Mercury Determination in Seaweed, CD200, USEPA Method 7473, Using the Teledyne Leeman Labs Hydra II_C Combustion CVAAS

Jeff Forsberg, Product Manager, John McQuatters, Mercury Product Specialist, Teledyne Leeman Labs, Hudson, NH

Introduction

The brown algae, *Fucus vesiculosus*, known by the common name "bladderwrack", is a seaweed found on the coasts of the North Sea, the western Baltic Sea, and the Atlantic and Pacific Oceans.[1] Among the three groups of algae (brown, red and green), *Fucus vesiculosus* has been demonstrated to be an efficient class of biosorbent for toxic elements including mercury (Hg) in water and wastewater due to its high uptake capacity. Consequently, analysis of *Fucus vesiculosus* can be used for environmental monitoring, and in particular, water quality control. To this end, some European countries have employed *Fucus vesiculosus* as a marine bioindicator.

Conversely, *Fucus vesiculosus* is also used in the preparation of foods, cosmetics and medicines for its nutritional and therapeutic properties, and monitoring it for levels of trace elements is of great interest to analysts and scientists concerned with product safety.[2]

This application note will demonstrate the ability of the Teledyne Leeman Labs Hydra II_C Mercury Analyzer to determine total mercury by USEPA Method 7473 in the Certified Reference Material (CRM) Seaweed (CD200). Seaweed (CD200) is a powdered bladderwrack material certified for the mass fraction of the total content of As, Cd, Cu, Hg, Pb, Se and Zn and is produced by the European Commission, Joint Research Centre Institute for Reference Materials and Measurements (IRMM) Geel, Belgium.[2] USEPA Method 7473 is approved for both laboratory and field analysis for mercury in solids, semi-solids and solutions using thermal decomposition, amalgamation and Atomic Absorption (AA) spectroscopy.[3]

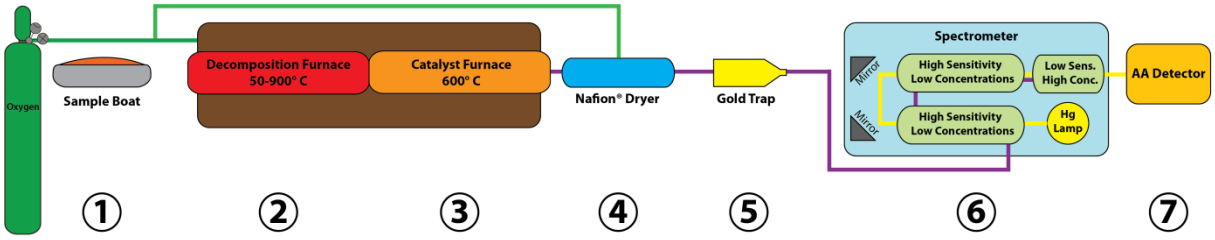
Instrumentation

The Teledyne Leeman Labs Hydra II_C is a fully automated mercury analyzer that measures mercury in diverse sample matrices directly with little to no sample preparation. Instead, it employs sample combustion (thermal decomposition), mercury concentration by gold amalgamation and detection by Cold Vapor Atomic Absorption Spectroscopy (CVAAS). The instrument operates using a universal power supply compatible with main power input 110/220 V, 50/60 Hz power outlet and oxygen supplied at 15 to 20 psig. All 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 operational parameters, mercury determination can be performed on a diverse sample set across a dynamic range consisting of absolute per sample mass of mercury from 0.001 ng to 1500 ng. The *Hydra II_C Mercury Analyzer Operator's Manual* provides extensive guidance on parameter optimization.

Figure 1 depicts the analytical process with gas flowing from left to right. The Hydra II_C mercury analyzer employs combustion of a sample at high temperatures with oxygen. The gases resulting from this 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 allowing the other gases to pass through.

The amalgamator is then heated to release the accumulated Hg^0 into a carrier gas which transports it into the Cold Vapor Atomic Absorption Spectrometer. 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. Waste gases exiting the system are chemically "scrubbed" with a carbon trap or exhausted safely 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 (combustion is customizable, controlling temperature and duration) for each individual sample to facilitate analysis of mercury in various sample matrices. For this experiment, the system was calibrated up to 4 ng. The operating conditions for the instrument used during sample analyses are shown in Figure 2 and Table I.

