Mercury Determination in House Dust, NIST SRM-2584, USEPA Method 7473, Using the Teledyne Leeman Labs Hydra II_C Combustion CVAAS

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Introduction

Mercury (Hg) is one of several wide-spread environmental toxins capable of causing a variety of negative health effects in humans. Because of its potential neurotoxic effect on children, chronic low-dose mercury exposure has become an increasing concern and dust ingestion during childhood is regarded as a key means of exposure to metals and metalloids (including mercury) that are derived from vehicular traffic and numerous industrial sources.

Soil and dust often become the primary resting places for these toxins through atmospheric deposition. Urban inhabitants in particular have a higher rate of exposure to contaminated dust by inhalation, ingestion and dermal contact.

Considering these factors, dust ingestion is often regarded as a primary source of low-dose mercury for urban children who spend much of their time indoors and ingest dust through normal, repetitive hand-to-mouth activities. Accordingly, knowledge of the chemical composition of dusts is required to accurately estimate childhood exposures.

This application note will demonstrate the ability of the Teledyne Leeman Labs Hydra II_C Mercury Analyzer to determine total elemental mercury (Hg^0) in National Institute for Standards and Technology (NIST) Standard Reference Material (SRM) 2584 - Trace Elements in House Dust using EPA Method 7473. EPA Method 7473 is approved for both laboratory and field analysis for mercury in solids and solutions using Thermal Decomposition, Amalgamation and Atomic Absorption Spectroscopy.

Instrumentation

The Hydra II_C is a fully automated (70 position) mercury analyzer that measures mercury in solid and semi-solid sample matrices directly without acid digestion (sample preparation). It employs sample combustion (thermal decomposition), mercury concentration via gold amalgamation and detection by Cold Vapor Atomic Absorption Spectroscopy (CVAAS). It operates using a single 110/220 V, 50/60 Hz power outlet and oxygen supplied at 15 to 20 psig. All instrument operating parameters (including furnace/catalyst temperature, gas flows, autosampler control) and sample cycle stages are computer controlled for ease-of-use. Through proper selection of the instrument'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. The Teledyne Leeman Labs *Hydra II_C Mercury Analyzer Operator's Manual* provides extensive guidance on parameter optimization.

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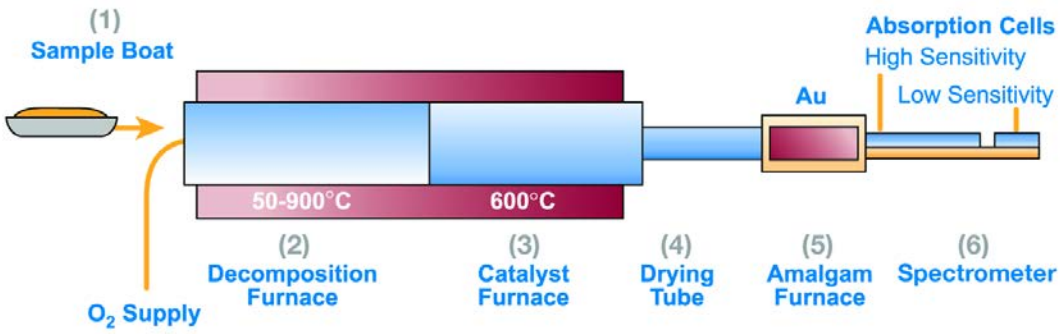
The Hydra II_C mercury analyzer employs combustion (decomposition) of a sample at high temperatures with oxygen. The gases resulting from the decomposition are carried through a heated catalyst to remove halogens, nitrogen oxides, and sulfur oxides. The remaining combustion products, including elemental mercury (Hg^0), are swept through a dryer and then to a gold amalgamation tube which captures the mercury while letting the other gases pass through. The amalgamator is then heated to release the Hg^0 into a carrier gas which transports it into the Cold Vapor Atomic Absorption Spectrometer (CVAAS). The transient signal is measured in series by a high-sensitivity cell followed by a low-sensitivity cell. 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 that provided by a single optical cell path length. Figure 1 depicts the analytical process with gas flowing from left to right. Waste gases exiting the system are chemically "scrubbed" with a carbon trap or exhausted out of the lab at the end of the process.

