

Direct Measurement of Mercury in Environmental Samples Without Sample Digestion

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Introduction

Mercury has long been recognized as an important global pollutant. Government organizations, researchers, and concerned citizens around the world strive to understand its entry into, and impact upon our ecosystem. Unlike most other pollutants, mercury is mobile, non-biodegradable, and bio-accumulative; it is therefore a global concern that will not go away. In an effort to better understand the sources, fate and bio-accumulative effects of Hg, researchers need to measure it in a wide variety of sample types. Some of these include: air, water, soil, fish, fowl, mammals, foods, fertilizers and fuels to name just a few.

Historically, the vast majority of mercury analyses have been performed by first digesting a sample [often a solid] using a combination of strong mineral acids and oxidizing agents to liberate the mercury and transform the sample into a liquid. Free mercury (Hg^{+2}) in the liquid sample is then chemically reduced to Hg^0 [typically with stannous chloride] and swept out of the liquid sample into an atomic absorption detector. This approach is classically referred to as cold vapor atomic absorption or CVAA and is in widespread use today. Another variant on this approach uses Atomic Fluorescence detection (CVAF) which carries with it improvements in both detection limits and dynamic range.

This article describes the application of a new instrument that allows today's analyst to measure the Hg content in solid or liquid samples, without the need to first digest the sample. This approach is based on thermal decomposition (combustion) of the sample prior to measurement of its Hg content. Using this technique the researcher can analyze a wide variety of sample types (including liquids) without modifying methodology.

Thermal Decomposition Technique

To fully appreciate the benefits of the thermal decomposition approach to mercury analysis, it is instructive to examine the various sample digestion requirements of the CVAA Hg methodologies in greater detail. Sample digestion protocols for CVAA can be found at www.leemanlabs.com as well as in a variety of environmental methodologies, such as EPA methods 245.1, 245.5, 7470A, 7471B.

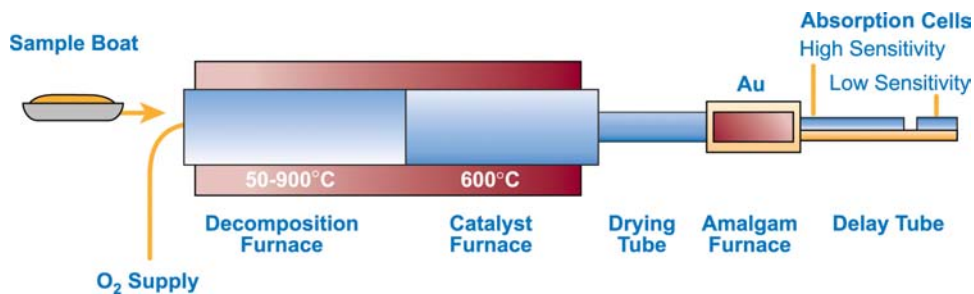
The instrument referred to throughout the remainder of this article is the Hydra-C from Teledyne Leeman Labs (See Figure 1).

Figure 1: The Hydra-C Mercury Analyzer Determination via Thermal Decomposition



Hydra-C is a fully automated mercury analyzer employing the thermal decomposition technique as described in EPA method 7473 and ASTM method 6722-01. Figure 2 depicts the analytical process used in Hydra-C. Briefly, a small amount of sample (typically 0.05 to 1 gram) is weighed and deposited into a sample boat. The weighed sample is then introduced into the Hydra-C where oxygen begins to flow over the sample. The decomposition furnace temperature is then increased in two stages; first to dry the sample, then to decompose it. The evolved gases are carried through a heated catalyst to produce free mercury while removing halogens, nitrogen oxides, and sulfur oxides. The remaining combustion products including elemental mercury (Hg^0) are swept through a gold amalgamation trap where elemental Hg is trapped and concentrated. After the amalgamation step, the trap is heated to release the mercury into a carrier gas which transports it into an atomic absorption spectrometer.

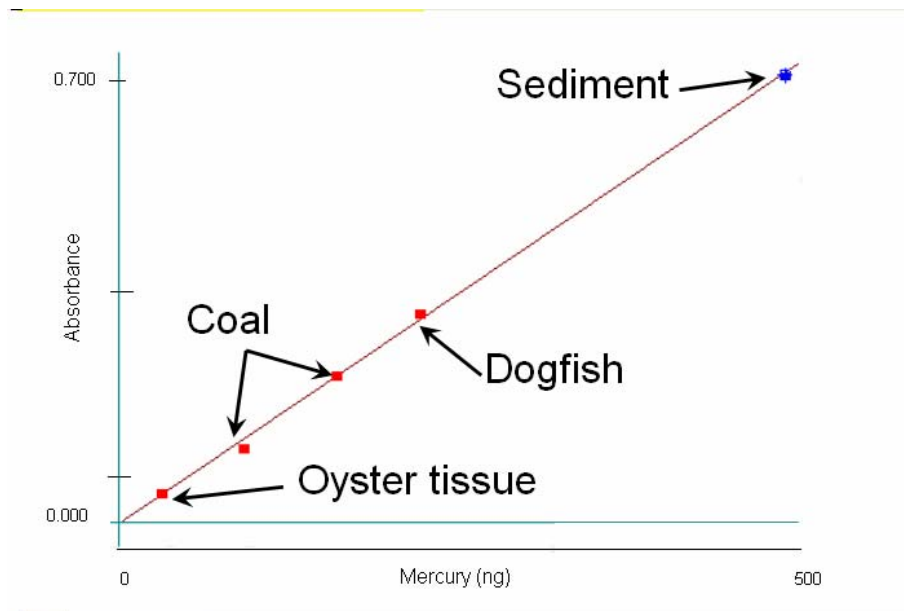
Figure 2: The Hydra-C Analytical Process.