Figure 2 Operational Conditions

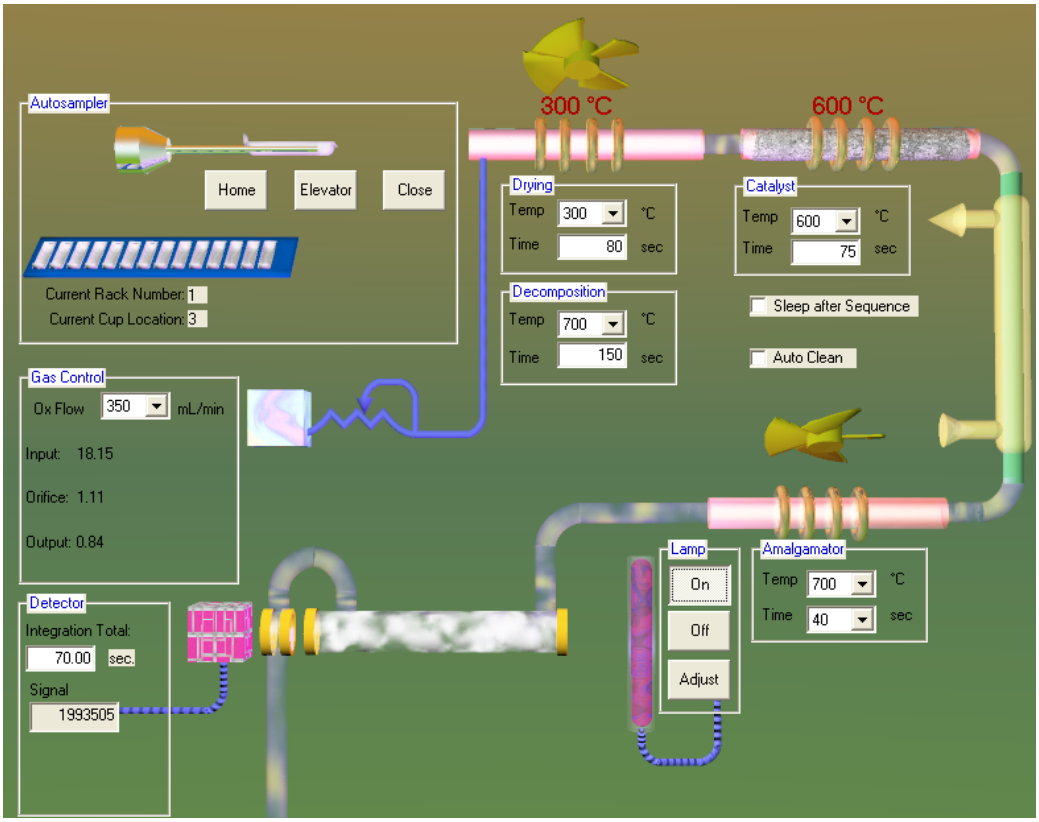


Table I Operational Conditions		
Sample	**Method Parameter**	**Parameter Value**
Seaweed (CD200)	Oxygen Flow	350 mL/minute
	Integration Time	70 Seconds
	Drying Temperature	300 °C
	Drying Time	80 Seconds
	Decomposition Temperature	700 °C
	Decomposition Time	150 Seconds
	Catalyst Temperature	600 °C
	Wait Time	75 Seconds
	Amalgamator Temperature	700 °C
	Amalgamator Time	40 Seconds

Seaweed (CD200) CRM was used for this analysis. According to the European Commission, Joint Research Centre Institute for Reference Materials and Measurements (IRMM) the CRM was prepared as follows, "Approximately 60 kg of brown algae seaweed (bladderwrack, fucus vesiculosus) was collected in Galway (Ireland) and processed at IRMM (Belgium) to produce a Certified Reference Material (CRM) of seaweed powder. The produced vials containing the processed seaweed were carefully capped, sealed and stored for further certification studies. Between-unit homogeneity was quantified as well as stability during dispatch and storage in accordance with ISO Guide 35:2006. Within-unit homogeneity was also quantified to determine the minimum sample intake. The material was characterized by an inter-laboratory comparison among laboratories of demonstrated competence and adhering to ISO/IEC 17025. Technically invalid results were removed but no outlier was eliminated on statistical grounds only. Uncertainties of the certified values were calculated in compliance with the Guide to the Expression of Uncertainty in Measurement (GUM) including uncertainty contribution related to possible heterogeneity and instability of the material as well as to the characterization." [2]

Note: The only sample preparation involved with CD200 was the thorough mixing of the bottle initially and between each sample weighing to assure and maintain homogeneity.

