

The Determination of Mercury in Soil and Water According to U.S. EPA SOW 846 & Method 7473 by Thermal Decomposition, Amalgamation and Cold Vapor Atomic Absorption

INTRODUCTION

The accurate determination of mercury in soils and waters is critical to the remediation of contaminated sites. The **Hydra II_C** Direct Mercury Analyzer provides a simple and convenient way to analyze these materials in about 7 minutes without any sample digestion or creation of hazardous chemical waste to be disposed.

The **Hydra II_C** heats samples in an oxygen stream to decompose any mercury compounds which are then collected on an amalgamator. After all of the sample's mercury has been collected, the amalgamator is heated releasing the trapped mercury for determination by cold vapor atomic absorption (Figure 1).

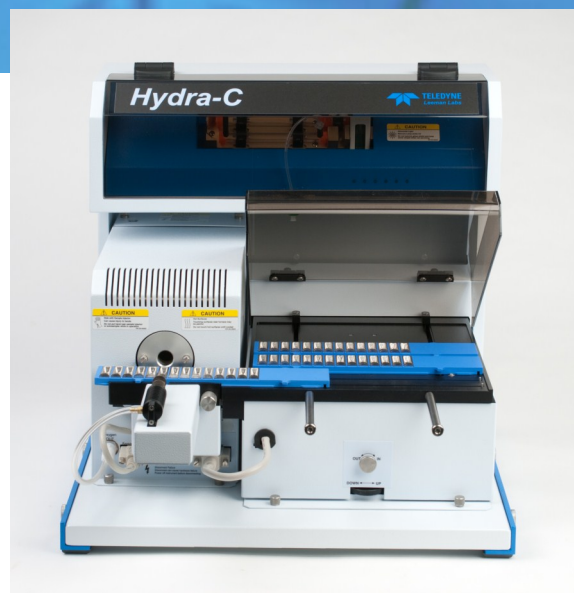
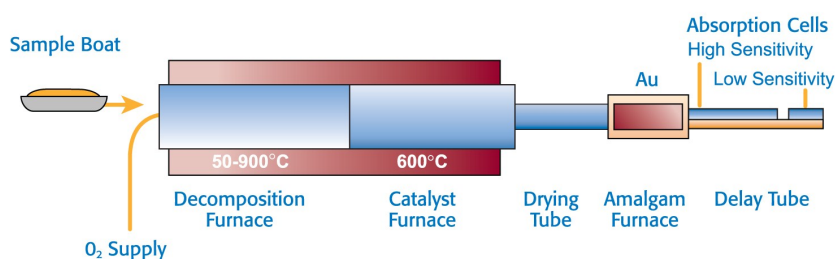


Figure 1

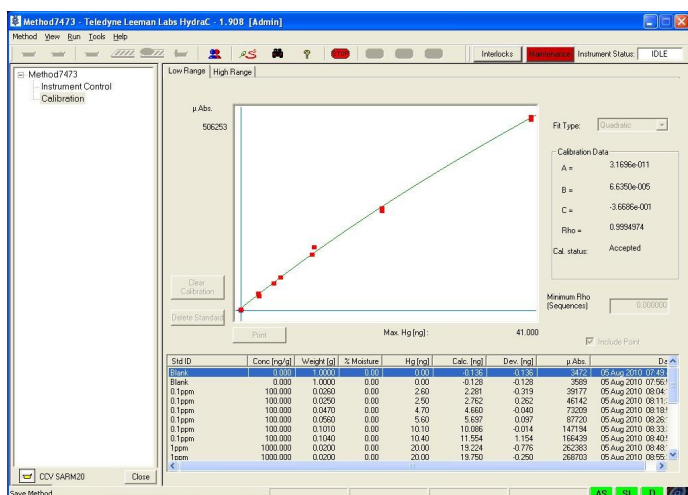
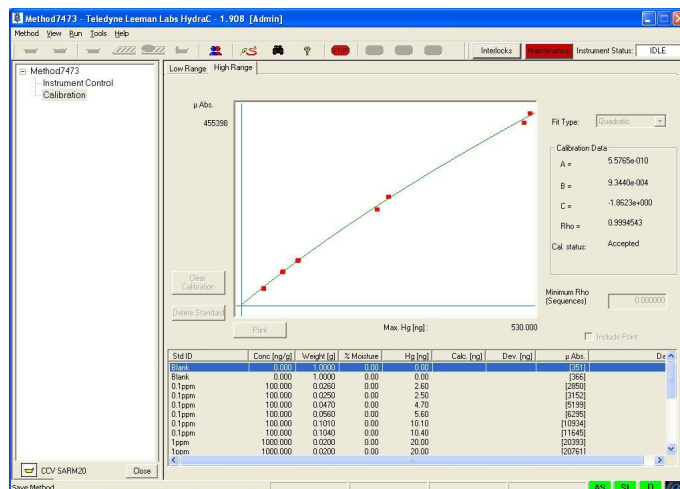


INSTRUMENTAL

Table 1 shows the instrument parameters employed for the calibration. Some of the sample matrices analyzed required slightly different drying and decomposition conditions for optimum results.

