in the detector, mercury vapor absorbs light at 253.7 nm creating fluorescent light at the same wavelength. Fluorescence detection is made at 90 degrees to the incident beam to minimize any incidental light scatter from the excitation source itself. The intensity of the fluorescent light is directly proportional to the concentration of mercury in the sample.

Teledyne Leeman Lab’s QuickTrace M-8000 CVAF Mercury Analysis System

Teledyne Leeman Labs QuickTrace® M-8000 CVAF mercury analyzer is shown in Figure 5. The QuickTrace® M-8000 mercury analyzer easily achieves the ultra-trace mercury detection limit of < 0.05 ng/L required by customers employing EPA Method 1631. The QuickTrace® M-8000 is also versatile enough to analyze samples >400 µg/L without dilution and supports three modes of operation without hardware or tubing configuration changes:

- Mode 1: Cold Vapor Atomic Fluorescence (CVAF)
- Mode 2: Cold Vapor Atomic Fluorescence Single Gold Trap Amalgamation (CVAF-SGTA)
- Mode 3: Cold Vapor Atomic Fluorescence Double Gold Trap Amalgamation (CVAF-DGTA)

Less than 0.02 ng/L Instrument Detection Limits (IDLs) are typical for the QuickTrace® M-8000 gold trap modes utilizing less than 25 mL of sample. Non-gold trap IDLs of less than 0.1 ng/L utilizing less than 10 mL of sample can be achieved.
How the QuickTrace® M-8000 Works

The QuickTrace® M-8000 is a mercury analyzer based on methods US EPA 1631, US EPA 245.7 and other CVAF methodologies. The M-8000 system is a valve-based atomic fluorescence mercury analyzer that allows for determination of total mercury with or without pre-concentration of the sample by amalgamation on either one or two gold traps. Refer to Figure 6 to trace the processes of the QuickTrace® M-8000 mercury analyzer. An acidified digested aqueous sample from the autosampler is introduced, via peristaltic pump, as Hg$^{2+}$ dissolved in solution (1). An optional Hydroxylamine Hydrochloride (NH$_2$OH HCL) addition to the sample stream occurs at the first mixing tee (2). Simultaneously, a reducing agent (10% SnCl$_2$ in 7% HCl) is introduced via a parallel pump channel and is mixed with the sample stream at the second mixing tee (3). The liquid mix then enters the liquid mix tube (4). Stannous Chloride (Sn$^{2+}$) reduces Hg$^{2+}$ in solution to Hg$^{0}$ while the mixture is en route to the Gas Liquid Separator (GLS) (5). At this stage (prior to the GLS) the analyte is present as a finely dispersed emulsion of liquid (metallic) Hg$^{0}$ micro-droplets, in excess SnCl$_2$ solution medium. The finely dispersed Hg$^{0}$/SnCl$_2$ emulsion is introduced into the top of the GLS. The Hg$^{0}$/SnCl$_2$ emulsion flows over the frosted GLS center post in a thin film, covering the entire post from top to bottom. A carrier gas simultaneously enters the bottom of the GLS tangentially. The carrier gas swirls around the wetted center post and upwards toward the GLS gas exhaust port.

Hg$^{0}$ droplets in the thin emulsion film quickly evaporate into the gas vortex surrounding the post. The carrier gas stream efficiently sweeps this Hg$^{0}$ vapor (along with some evaporated water) upward and out of the GLS gas exhaust to the Nafion® dryer (6). The dried gas can then be directed to either one or two optional gold traps (7) that capture the mercury while letting the other gases pass through. The gold trap(s) is/are then heated to release the Hg$^{0}$. Finally, the dry Hg$^{0}$/carrier gas mixture exits the dryer and enters the sample cell in the spectrometer (8) for a fluorescence measurement by the AF Detector (9). Ultimately, the gas stream exits the sample cell and is exhausted to a solid KMnO$_4$ trap where Hg$^{0}$ is absorbed and clean carrier gas passes to the lab atmosphere. The majority of the water bulk containing excess reducing agent, acid, any non-participating spectator ions, and reaction by-products drains out the bottom of the GLS and is pumped to waste.
DIRECT ANALYSIS BY THERMAL DECOMPOSITION

Desirable characteristics of thermal decomposition include:

1. Direct analysis of the sample in native form eliminating the sample digestion step required by both CVAAS and CVAFS techniques. Additionally, since there is no chemical pretreatment of samples, there is no need to matrix match standards allowing one calibration curve to be suitable for a variety of sample types.

