

Enhanced Moisture Control for USEPA Method 7473 Using the Hydra II_c, CVAA Combustion Mercury Analyzer

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INTRODUCTION

Total, inorganic, and methyl mercury determination is an important tool for monitoring mercury uptake and bioaccumulation in ecosystem flora and/or fauna. By quantifying environmental mercury contamination, the dangers of human exposure can be adequately assessed.

The heavy metal mercury (both organic and inorganic) is known to have toxic effects on human nervous, digestive and immune systems, and is a particular threat to fetal and early childhood development resulting in impaired neurological development.¹

This application note will demonstrate the capabilities of the Hydra II_C for total mercury determination by direct combustion of aqueous samples using USEPA Method 7473 with an enhanced moisture control system.



The enhanced moisture control system was used to lower the Method Detection Limit (MDL) by increasing the aqueous sample volume used to determine mercury concentration. To fully investigate the performance of the modified system and the accuracy of the analytical results, the following studies were conducted:

- Validation of the effectiveness of the enhanced moisture control system
- Calibration of the instrument with carryover study
- Post-calibration method validation including method detection limit, precision study and sample vessel bias study

INSTRUMENTATION

The Hydra II_c, CVAA Combustion Mercury Analyzer is an independent stand-alone analyzer that uses Cold Vapor Atomic Absorbance (CVAA) spectroscopy to obtain reliable quantitative data from simple to complex matrices by direct combustion combined with a proprietary catalyst to remove interfering compounds such as sulfur and nitrogen oxides. The combustion process includes a continuous linear flow of carrier gas through the entire system including both the decomposition and catalyst furnaces. The system components are shown in Figure 1.





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First a weighed sample (1) is introduced to a decomposition furnace (2) with oxygen (or air) flowing over the sample itself. The furnace temperature is then raised in two stages to first dry the sample, then to combust or decompose the sample. Post combustion, the elemental mercury is passed through the proprietary catalyst (3) then through a heated NafionTM Perma Pure[®] drying system (4) with counter flow to assist in water removal from the sample gas stream. The flow path continues with the concentration of Hg⁰ onto gold-coated quartz sand (5). The gold sand trap is heated to temperatures greater than 600 °C to liberate the elemental mercury. Once liberated, the elemental mercury is swept by the combustion carrier gas through the external dryer tube filled with magnesium perchlorate Mg(ClO₄)₂ and then on to the analytical absorbance cells (6) where it is measured at 253.7 nm for determination of sample concentration (7). The placement of the enhanced moisture control system directly between the gold trap sample "exit" port (5 – 6) and the detector cell "sample gas in" port ensures that moisture does not enter the detector cells causing baseline drift and absorbance of light. By removing the excess moisture, false positives are eliminated in mercury determination at the ultra-trace concentration levels.

The analytical working range for the Hydra II_C, CVAA Combustion Mercury Analyzer is from <0.05 ng to >1500 ng. This dynamic quantitative range allows mercury concentrations to be determined in a broad range of sample substrates without dilution or pre-concentration. An autosampler accompanied the Hydra II_C, CVAA Combustion Mercury Analyzer allowing hands-free sample batch analysis.

EXPERIMENTAL

The Hydra II_C, CVAA Combustion Mercury Analyzer is operated by the Envoy software, which provides method specific control of the system. Parameter optimization allows for the quantitation of mercury in the trace ng range. The goal of this application note is to optimize instrument parameters to analyze aqueous samples without disruption by water vapor, and to determine the Method Detection Limit (MDL) using the final system parameters and setup.

Excess water vapor is known to disrupt the ultra-trace analytical range in any dedicated mercury determination system, but an area of greater concern is water vapor condensation occurring in cold zones within the closed direct combustion system. These cold zones allow the potential for water vapor to condensate (drop out) and collect, and can occur in any system with heated optics and gold traps operated at temperatures at or above 200 °C hold temperature and 600 °C desorption temperature. Once water vapor begins to collect, elemental Hg in the sample will concentrate in the condensate reducing the detectable quantity of elemental Hg and increasing the MDL. The continuing collection of condensate water vapor can eventually render the system inoperable, even after a short sample run, and require a period of equilibration to return to a dry state prior to the next analysis. Consequently, removal of excess water vapor is imperative.