Figure 1 Hydra II_C Mercury Analyzer Principle of Operation



Experimental

The Hydra II_C is operated by the Teledyne Leeman Labs Envoy software that provides sample specific control of the system. The software's parameters can be optimized for sample drying and decomposition (both temperature and duration) for each individual sample to facilitate accurate analysis of mercury in various sample matrices. For this experiment, the system was calibrated up to 200 ng. Operating conditions for the instrument used during sample analyses are shown in Figure 3.

SRM 2584 - Trace Elements in House Dust was obtained from the National Institute for Standards and Technology (NIST). Approximately 65% of the material used for SRM-2584 was derived from HEPA® vacuum cleaners that removed dust and other surface debris from specific households in Montana, New Jersey, Ohio, and Wisconsin. This material was mixed with material taken from the sources used in the preparation of SRM-2583, which consisted primarily of vacuumed dust from cleaning services, motels, and hotels from North Carolina, Maryland, Ohio, and New Jersey. The material was sent out for radiation sterilization, and then shipped to NIST for final processing and blending. The raw materials were mixed and tumbled and the dust was separated from unwanted debris then screened through a 90 µm stainless steel sieve using vibration and a vacuum. Processed sub-lots of approximately 5 kg each were set aside and analyzed in order to develop a blending protocol. Selected sub-lots were blended in a cone blender and then bottled. Certification analyses were performed in the NIST Analytical Chemistry Division. Reference values for Hg were obtained using CVAAS and instrumental neutron activation analysis.

The only sample preparation involved with the SRM was the thorough mixing of the SRM bottle between sample weighings. Separate disposable scoopulas were used for SRM-2584 and the Coal Fly Ash (SRM-1633b) which was used as a calibration verification QC analyzed before and after samples. Also, differing amounts of the 1000 ug/L (1.000 mg/L) solution, used during calibration, were analyzed as calibration verification QCs before and after the samples.

The NIST SRM-2584 Certificate did not list moisture content and instructed that it should be determined in-house. A tared sample boat was loaded with ~.100 grams (as-received weight), dried, and then weighted again (dry weight). The percent moisture was determined to be 2.26%.

Calibration Standardization

Quartz boats were cleaned prior to calibration by running them through the same method created for the experiment with any unnecessary dry time removed. While the boats were being cleaned, standards were prepared by serial dilutions of a 1000 mg/L (1,000,000 ug/L) certified primary standard purchased from LabChem® as shown in Table I. A 0.2% HNO_3 solution, made using 18 Mohm DI water, was used as diluent for all dilutions. Calibration standards were prepared in the following manner:

- A 10,000 ug/L standard was made from the primary standard by performing a 100x dilution (.1 ml into a total volume of 10 ml).
- The 1000 ug/L, 100 ug/L and 10 ug/L standards were made by 10x serial dilutions (1ml of previous standard into a total volume of 10ml).
- The 5 ug/L standard was made by performing a 2x dilution of the 10 ug/L (3 mls into a total volume of 6 ml).

Table I Serial Dilutions (0.2%NHO_3 as Diluent)