2. Fast analysis times
3. A Detection limit of approximately 0.001 ng

For laboratories that analyze large numbers of solid samples or that would simply rather not perform the digestion typically associated with CVAAS and CVAFS, direct analysis can be an ideal solution. However, the analysis of large quantities of samples in aqueous solution by combustion does not yield detection limits comparable to CVAAS or CVAFS. This is primarily due to the relatively small liquid volumes that can be processed using direct analysis (typically well under 1 ml per sample). Consider, for example, that the total mercury in 1 mL of a sample that contains 5 ng/L of mercury is equivalent to 0.005 ng mass of mercury. This quantity is slightly above the detection limit for direct analysis by thermal decomposition. In contrast 5 ng/L is a concentration that is trivial to measure by CVAFS. However, when dealing with solid samples, the sensitivity difference is quite small since the digestion required to put the sample into solution will introduce a large dilutive effect.

Teledyne Leeman Labs Hydra II C Direct Analysis Combustion Mercury Analysis System

The Teledyne Leeman Labs Hydra II C direct analysis combustion mercury analyzer is shown in Figure 7. The Hydra II C is based on US EPA method 7473 and ASTM 6722 and 7623. Analysis requires no sample digestion and employs a gold trap for pre-concentration of the sample. Through proper selection of the Hydra II C’s operational parameters (furnace/catalyst temperature and time, gas flows, etc.), accurate analysis can be performed across a dynamic range of 0.001 ng to 1500 ng. By quickly changing the analyzer’s modules it can be converted to a liquid sample CVAAS analyzer.

The Hydra II C Operation’s Manual provides extensive guidance on optimizing the analyzer.
How the Hydra II C Mercury Analyzer Works

The Hydra II C mercury analyzer employs combustion (decomposition) of a sample at high temperatures with oxygen (or air).

**NOTE**

Organic samples may be incompletely oxidized when air is used in place of pure oxygen.

Refer to Figure 8 to trace the processes of the Hydra II C direct combustion CVAA mercury analyzer. First a weighed sample (1) is introduced to a decomposition furnace (2) with oxygen (or air) flowing over the sample itself. The furnace temperature is then raised in two stages to first dry the sample, then to combust or decompose the sample.

The gases resulting from the decomposition are carried through a catalyst furnace to remove halogens, nitrogen oxides, and sulfur oxides (3). The remaining combustion products, including elemental mercury (Hg⁰), are swept through a Nafion® dryer and then to a gold trap (5) that captures the mercury while letting the other gases pass through. The gold trap is then heated to release the Hg⁰ into a carrier gas which transports it to the spectrometer (6). In the spectrometer, the gas is directed through two 5” high-sensitivity (for low concentrations) optical cells, and then one 1” low-sensitivity (for high concentrations) optical cell. The light from the Hg Lamp travels through the cells using a system of reflective mirrors. The transient signal is measured by the AA Detector (7). The two peaks are integrated and reported against the best calibration of the two cells available. The use of two cells provides the best detection limit with a wider dynamic range than a detection limit provided by a single optical cell path length. Waste gases exiting the system are chemically scrubbed with an activated carbon mercury trap or exhausted out of the lab at the end of the process.

*Figure 8  Teledyne Leeman Labs Hydra II C Process Diagram*
WHAT ABOUT OTHER ATOMIC SPECTROSCOPY TECHNIQUES LIKE AA, ICP-OES OR ICP-MS?

Other atomic spectroscopy techniques can be used for the analysis of mercury, but techniques other than traditional cold vapor are problematic for a variety of reasons. In the case of ICP-MS and ICP-OES, special sample preparation handling is often required, including the addition of a small amount of metallic gold. The metallic gold is used to minimize the memory effects mercury exhibits within the intricate components of the ICP-MS and ICP-OES systems. Additionally, ICP-MS can have a spectral interference due to tungsten isotopes combining with oxygen to form the polyatomic ion of tungsten oxide (WO⁺) as they exit the plasma and enter the cool down phase in mass detector.

For example, the isotopes of tungsten that exhibit the spectral interference have a mass of 182, 183, 184, and 186 and when combined with oxygen atomic mass 16 to form a polyatomic ion, the mass becomes 198, 199, 200 and 202 which is the isotopic mass of stable mercury isotopes in the greatest abundance: 198, 199, 200 and 202.

NOTE

Mercury does have an isotope that is not affected by the tungsten spectral interference of 201, but this mercury isotope is in lower abundance.

ICP-MS can achieve detection limits of 1 to approximately 20 ng/L, but the issues presented by determining mercury concentration by ICP-MS ultimately require an experienced spectroscopist that understands the complexity of ICP-MS mercury analysis.

It is rarely practical to utilize ICP-OES or AA for the analysis of mercury due to their inability to offer the level of sensitivity routinely required for mercury determination. For example, a typical ICP-OES detection limit for mercury would be from 1 to 20 µg/L and traditional AA systems can only achieve detection limits around 50 to 100 µg/L.