The Seaweed (CD200) CRM certificate, included with the material, did not list moisture content and instructed that it should be determined in-house on a separate portion of the material that would not be used for analyte determination. A cleaned, dried and tared sample boat was loaded with ~0.200 grams (as-received weight), dried at ~105 °C, and then weighted after 2 hours per the certificate's instructions. The percent moisture was determined to be 5.0 percent.

Calibration Standardization

Nickel boats loaded with diatomaceous earth were cleaned just prior to calibration by running them through the same method created for the analysis (unnecessary dry time was removed). While the boats were being cleaned, Intermediate Standards were prepared by serial dilutions of a 1000 mg/L certified primary standard purchased from Sigma Aldrich® as shown in Table II. The final analyzer Calibration Standards were prepared as shown in Table III.

Laboratory 18.2 Mohm-cm resistivity DI water was used for the first Intermediate Standard dilution so that its resulting Nitric Acid (HNO_3) concentration would be 0.12%. Also, a 0.12% HNO_3 solution was made using 18.2 Mohm-cm resistivity DI water as diluent for the second Intermediate Standard and the final analyzer Calibration Standards. This protocol allowed for the same volume and concentration of HNO_3 preservative for each Calibration Standard as shown in Table III. The Intermediate Standards and Calibration Standards were prepared in the following manner:

- A 10,000 µg/L Intermediate Standard was made from the commercial primary standard (preserved in 12% HNO_3) by performing a 100x dilution using 18.2 Mohm-cm resistivity DI water.
- A 1000 µg/L Intermediate Standard was made by performing a 10x serial dilution using the prepared 0.12% HNO_3 diluent solution (1 mL of the 10,000 µg/L standard into a total volume of 10 mL).
- Using a microliter pipettor for best accuracy, 40, 20, 10, 5 and 2.5 µg/L analyzer Calibration Standards were made by diluting 400 µl, 200 µl, 100 µl, 50 µl and 25 µl of the 1000 µg/L Intermediate Standard into a total volume of 10 mL in separate tubes using the prepared 0.12% HNO_3 diluent solution.
- 0.12% HNO_3 diluent solution was used for the analyzer Calibration Blank.

Table II Serial Dilutions for Intermediate Standards

	Primary Standard	100x Dilution	10x Dilution
Hg Conc. in µg/L	1,000,000	10,000	1,000
HNO_3 Conc. in %	12	0.12	0.12

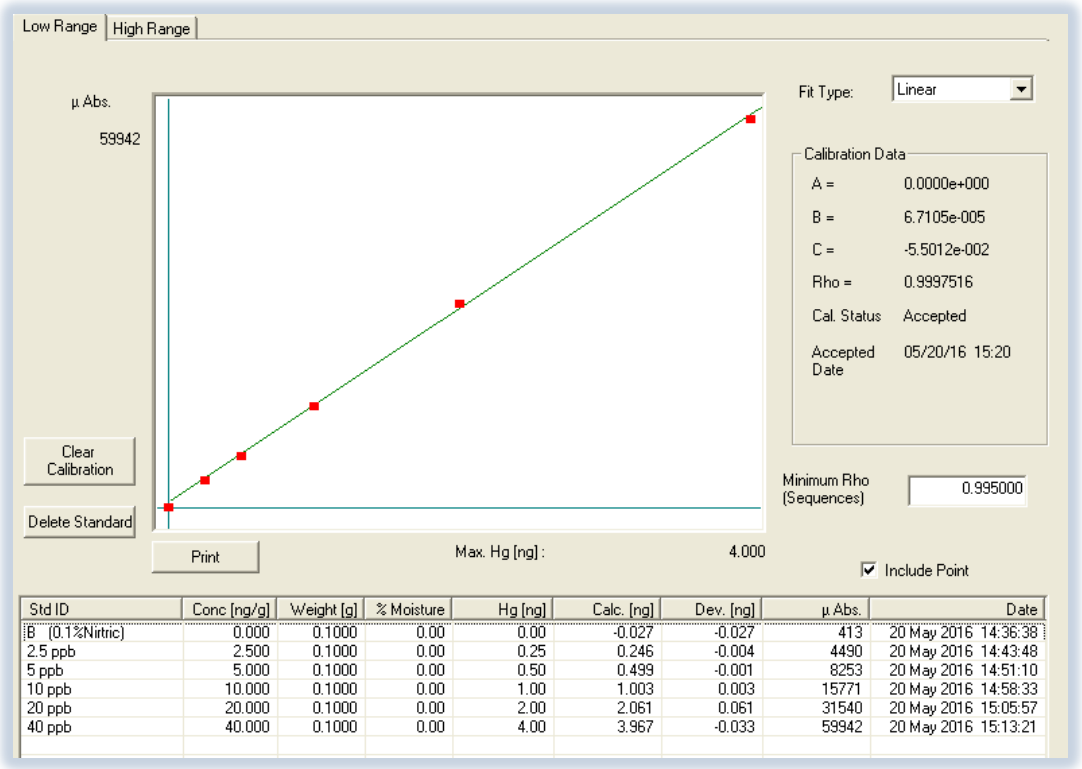
Using the pre-cleaned Nickel boats with diatomaceous earth, 0.100 mL aliquots from the mercury Calibration Standards in Table III were analyzed using the operating conditions shown in Table I to create a linear-fit calibration curve in the low-calibration (high-sensitivity) cell. The system developed a curve covering a range of 0.0 – 4.0 ng of mercury and is presented in Figure 3. The Envoy Software displays calibration plots as mass of mercury in nanograms versus micro absorbance of Hg.

