

Measurement Techniques for Mercury: Which Approach is Right for You?

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The United States Environmental Protection Agency classifies mercury as a persistent, bio-accumulative toxin⁽¹⁾, indicating that its toxicity does not diminish through decomposition or chemical reaction, and that it is absorbed faster than it can be excreted. Recently, efforts to minimise the release of mercury, and to track its migration when released, have demanded more sensitive analytical techniques for its measurement. As these techniques have become available, regulatory agencies around the world have written new analytical methods for their use. Table 1 shows a listing of many of the regulatory methods that are available for use with today's technologies.

Let's take a look at the analytical techniques in a bit more detail and then we'll come back to the question of which technique is right for you.

Cold Vapour Atomic Absorption Spectroscopy (CVAAS)

In many parts of the world, CVAAS is still the most commonly used technique for the determination of mercury. Hallmarks of this approach include: detection limits in the single digit part per trillion (ppt) range, a dynamic range of 2 to 3 orders of magnitude and an abundance of analytical methods which allow for the measurement of Mercury in almost any sample matrix.

The technique was introduced in 1968 by Hatch and Ott⁽²⁾ on the heels of the first commercially available atomic absorption spectrometer. In their work they described an attachment for flame AA that enabled them to reduce mercuric ions in solution to ground state atoms and transport that mercury to the optical path of the spectrometer for measurement. Thus, cold vapour atomic absorption was born. Very quickly CVAAS became the reference technique for mercury determinations. Within a few years, the US EPA adopted the technique for the determination of mercury in water, soil, and fish. Now, almost 40 years later, CVAAS remains one of the primary techniques for mercury analysis and is the reference technique for drinking water monitoring per the Safe Drinking Water Act⁽³⁾.

In contrast to those early systems, most modern CVAAS instruments are: more sensitive, more automated, smaller, faster and less expensive than generic flame spectrometers with cold vapour attachments. Today's CVAAS systems provide detection limits of just a few ppt, analyse samples in about one minute, require very little operator interaction and take up just a couple of square feet of bench space. Figure 1 provides an overview of a cold vapour atomic absorption system along with a photograph of a typical instrument. With CVAAS instruments a peristaltic pump is typically used to introduce sample and stannous chloride into a gas liquid separator where a stream of pure, dry gas is bubbled through the mixture to release mercury vapour. The mercury is then transported in the carrier gas through a dryer and then into an atomic absorption cell. Once in the absorption cell mercury absorbs 254 nm light in proportion to the concentration of mercury in the sample.

Cold Vapour Atomic Fluorescence Spectroscopy (CVAFS)

Hallmarks of CVAFS based mercury analysers include sub ppt detection limits and a much wider dynamic range than can be achieved by CVAAS; typically 5 orders of magnitude for CVAFS versus 2 to 3 for CVAAS. CVAFS instruments are available in two configurations; one which employs simple atomic fluorescence and one which employs a gold amalgamation system to preconcentrate mercury prior to measurement by atomic fluorescence. The detection limit for the simple fluorescence approach is about 0.2 ppt whereas using the preconcentration approach with fluorescence detection can be as low as 0.02 ppt. The US EPA has promulgated methods for each of these approaches; Method 245.7⁽⁴⁾ is for use without preconcentration and 1631⁽⁵⁾ is with preconcentration.

These methods were developed to satisfy the need for quantitation at the National Recommended Water Quality Criteria for Mercury⁽⁶⁾. 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 to 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>

Figure 2 provides an overview of a cold vapour atomic fluorescence instrument; in this case both with and without a gold amalgamation system for preconcentration. With CVAFS instruments a peristaltic pump is typically used to introduce sample and stannous chloride into a gas liquid separator where a stream of pure, dry gas (typically argon) is bubbled through the mixture to release mercury vapour. The mercury is then transported in the carrier gas through a dryer and then to a valve which selects between simple fluorescence or the preconcentration approach. With fluorescence the drying stage is quite important as water vapour and other molecular species can interfere with the fluorescence measurement. Once in the detector, mercury vapour absorbs 254 nm light and fluoresces at the same wavelength. Measurement of the fluorescence signal is usually made at 90 degrees to the incident beam to minimise scatter from the excitation source. The intensity of the fluoresced light is directly proportional to the concentration of mercury.