Enhanced Moisture Control System Modifications

For this study, the Hydra II_C's standard Nafion[™] Perma Pure[®] drying system was enhanced by the addition of an external, in-line moisture control measure to remove excess water vapor prior to the detector cells. A Teledyne Leeman Labs chemical dryer tube (SP5653) was filled with the chemical drying agent Mg(ClO₄)₂ sieved on a # 20 sieve (pore size ~0.85 mm) shown in Figure 2. The external drying tube was installed between the gold trap "sample exit port" and the detector cell "sample gas in" port.

Figure 2 Teledyne Leeman Labs Dryer Tube, Sieve and Magnesium Perchlorate Mg(ClO₄)₂





Because of the Hydra II_c's modular design, installation of the external drying tube was very simple. The installation is detailed below and shown in (Figure 3).

- 1. Locate and disconnect the gold trap module Hg gas transfer line (1, 2).
- 2. Connect the external dryer tube to the gold trap module exhaust (3).
- 3. Connect the gold trap Hg gas transfer line to the open connection on the external dryer tube (4, 5, 6).

Figure 3 Connecting the External Dryer Tube with Mg(CIO₄)₂





After adding the external dryer tube, additional modifications were made to the system to further improve moisture removal. Taking advantage of the Hydra IIc's ability to use an alternative counter-flow gas for the Nafion[™] Perma Pure[®] dryer, argon was supplied at 34 psi (210 kPa) to facilitate efficient drying of the wet oxygen gas. A collection container was added to receive the excess water vapor exiting the dryer counter flow (Figure 4).

Figure 4 Collection Container for Dryer Counter Flow





To eliminate cold zones in which water vapor could potentially condensate, system default temperatures were customized by revising or adding a "Data Key" entry followed by adding or revising the "Data Value" in the Hydra IIc's system "initialization" file (.ini suffix). The Nafion[™] Perma Pure[®] dryer temperature was elevated to a maximum temperature of ~ 70 °C while the gold trap was placed in an elevated temperature hold state of ~ 220 °C using the following procedures:

1. Navigate to the main Envoy SW folder then open the Startup.ini file.



 Type in the "Data Key" with a space, and then enter the "Data Value" needed to facilitate the change. The "Data Key" and "Data Value" for the Nafion[®] dryer is "NafionFurnaceTemp 600" and the gold trap "Data Key" and "Data Value" is "EluteWarmTempOverride 220" as depicted in Figure 5.

Figure 5 "Data Key" and "Data Value" Changes for System Startup

Startup.ini - Notepad	
File Edit Format View Help	
InstPresent yes SimDetector no SimAutosampler no SimSampleIntro no SimSamplePump no	
; Rename balance specific dll (i.e. SARTORIOUS.DLL) to SCAN Scale no	_E.DLU
Plunger 0,5700,20220 Pusher 13601,9246 Slider 5330 Elevator 0, 4000	
; Change Plunger Speed to remove vibration MotorSpeed 0,4,3,3 LowPeakAbsLimit 380000	
NafionFurnaceTemp 600	
EluteWarmTempOverride 220	
overRangeLimit 15	

Validation of the Enhanced Moisture Control System

Once system modifications were completed, aqueous samples were run at volumes of 100, 200, 400, 600, 800, and 1000 μ L in un-calibrated groups of 42 to study water vapor breakthrough into the detector cells. At the completion of each group, the system was dismantled and inspected for condensation in all potential cold zones. Based on these findings the system and system parameters were optimized to maximize aqueous volumes, minimize the time from sample pick up to drop off, and achieve the lowest possible MDL.

Sample Boat Cleaning

To ensure the cleanliness of each sample boat prior to calibration and MDL analysis, the vessels were sequenced and subjected to a fast analytical protocol consisting primarily of a combustion and gold trap elution stages.