Table 1: System Parameters

Parameter	Water	Biological	Coal	Soil
Dry	300°C for 30-140 sec.	300°C for 70 sec.	300°C for 30 sec.	300°C for 30 sec.
Decomposition	800°C for 150 sec.	800°C for 150 sec.	800°C for 250 sec.	800°C for 150 sec.
Catalyst	600°C			
Catalyst Wait Period	60 sec.			
Gold Trap	600°C for 30 sec.			
Measurement	100 sec.			
Oxygen Flow	350 ml/min			

Figure 3. Hydra II_c Low Concentration Range (0—40 ng)Figure 4. Hydra II_c High Concentration Range (40—500 ng)

SAMPLE PREPARATION AND CALIBRATION

The **Hydra II_c** employs two optical paths of differing lengths for extended dynamic range. Its software automatically selects the best analytical signal for each measurement. The calibration curves are displayed in Figures 3 and 4 as micro absorbance vs. total mercury injected.

These calibration curves were generated using weighed deposits of aqueous standards in concentrations of 0.1, 1.0 and 10.0 ppm (w/w) mercury. About 0.1—0.2 gm of each sample was placed into a tared nickel boat for analysis.

RESULTS

Before any analysis began the Instrument Detection Limit (IDL) and Method Detection Limit (MDL) were determined. The IDL was obtained by analyzing seven replicate blanks and the MDL was determined by analyzing seven replicates of NIST SRM8437 (Hard Red Spring Wheat Flour). Using 3.14 times the standard deviation*, the IDL was determined to be 0.005 ng and the MDL was determined to be 0.02 ng. The data used to calculate the IDL and MDL are presented in Table 2. Certified reference materials (CRMs) for water, coal, biological tissue and soil matrices were analyzed. Certified and measured concentrations are provided in Table 3.

Table 2: IDL and MDL Results

Replicate	IDL (ng Hg)	MDL (ng Hg)
1	0.010	0.192
2	0.011	0.179
3	0.010	0.179
4	0.014	0.189
5	0.013	0.195
6	0.011	0.180
7	0.012	0.182
Std Dev (S.D.)	0.0015	0.0067
3.14(S.D.)	0.0047	0.021

Table 3. Certified reference material results

Sample Matrix	Name	Average sample weight (g)	Certified Concentration (PPM)	Measured Concentration (PPM)
Water	ERA WasteWatR	0.215	0.015	0.016
Coal	SABS SARM20	0.133	0.250	0.233
Biological	NIST 1515	0.135	0.044	0.043
Soil	NIST 2704	0.121	1.480	1.451

*Student t-test for 99% distribution with seven replicates (6 degrees of freedom).

Each sample type was analyzed in duplicate and a spike was analyzed to determine recovery. Sample spike (MS) recovery and spike duplicate (MSD) relative percent difference are presented in Table 4. Both the spike recovery and the relative percent difference between the spike and spike duplicate must be within $\pm 20\%$. The average sample weight analyzed also is displayed in Table 4.

Quality control checks were analyzed every ten samples for both the low and high curves. The method requires the results for the quality control checks to be within $\pm 20\%$. Results were consistently within $\pm 10\%$.

CONCLUSIONS

All the quality control requirements of U.S. EPA Method 7473¹ were satisfied. Sample results obtained showed excellent precision and recovery. All CRM's showed good accuracy without any sample pretreatment and required only about 7 minutes per sample analysis. Proper drying and decomposition conditions produce a matrix independent analysis of mercury in many sample types.

MORE ABOUT THE HYDRA II_C

The **Hydra II_C** provides a 70 position autosampler and has on-the-fly loading capability for virtually unlimited capacity. Additionally, a conversion kit is available which employs chemical reduction to satisfy the monitoring of drinking water in accordance with USEPA Method 245.1 and European Standards EN1483 and EN13806.

Table 4: Recovery and precision study

			A	B	C		
Sample Type	Sample Conc. (ng/g Hg)	Sample Weight (g)	Sample Mass (ng Hg)	MS Result (ng Hg)	Spike Added (ng Hg)	Recovery* (%)	Relative Percent Diff.** (%)
Waste water	269	0.127	34.16	55.91	25	87.0	1.0
		0.143	38.47	60.43	25	87.9	
Coal	27.1	0.138	4.0	33.63	31.75	94.1	7.4
		0.135	7.74	25.22	24.66	87.4	
Leaf	10.15	0.090	0.91	3.56	2.95	89.8	11.4
		0.081	0.82	5.41	4.57	100.4	
Soil	56.5	0.697	39.4	76.62	40.32	92.3	15.0
		0.727	41.1	88.5	44.1	107.5	

**MS % Recovery is calculated by subtracting the sample result from the spike result and dividing the difference by the spike added. To report as a percentage, the calculated value is multiplied by 100. % Recovery = $100 \times (B-A)/C$.*

***MSD Relative Percent Difference is calculated by multiplying the difference in the duplicate recoveries by 200 and dividing the result by the sum of the duplicate recoveries.*

¹www.epa.gov/osw/hazard/testmethods/sw846/pdfs/7473.pdf