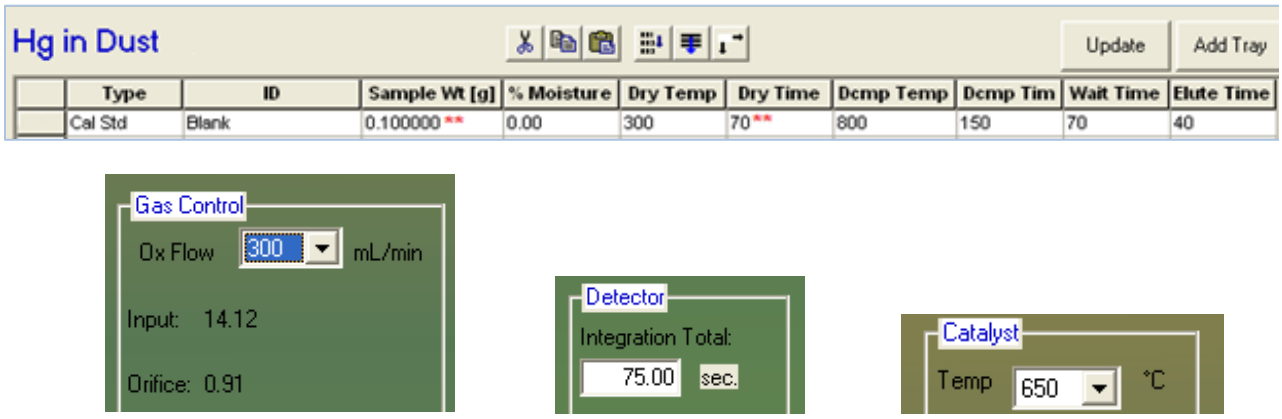
	Primary Standard	100x Dilution	10x Dilution	10x Dilution	10x Dilution	2x Dilution
Conc. in ug/L	1,000,000	10,000	1,000	100	10	5

Using the pre-cleaned quartz boats, aliquots from the mercury standards in Table I were introduced into the system to create two linear-fit calibration curves. The system developed a low curve covering the 0.50 - 10 ng mercury levels and a high curve that covers samples in the 10 - 200 ng range. The calibration plots are displayed as mass of mercury in nanograms (x-axis) versus micro absorbance of Hg (y-axis). Operating conditions for the instrument used during calibration and subsequent analyses are shown in Figure 2 and Figure 3. The two resulting calibration curves are presented in Figure 4**.**

Table II Calibration Standardization

Calibration Point	Aliquot
Blank	0.100 ml of 0.2% HNO_3 diluent
0.5 ng	0.100 ml of the 5 ug/L solution
1.0 ng	0.100 ml of the 10 ug/L solution
5.0 ng	0.050 ml of the 100 ug/L solution
10.0 ng	0.100 ml of the 100 ug/L solution
50.0 ng	0.050 ml of the 1,000 ug/L solution
100.0 ng	0.100 ml of the 1,000 ug/L solution
200.0 ng	0.020 ml of the 10,000 ug/L solution

Figure 2 Calibration Operational Conditions



** As a general rule, when calibrating with or analyzing liquids, a ratio of 70 seconds per 100 microliters is strongly suggested.