The concentration of standards and samples with this technique

Analytical Techniques	Cold Vapour Atomic Absorption (CVAAS)	Cold Vapour Atomic Fluorescence (CVAFS)	Direct Analysis or Thermal Decomposition
	245.1	245.7	7473
245.5	1631	6722-01	
7470			
Analytical Methods	7471	EN13506	
	3111B	EN12338	
	EN1483	ISO 17852:2008	
	EN13806		

Table 1: Commonly Used Regulatory Methods

are typically 100–1000x lower than those used with CVAAS, demanding much cleaner reagents. To ensure reagents are low in mercury, methods such as EPA Method 1631 describe techniques to remove mercury from salts and some solutions.

Direct Analysis by Thermal Decomposition

Hallmarks of the direct analysis approach include: elimination of the sample digestion step, fast analysis times and a detection limit of about 0.005 ng. Elimination of sample digestions means solid samples can typically be run in their native form. For laboratories that analyse large numbers of solid samples, or that would simply rather not perform the digestion typically associated with CVAAS and CVAFS, direct analysis may be ideal. It is noteworthy that this approach also carries with it the benefit of generating less acid waste than the solution-based techniques. However direct analysis is not well suited for the laboratory whose primary need is to run large numbers of samples that are already in aqueous solution. For liquid sample analysis, the detection limit available using direct analysis is not typically comparable with those of CVAAS or CVAFS. This is primarily due to the relatively small liquid volumes that can be processed using direct analysis; which are typically well under 1 ml per sample. Consider, for example,



Figure 1b: Hydra II AA CVAAS Mercury Analyzer

that the total mercury in 1 ml of a sample that contains 5 ppt (ng/L) of mercury is only 0.005 ng - which is right at the detection limit for direct analysis.

In contrast 5ppt is a concentration that is trivial to measure by CVAAS. When dealing with solid samples however, the sensitivity difference is quite small since the digestion required to put the sample into solution typically introduces a significant dilution.

Figure 3 shows an overview of the direct analysis technique. With this approach, a weighed sample is introduced into the decomposition furnace with oxygen (or air) flowing over the sample. The furnace temperature is ramped in two stages; first to dry the sample and then to decompose it. As the evolved gases are released, they are carried into a catalyst where further decomposition occurs and elemental mercury is released. When the gas stream leaves the catalyst elemental mercury is captured on the surfaces of a gold amalgamation trap. After the sample's mercury has been collected, the gold trap is heated and the accumulated mercury proceeds to an atomic absorption detector for quantitation.

ICP or ICP-MS

Although some analysts prefer to utilize inductively coupled plasma mass spectrometry (ICP-MS) for the determination of mercury, it does involve special sample handling including the addition of small amounts of gold to the sample to expedite baseline recovery. And, the cost of such equipment can be as much as 3 to 5 times higher than dedicated CVAAS or CVAAS systems. Note: Although inductively coupled plasma optical emission spectrometry (ICP-OES) based instruments can be used to measure mercury, trace level analysis is problematic due to poor sensitivity.

Which Technique is right for you?

Selecting the right technique really depends on your analytical needs. For some laboratories, the decision will be driven solely by the need to comply with a specific regulatory method. For example, if your lab is required to analyse samples using EPA method 245.1, then you will need to use the technique of CVAAS. If you are required to follow specific regulatory methods you may find Table 1 helpful as a reference.

If your lab is not constrained by 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
- your preferences regarding digesting the sample or not
- your budgetary constraints.