Calibration

With the thermal decomposition technique the calibration process is simple and can be performed using either liquid or solid standards. Figure 3, shows a linear calibration curve generated from a variety of different certified reference materials (CRM). Alternatively, the calibration curve may be generated using aqueous standards with CRMs employed as quality control checks. Either way, it is clear that a variety of sample types can be analyzed without the need for recalibration.

Figure 3: Calibration Using a Variety of Certified Reference Materials



Operating Conditions

Hydra-C is typically run using one set of operating conditions for most sample matrices. Table 1 shows the conditions used to obtain the results for the certified reference materials displayed in Table 2. The one parameter that may need modification is dry time. For example, superior recoveries are obtained when boiling of liquid samples is avoided. The required minimum dry time for liquid samples is directly proportional to the amount of liquid injected. A good rule of thumb is to allow at least 0.7 seconds for every milligram of aqueous sample injected.

Table 1: Standard Operating Conditions

Parameter	Time (s)	Temp. (°C)
Dry	60*	300
Decomposition	120	800
Catalyst	110	600
Amalgam	30	700
Integration	75	N.A.

* Dry times vary for aqueous samples as a function of volume deposited (0.7sec/mg).

Table 2: Certified Reference Materials from Aqueous Calibration

SAMPLE	No.	Certificate	Measured	Recovery
Tissue		(ppm)	(ppm)	(%)
Bovine Liver	1577	0.016	0.0178	111.7
Blood				
	Lypho 1	9.6	9.08	94.8
	Lypho 2	39	35.5	90.9
	Lypho 3	73	66.7	91.4
Marine				
Dogfish	Dorm-2	4.64	4.34	93.5
Dogfish	Dolt-2	1.99	1.79	90
Oyster Tissue	1566	0.057	0.061	107
Sediments & Soils				
	8406	0.06	0.061	101.7
	2709	1.4	1.52	108.6
Coal				
	HC-5150	0.176	0.177	100.6

Correlation of Reduction and Thermal Decomposition Techniques

Despite the fundamental differences between the reduction approach to Hg analysis and the thermal decomposition approach, excellent correlation is achieved between the two techniques. Table 3 contains the results for several coal samples analyzed using the two techniques. The specific methodologies followed were ASTM D6414-99 (wet digestion)

and ASTM 6722-01 (thermal decomposition) for the determination of mercury in coal and combustion residue. A Hydra AA and a Hydra-C (Teledyne Leeman Labs, Hudson, NH, USA) were employed for the reduction and thermal decomposition experiments described in this work. For each sample, the difference in the reported values between techniques is well within confidence limits of either technique (less than 1.0 standard deviation). Similar correlation between methods is typically observed in other matrices.

Table III: Comparison of Techniques

Hydra AA with digestion runs 1-5				
	20025B	20100B	30075B	40150B
Run1	81.5	64.5	58.5	ND
Run2	85.0	78.9	56.2	ND
Run3	75.2	73.8	56.5	ND
Run4	79.0	65.2	48.6	ND
Run5	81.3	64.0	51.1	
Average	80.4	69.3	54.2	ND
Std Dev	3.62	6.71	4.16	NA
Hydra-C solid analysis 5 replicates				
	20025B	20100B	30075B	40150B
Run1	80.4	76.4	65.6	3.1
Run2	77.5	84.9	54.7	2.8
Run3	84.1	69.1	46.4	2.4
Run4	77.1	70.1	60.0	2.5
Run5	75.0	71.0	53.3	2.3
Average	78.8	74.3	56.0	2.6
Std Dev	3.54	6.57	7.22	0.32

Although this is not always the case, it is interesting to note that the thermal decomposition technique is capable of determining mercury in coal samples to lower concentrations than the aqueous or reduction technique. In the case of coal samples, the wet digestion process results in about a 50-fold dilution of the sample while no dilution occurs with thermal decomposition. With liquid samples, the reduction technique offers the better detection limit since very little dilution results from the addition of digestion reagents.

Safety and “Green Chemistry”

The thermal decomposition technique has two additional benefits that laboratories appreciate. First, with thermal decomposition no concentrated mineral acids or strong redox reagents are used. Such chemicals must be handled with care by qualified personnel and with appropriate attention to safety. Second, because the aqueous digestion step is eliminated, no aqueous hazardous waste is produced. Specifically, there are no acidic wastes high in metal content (tin, manganese, sodium & potassium) to be disposed of.

Conclusions

Hydra-C and the thermal decomposition approach to mercury analysis are attractive options for laboratories measuring mercury in a variety of sample matrices. Results obtained by thermal decomposition correlate well with earlier techniques such as CVAA. Comparative results presented here showed no analytical bias and were within confidence limits for the two techniques.

Hydra-C greatly simplifies the sample handling and pretreatment phase of the analysis and virtually eliminates the need for the analyst to have the necessary chemistry background to carry out sample digestions. Further, because its methodology is not customized for sample type the QC steps associated with method blanks, reagent blanks, etc. are eliminated. These benefits, combined with the fact that Hydra-C can provide the analyst with lower limits of quantization for solid samples than the standard CVAA approach, make this an option that should be seriously considered for any Hg analysis challenge.