Figure 3 Sample Analysis Operational Conditions

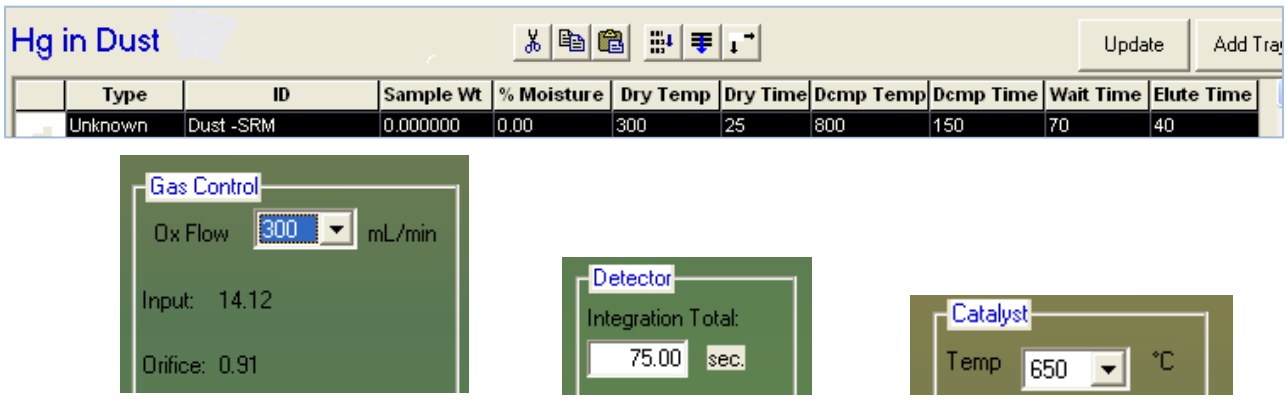
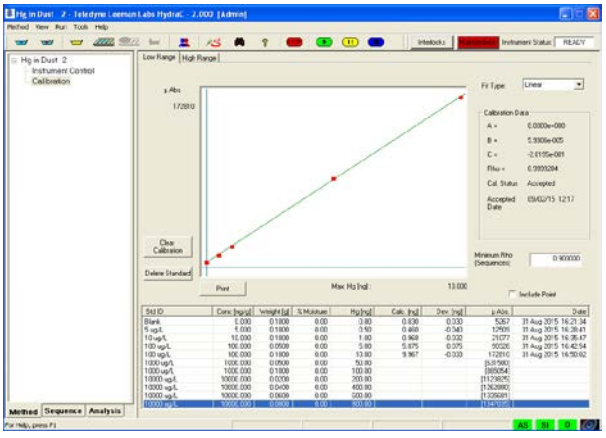
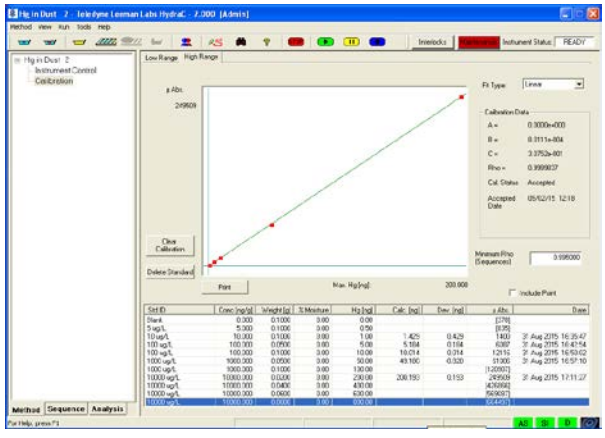


Figure 4 Calibration Curves



Low-Range Calibration Curve



High-Range Calibration Curve

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Procedure

The same procedure used to clean the quartz boats was used to clean sufficient nickel boats for sample analysis. With thorough mixing of the SRM bottle between each sampling, ~0.025 grams of sample was transferred into the pre-cleaned nickel boats. Exact weights for each individual sample were recorded and entered into the Hydra II_C's Envoy software. A total of seven samples were prepared in this manner and then loaded onto the boat shuttles for unattended analysis. The integrated cover over the shuttles was closed to prevent airborne particulates from contaminating the samples in the boats while they were waiting to be analyzed.

Note that an Envoy time-saving feature can be employed at this point. Once sufficient samples have been weighed and the weights entered, the analyzer can begin analysis while any remaining samples are then added to the end of the sequence. Alternatively, samples can be analyzed individually by loading the weighed sample boat directly onto the injector and entering the weight when prompted by the Envoy software.

Results

Using the Teledyne Leeman Labs Hydra II_C Mercury Analyzer for measurement of mercury in this sample matrix resulted in an excellent correlation with the certified value for NIST SRM-2584.

Seven replicates of the SRM were analyzed using the instrument operating conditions shown in Figure 3. The results listed are corrected for moisture content. The mean concentration and standard deviation were calculated and listed. Individual analyses, giving a final result of 5.189 mg/kg ± 0.643 (dry basis), are shown in Figure 5 and Figure 6. NIST SRM-2584 has a certified concentration of 5.2 mg/kg with an uncertainty of ±0.24 mg/kg. An example house dust sample peak is shown in Figure 7.