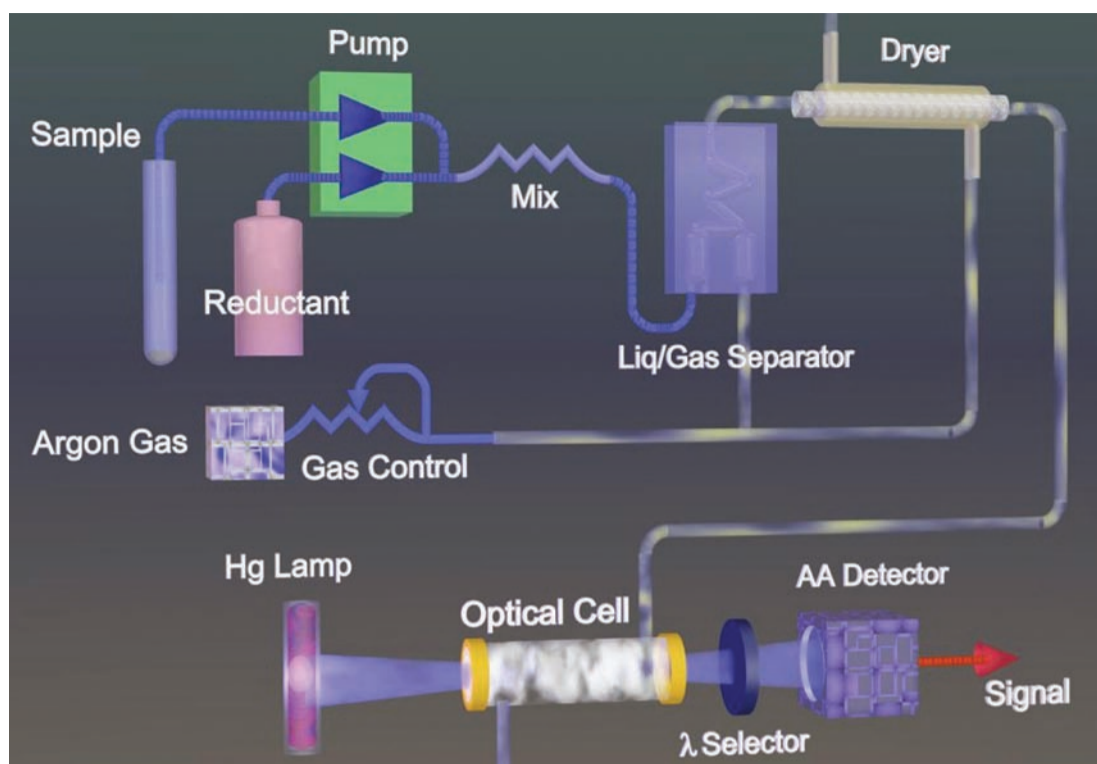


Figure 1: An overview of cold vapour atomic absorption

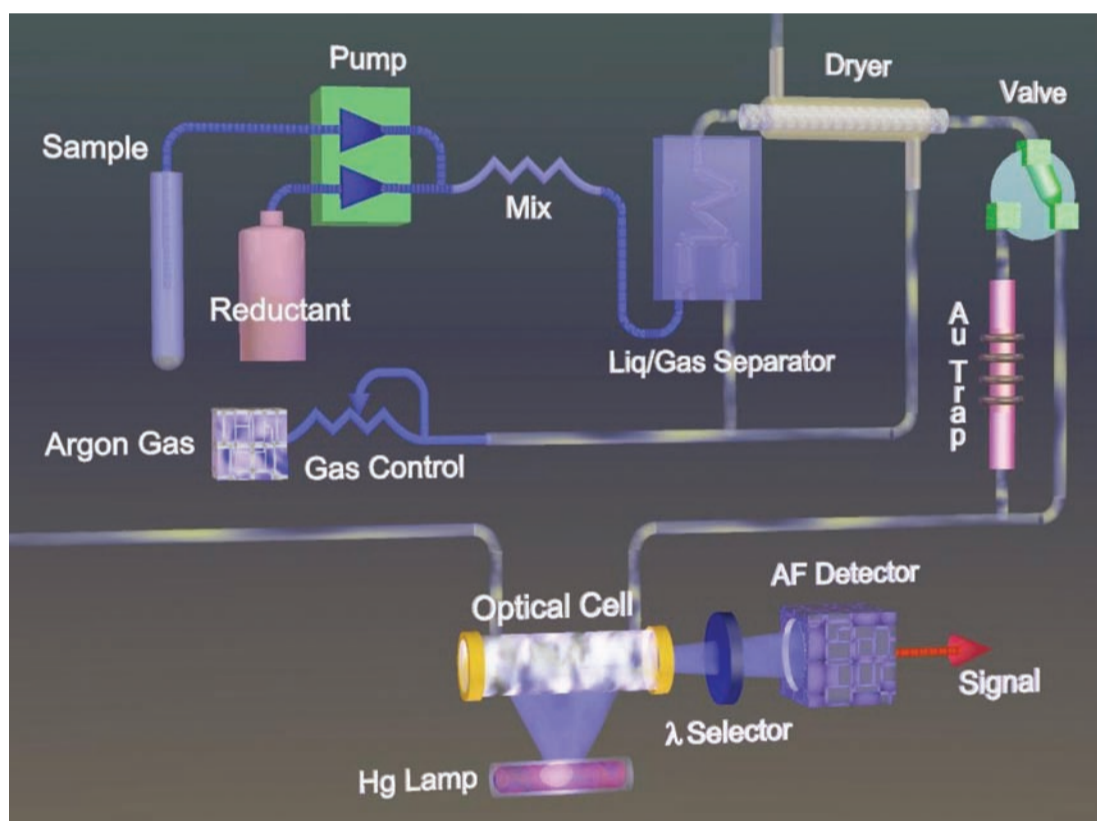


Figure 2: An overview of cold vapour atomic fluorescence

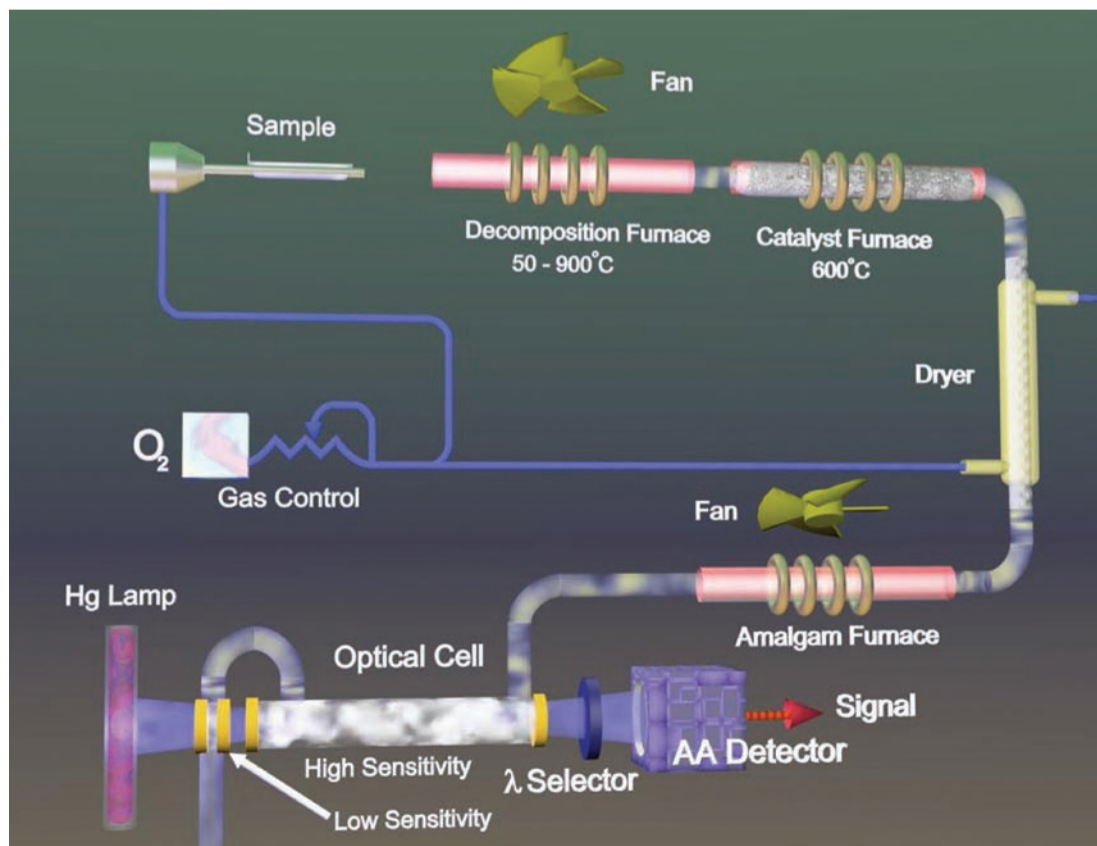


Figure 3: An overview of direct analysis using thermal decomposition.



Hydra-C Mercury Analyzer with Thermal Decomposition

Answering a few simple questions will guide you in the direction of the technique which is right for you.

The fundamental question is, is your sample a solid or a liquid?

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 of CVAAS or CVAFS.

At this point you can let your detection limit requirements drive