System Calibration

After system optimization, a calibration was prepared with a system MDL performed in order to validate the modified system. Calibration standards were prepared in 0.1 % HNO₃/ultra-pure deionized water matrix. Appropriate aliquots of 1, 10, 100, 1000 and 10,000 μ g/L working standards were used to prepare the calibration curve that consisted of one blank and thirteen non-zero standards ranging from 0.1 ng to 1000 ng. Prior to addition of "working" standards to the pre-cleaned sample boats, 100 μ L of 0.03 % (w/v) Cysteine Hydrochloride/ultra-pure deionized water matrix was added to stabilize the mercury standards in the nickel boats (Figure 6).



Figure 6 L-cysteine (F.W 175.64)

Cysteine Hydrochloride (L-2-Amino-3-mercaptopropanoic Acid Hydrochloride)

Monohydrate, U.S.P.

Carryover Study

Due to the large dynamic range, the calibration sequence consisted of sequential standards separated by empty positions to identify bias caused by carryover between high and low samples (Figure 7). Mercury was detected using a band pass filter with selectivity for wavelength 253.652 nm.

Figure 7 Calibration Boat Shuttle Load



Post-Calibration Method Validation

After calibration, a post-calibration method validation was performed including:

- 1. Method Detection Limit Study
- 2. 1 µg/L Precision Study
- 3. Bias response study at 0.1 μ g/L to compare the use of quartz boats, nickel boats loaded with diatomaceous earth, and nickel boats with L-cysteine as the mercury stabilizer.

CALIBRATION STANDARDIZATION

Calibration intermediate "working" standards were prepared with serial dilutions starting with a 1000 mg/L certified stock standard preserved in 12 % HNO₃ (Table I). All "working" standards were prepared using a final volume of 10 mL by additions of 1 mL of standard and 9 mL of 0.1 % HNO₃/ultra-pure purged DI water.



Table I Intermediate "Working" Calibration Standard Preparation							
Standard Concentration	Stock 1000 mg/L	100 mg/L	10 mg/L	1 mg/L	0.1 mg/L	0.01 mg/L	0.001 mg/L
0.1 % HNO₃	-	9 mL	9 mL	9 mL	9 mL	9 mL	9 mL
Standard Added	-	1 mL Stock	1 mL 100 mg/L	1 mL 10 mg/L	1 mL 1 mg/L	1 mL 0.1 mg/L	1 mL 0.01 mg/L
Total Volume	-	10 mL	10 mL	10 mL	10 mL	10 mL	10 mL
~ % acid	12 %	1.3 %	0.22 %	0.12 %	0.1 %	0.1 %	0.1 %

Instrument calibration standards were prepared by combining an intermediate "working" standard with 0.1 % HNO₃ matrix blank and 100 μ L of L-cysteine solution (Table II). A volume of 600 μ L was maintained to minimize any matrix bias that may exist in the large dynamic calibration range.

Table II Instrument Calibration Standards Preparation					
Standard (ng Hg)	0.1 % HNO3	Intermediate Standard/Volume	L-cysteine	Total Volume	
Blank	500 µL	-	100 µL	600 µL	
0.1 ng	400 µL	0.001 mg/L - 100 µL	100 µL	600 µL	
0.5 ng	-	0.001 mg/L - 500 µL	100 µL	600 µL	
1 ng	400 µL	0.01 mg/L - 100 μL	100 µL	600 µL	
5 ng	-	0.01 mg/L - 500 μL	100 µL	600 µL	
10 ng	400 µL	0.1 mg/L -100 µL	100 µL	600 µL	
20 ng	300 µL	0.1 mg/L - 200 μL	100 µL	600 µL	
50 ng	-	0.1 mg/L - 500 μL	100 µL	600 µL	
100 ng	400 µL	1 mg/L - 100 µL	100 µL	600 µL	
200 ng	300 µL	1 mg/L - 200 µL	100 µL	600 µL	
400 ng	100 µL	1 mg/L - 400 µL	100 µL	600 µL	
600 ng	440 µL	10 mg/L - 60 µL	100 µL	600 µL	
800 ng	420 µL	10 mg/L - 80 µL	100 µL	600 µL	
1000 ng	400 µL	10 mg/L - 100 µL	100 µL	600 µL	