WHICH TECHNIQUE IS RIGHT FOR YOU?

Selecting the right mercury analysis technique ultimately depends on your specific analytical needs. For many laboratories, particularly those involved in environmental analysis, the decision will be driven solely by the need to comply with a specific regulatory method. For example, if your lab is required to analyze samples using EPA method 245.1, then you will need to use CVAAS. If you are required to follow specific regulatory methods refer to Table 2-1 "Commonly Used Regulatory Methods".

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If your lab is not required to follow a regulatory method, the driving force for the decision will more likely be criteria such as:

- The characteristics of your sample matrix (i.e. solid or a liquid)
- The detection limits you need to reach in that matrix
- Whether you prefer to digest the sample, versus analysis in the native state
- Budgetary constraints
MERCURY ANALYSIS QUESTIONNAIRE

Answering a few simple questions below will help you decide which technique is right for you!

Are Your Samples Liquid or Solid?

- If your sample is a liquid (e.g. wastewater, drinking water, etc.) then you will most likely be best served by one of the chemical reduction techniques, either CVAAS or CVAFS. Direct analysis by thermal decomposition can be used, but requires additional time to dry aqueous samples prior to decomposition. Typically, drying aqueous samples by this technique requires a minimum of 0.7 seconds/microliter of sample. For example, a 0.2 gram aqueous sample deposit would require approximately 2.5 minutes to dry.

  **NOTE**

  If you have a liquid sample matrix that is high in a chemical interference such as gold or iodine, direct analysis may still be the best choice. These interferences impede the chemical reduction of mercury and can produce erroneously low results.

- If your sample is a solid you have the choice of digesting the sample and then analyzing it by CVAAS or CVAFS, or eliminating sample digestion completely by employing direct analysis by thermal decomposition.

- If your laboratory analyzes both liquid and solid samples, consider a mercury analyzer that can be converted between direct analysis by combustion (decomposition) and liquid sample analysis using CVAAS, such as the Teledyne Leeman Labs Hydra II mercury analyzers. The liquid sample introduction components and autosampler are easily exchanged for a solids autosampler and furnace module. The AA detector is quickly converted by changing the spectrometer’s optical cell tubing configuration.

What is the Detection Limit You Need?

If your sample is a liquid, detection limit requirements will drive your decision. CVAAS will provide a detection limit of approximately 5 ng/L for the Hydra II AA or 0.5 ng/L for the QuickTrace® M-7600. CVAFS will provide a detection limit of approximately < 0.1 ng/L (or as low as 0.01 ng/L when employing pre-concentration using the two optional gold traps) for the QuickTrace® M-8000.

With that said, unless you have a preference for CVAAS, you should probably consider CVAFS for the following reasons:

- Superior detection limits allow the ability to report lower levels
- Wider dynamic range can significantly reduce the time spent performing sample dilutions

Do You Want to Digest Your Samples?

The digestion process for most waters is straight forward and laboratories often have all the equipment necessary to complete defined water digestions. Waters known to contain gold, iodide or other interferences may be accurately analyzed after digestion, if the sample is sufficiently diluted or the Method of Standard Additions (MSA) is employed.

Just as the reduction techniques have certain matrix interferences that can be troublesome, direct analysis by thermal decomposition may not be the right choice even when the sample is a solid. For example organic samples can be an explosive risk and the process with such matrices should be characterized using quite small sample volumes (typically 0.01 mg) prior to full-scale sampling.
How Much Will Direct Analysis Cost?
For many labs the simplicity of direct analysis is very appealing. For labs that already have digestion procedures in place, the higher capital cost of direct analysis relative to CVAAS or CVAFS, may not justify the additional expense. For others, while direct analysis requires a higher initial investment, it does provide advantages that can lead to cost savings during the system’s life-span:

- Direct analysis eliminates exposure to concentrated mineral acids and strong reducing agents, minimizing the risk of an accident
- The cost of hazardous waste remediation can be drastically reduced

**NOTE**
With direct analysis by decomposition, the only hazardous material requiring proper disposal are the catalyst tubes used (typically requiring replacement every 3 to 6 months). Of course, if the sample itself is a hazardous material, its remnants after thermal decomposition may also be hazardous.

What Other Matrix Considerations are Important?
Other factors, such as the sample heterogeneity or volatility may also be important considerations. Because direct analysis by thermal decomposition is limited to a relatively small quantity of sample, samples that are not homogeneous or cannot be homogenized for one reason or another are best handled by digesting a larger quantity and then analyzing with CVAAS or CVAFS.