your decision; with the knowledge that CVAAS will provide a detection limit of about 2 ppt and CVAFS will provide a detection limit of about 0.2 ppt (or as low as 0.02 ppt with gold amalgamation). With that said, unless you have a preference for CVAAS, our recommendation is that you consider CVAFS. Its superior detection limits will allow you to report to lower levels and its wider dynamic range will be a real time saver from the perspective of not having to do as many sample dilutions.

If your sample is a solid you have the choice of digesting the sample and then analysing it by CVAAS or CVAFS. Alternatively you may be able to skip the digestion step and go with direct analysis by thermal decomposition.

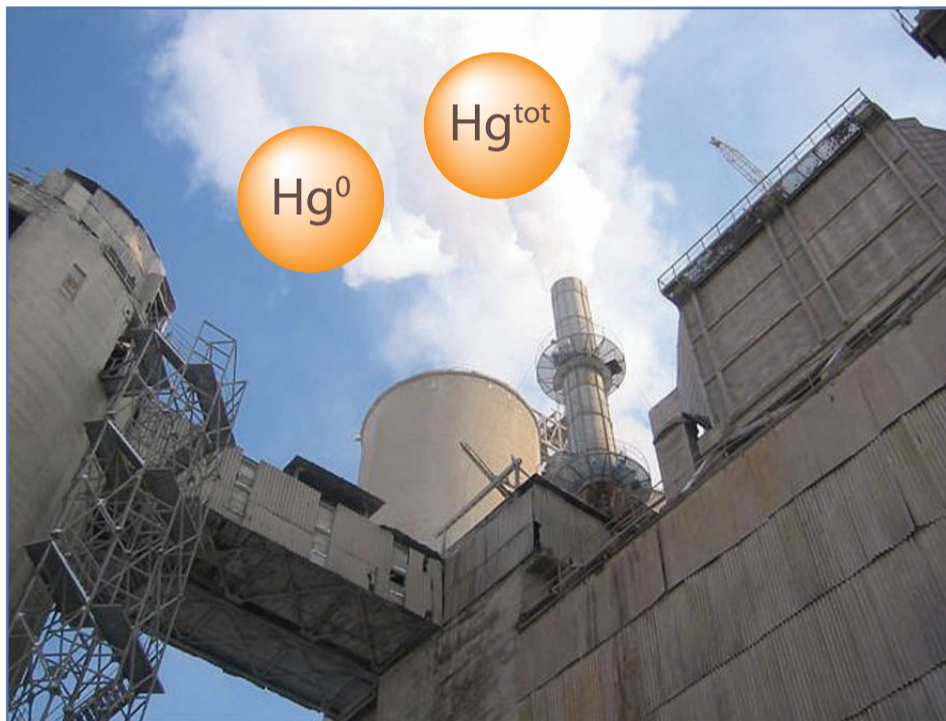
For many labs, the simplicity of direct analysis is very appealing. For labs that already have digestion procedures in place the higher capital cost of direct analysis relative to CVAAS (or CVAFS), could be up to \$10k, may drive the decision. Other factors, such as the sample heterogeneity or volatility may be important considerations as well. Because direct analysis is limited to a relatively small quantity of sample (about 1 gram), inhomogeneous samples may be best dealt with by digesting a larger quantity of sample followed by analysis using CVAAS or CVAFS.