Table III Prepared Analyzer Calibration Standards

Calibration Point / Nitric Concentration	Aliquot
Blank (0.12%)	0.100 mL of 0.12% HNO_3 diluent
0.25 ng (0.12%)	0.100 mL of the 2.5 µg/L standard
0.50 ng (0.12%)	0.100 mL of the 5.0 µg/L standard
1.00 ng (0.12%)	0.100 mL of the 10 µg/L standard
2.00 ng (0.12%)	0.100 mL of the 20 µg/L standard
4.00 ng (0.12%)	0.100 mL of the 40 µg/L standard

Note: As a general rule, when calibrating with, or analyzing liquids, a ratio of 70 seconds per 0.100 mL (at the typical temperature setting of 300 °C) is recommended for the Dry Time parameter.

Figure 3 Low-Range Calibration Curve



Std ID	Conc [ng/g]	Weight [g]	% Moisture	Hg [ng]	Calc. [ng]	Dev. [ng]	µ Abs.	Date
B (0.1%Nitric)	0.000	0.1000	0.00	0.00	-0.027	-0.027	413	20 May 2016 14:36:38
2.5 ppb	2.500	0.1000	0.00	0.25	0.246	-0.004	4490	20 May 2016 14:43:48
5 ppb	5.000	0.1000	0.00	0.50	0.499	-0.001	8253	20 May 2016 14:51:10
10 ppb	10.000	0.1000	0.00	1.00	1.003	0.003	15771	20 May 2016 14:58:33
20 ppb	20.000	0.1000	0.00	2.00	2.061	0.061	31540	20 May 2016 15:05:57
40 ppb	40.000	0.1000	0.00	4.00	3.967	-0.033	59942	20 May 2016 15:13:21

Procedure

The same procedure used to clean the Calibration Standard boats was used to clean sufficient empty nickel boats for sample analysis. With thorough mixing of the CRM bottle between each sampling, ~0.050 grams of sample was transferred into the pre-cleaned nickel boats. Exact weights for each individual sample were recorded and entered into the combustion method developed in the 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.

It is important to note that the Envoy software affords the time-saving ability to begin the analytical run (once sufficient samples have been weighed and the weights entered) while the remaining samples are weighed and 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

The Hydra II_C Mercury Analyzer's measurement of mercury in the CRM resulted in a successful correlation with the certified value for Seaweed (CD200).

Seven replicates of the CRM were analyzed using the instrument operating conditions shown in Table I. The results listed are corrected for the moisture content of 5.0%. The mean concentration and standard deviation were calculated and are listed in Table IV. Individual analyses, giving a final result of 19.8 µg/Kg ± 0.7 (dry basis), are shown in Figure 4. Seaweed (CD200) has a certified concentration of 18.6 µg/Kg with an uncertainty of ±1.6 µg/Kg. A representative Seaweed (CD200) sample peak is shown in Figure 5.

Table IV Seaweed, CD200 , 18.6 µg/Kg ± 1.6		
Sample	µg/Kg	
1	19.85	
2	20.17	
3	19.04	
4	19.95	
5	19.67	
6	20.10	
7	19.86	
Mean = 19.8		
Uncertainty = 0.7		
n = 7 Replicates	STDEV = 0.375	RSD% = 1.892