Figure 5 Results

House Dust, NIST 2584, 5.2 mg/Kg ± 0.24				
Sample Boat	mg/Kg			
1	5.752			
2	5.017			
3	5.501			
4	4.974			
5	4.811			
6	5.191			
7	5.076			
	Mean = 5.189			
	Uncertainty = 0.643			
	n = 7 Replicates	STDEV =	0.328	RSD% = 6.320

Figure 6 Results with Uncertainties

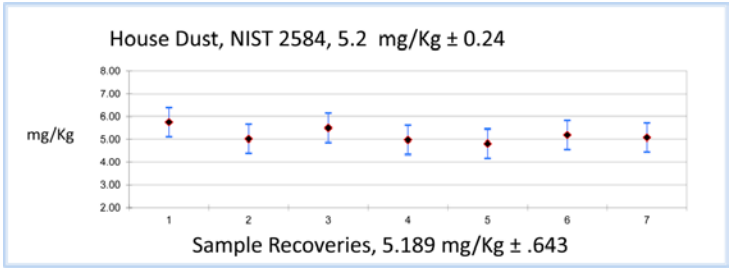
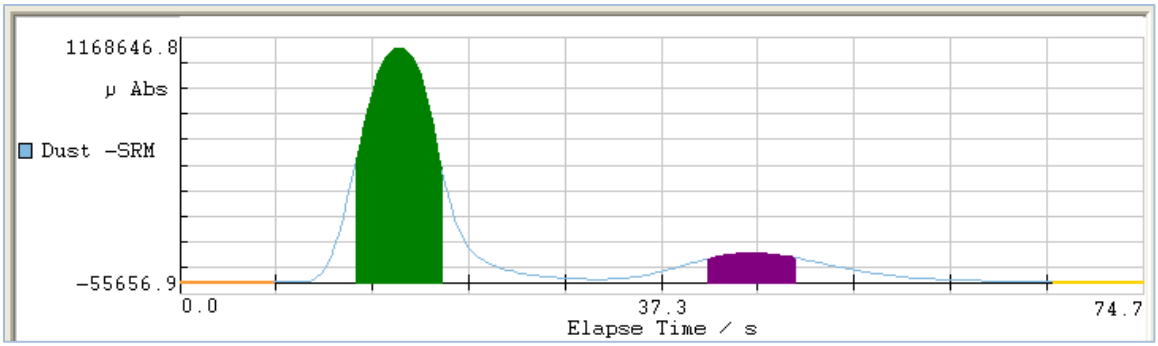


Figure 7 Example House Dust Sample Peak



The pre-sample and post-sample QC checks, consisting of both liquid and solid matrixes, are listed in Figure 8. The liquid QC checks were differing amounts of the 1,000 ug/L (1.000 mg/L) solution used during calibration. The solid QC checks were differing amounts of SRM-1633b (Coal Fly Ash) with a certified value of 1.005 mg/kg.

Figure 8 Quality Control Chart

Mercury Determination in Dust Quality Control			
	Quality Control (in ng/g)	**ng/g**	**% recovery**
Pre-Sample	Liquid Check -Low Curve (1000)	937	93.70%
	Solid Check-Low Curve(1005)	940	94.10%
Post-Sample	Liquid Check -High Curve(1000)	1008	100.80%
	Solid Check-High Curve(1005)	1035	103.50%
	Liquid Check-High Curve(1000)	998	99.80%

Conclusions

The Hydra II_C Combustion CVAAS Mercury Analyzer is the perfect tool for analyzing and determining total elemental mercury (Hg^0) concentrations in NIST SRM-2584 using the guidance in EPA Method 7473 and the instrument method parameters in this application note. Additionally, the integrated autosampler provides a fast, simple and convenient approach for the analysis of mercury. The use of combustion (decomposition) virtually eliminates sample preparation as well as the production of hazardous chemical wastes resulting in reduced technician time and operating expenses.

References

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