Additional assistance with your decision about which mercury analysis technique is right for you can be found at www.teledyneleemanlabs.com/hg_selector.

- (1) Persistent bioaccumulative and toxic chemical program, EPA.gov/pbt.
- (2) W.R. Hatch and W.L. Ott, Anal. Chim. Acta, 40, 2085-7 (1968).
- (3) Analytical Methods Approved for Drinking Water Compliance Monitoring of Inorganic Contaminants and Other Inorganic Constituents, http://water.epa.gov/scitech/drinkingwater/labcert/upload/methods_inorganic.pdf.
- (4) Method 245.7, Mercury in Water by Cold Vapor Atomic Fluorescence Spectrometry, Revision 2.0, February 2005, U.S. Environmental Protection Agency.
- (5) Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry, August 2002, U.S. Environmental Protection Agency.
- (6) National Recommended Water Quality Criteria (4304T), 2009, U.S. Environmental Protection Agency, (Federal Register: August 5, 1997 62[150]).

Monitoring Mercury Levels in the Environment Utilising both Laboratory and Process Instrumentation

For over 25 years **P S Analytical** (UK) has been at the forefront of environmental monitoring, with particular emphasis on mercury determination and speciation. PSA has developed Atomic Fluorescence instrumentation for both laboratory and process applications backed up by an in-house team of experts, worldwide distributor network and on-going R&D programme. Our expertise spans the ability to determine mercury in gases, liquids and solids at ultra low levels. Mercury can be present in many forms and by coupling to chromatographic techniques, the PSA Merlin Instrument forms an ideal detector for mercury speciation studies, providing data required to define suitable removal strategies.



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In the petrochemical industry mercury measurements are vital, since failure to detect the presence of mercury, even at low levels, has in the past led to catastrophic failures. PSA instrument routinely detects mercury levels at sub ppb levels over a wide range of matrices. Working closely with industrial and academia, P S Analytical has developed a range of systems excelling at the measurement of mercury in gaseous and liquid streams. Tailoring instrumentation to customer requirements enables systems to meet the local and international required safety standards for deployment in hazardous areas on production sites. P S Analytical has played an active part in the development of ISO/CEN standards for these measurements. In order to ensure the validity of the data recorded, PSA, in association with the National Physical Laboratory (NPL) has developed a vigorous calibration protocol that is traceable to fundamental principles. Integrating this tool into our process range of equipment ensures that reliable and authenticated data is being provided on a continuous basis.

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Mercury as a Global Pollutant

From July 28th – August 2nd 2013 the **11th ICMGP International Conference on Mercury as a Global Pollutant** will take place in Edinburgh, Scotland. www.mercury2013.com

Over 1,000 professional and academic experts on all aspects of Mercury behaviour and control will gather together to discuss a variety of Mercury monitoring and treatment topics.

The negotiations of the Global Mercury Treaty are to be completed in early 2013. The Edinburgh conference, therefore, presents a very timely opportunity for information sharing between the scientific community and policy makers based on the agreed text. Each day of the Edinburgh meeting will start with discussions that highlight some of the related challenges ahead in an effort to promote understanding and foster increased understanding of the treaty. The five day event will continue with parallel sessions and hundreds of posters covering all areas and aspects of mercury research. It will include research relevant to UNEP's Mercury Programme and actions that countries may need to take to implement the mercury treaty. Topics will include waste, chlor-alkali, coal combustion, gold mining, dentistry as well as the movement, behaviour and effects of mercury in our environment. Once again, the UNEP Global Mercury Partnership will host a special session dedicated to its work. The conference will be accompanied by the largest ever exhibition of organisations including commercial companies that provide services for mercury management, monitoring and control from all sources. There will also be public outreach activities to help bridge the gap between those that know and those that need to know. Edinburgh is one of the most beautiful and historic cities in the world. Where better to look from the past into the future?



11th International Conference on Mercury as a Global Pollutant

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