Figure 4 Results with Uncertainties

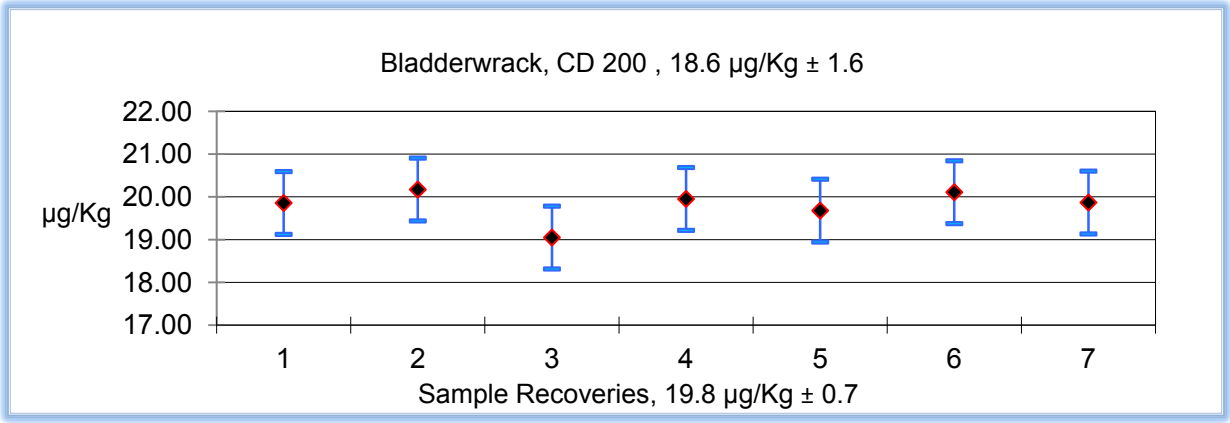
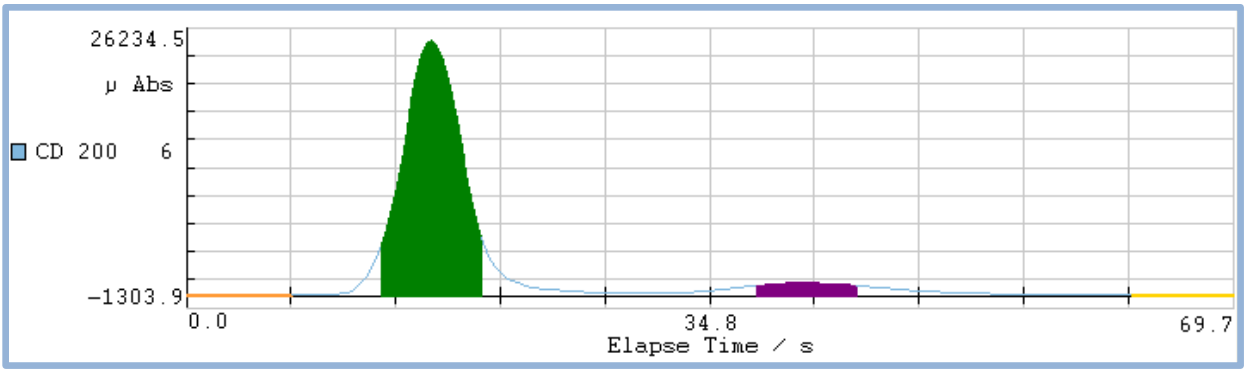


Figure 5 Representative Seaweed (CD200) Sample Peak



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The Quality Control (QC) Standards and Matrix Spikes are listed in Table VI with their recoveries. A Laboratory Control Sample (LCS), as required by USEPA Method 7473, was prepared from a second-source commercial standard, and analyzed before and after the samples. After the initial seven replicates, a Spike and Spike Duplicate were also analyzed by addition of 100 microliters of the 5 ug/L solution used during the calibration step.

Table VI Mercury Determination in Seaweed Quality Control

Quality Control (in µg/L) Standards	µg/Kg	% recovery
5 µg/L (0.5ng) LCS - pre sample	4.3	86
5 µg/L (0.5ng) LCS - post sample	4.1	82
Seaweed (CD200) Spk (0.5 ng)		111.0
Seaweed (CD200) SDup (0.5 ng)		113.0

Conclusion

The Hydra II_C Combustion CVAAS Mercury Analyzer is capable of analyzing and determining total elemental mercury (Hg^0) concentration in Seaweed (CD200) using the guidance in EPA Method 7473 and the operating conditions in Table I. 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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3. United States Environmental Protection Agency (USEPA). Mercury in solids and solutions by thermal decomposition, amalgamation, and atomic absorption spectrophotometry - EPA Method 7473-2007 - February 2007 Revision 0. [Online] https://www.epa.gov/sites/production/files/2015-12/documents/7473.pdf (accessed June 06, 2016)