PROCEDURE

- 1. Start the Hydra II_C in accordance the Hydra II_C Operations Manual.
- 2. Set the gas pressure to a value between 15 and 25 PSI. Teledyne Leeman Labs recommends that the oxygen carrier gas be purified by an in-line mercury trap. For this application note, a mercury trap (P/N 15-2145-003) was used to ensure that the scrubbed carrier gas stream contributed a minimal amount of mercury contamination to the system. The gas purification filter is typically used to purify argon gas in ultra-trace analysis using CVAF with gold pre-concentration of mercury in the sample.

	Carrier Gas Purification Mercury Trap (M-8000) - A pre-filter that uses a proprietary
15-2145-003	adsorbent to remove trace mercury vapor from the ultra-trace analytical carrier gas or ultra-
	trace solution purge gas.



- Prepare a new method by selecting Method "NEW" from the drop-down menu and name the method appropriately (e.g., Hydra II_C EPA 7473 or similar) (Figure 8). Set the method parameters to those shown in Table III. These parameters are the optimal parameters for aqueous analysis of samples up to 500 μL, based on the experimental findings of this study.
- **Note:** Each time the Hydra II_c is readied for analysis it is important to condition the catalyst by consecutively running a single boat with 100 mg of flour, a single boat with 500 μL of deionized water, and an empty sequence position.

Table III Optimal System Parameters					
Parameter	Setting	Time			
Drying	200 °C	210 s			
Catalyst	600 °C	30 s			
Decomposition	1000 °C	120 s			
Oxygen Flow	350 mL/min	-			
Integration	_	80 s			
Amalgamation	700 °C	30 s			





- 4. Click the Start Up Button to start the system, then allow 30 minutes for the instrument to stabilize at the method settings.
- 5. Prepare enough nickel boats by rinsing with DI water and firing in a muffle furnace at 800 °C for 15 minutes with flow though inert gas. Boats may also be cleaned by running them as unknowns on an un-calibrated method. Repeat this process until the boats are clean with a consistent µabs response. Store cleaned boats in a sealed plastic bag until use. After analysis is complete, repeat the cleaning process and store boats until next use.
- 6. Prepare the standards according to Table I and Table II. It should be noted that the calibration is usually stable over the life span of the catalyst. Verify the calibration after starting the analyzer (which includes catalyst conditioning) with a Certified Reference Material (CRM) for each calibration range. This can be accomplished by either varying the weights of the CRM or using an entirely different CRM.
- 7. Once the system has stabilized, the analysis of either calibration standards or quality control checks, samples and unknowns may begin.



RESULTS

Enhanced Moisture Control System Validation

Water vapor is known to cause false positives at the trace analysis level due to its light absorption at multiple wavelengths. The wavelengths are near 253.7 (but not exactly at 253.7) and the absorbency is weak, but can interfere at the trace levels of Hg analysis and determination. Additionally, the absorbance of light by water vapor affects the absorbency measurement process as a whole by destabilizing the baseline, which leads to erroneous results and poor precision. Removal of water vapor during the analysis of aqueous samples was a primary goal of this study.

Enhancement of the Hydra IIc's moisture control system by adding an external dryer tube with Mg(ClO₄)₂ resulted in improved system capabilities. Results were generated to validate that residual water vapor was removed from the gas stream and that the enhanced moisture control system did not allow water vapor to enter the detection cells regardless of sample volumes ranging from 100 μ L to 1000 μ L. The baseline was flat and stable through the entire sequence of 42 tap water samples run in incrementally increasing volumes (100, 200, 400, 600, 800, and 1000 μ L). Two representative examples of baseline stability are shown below. Figure 9 depicts sample 1 and 42 at 100 μ L. Figure 10 shows sample 1 and 42 at 1000 μ L of tap water, placed in a nickel boat and analyzed in an un-calibrated system solely to validate the enhanced moisture control system.



Figure 9 Forty Two Sample Tap Water Test at 100 µL

Figure 10 Forty Two Sample Tap Water Test at 1000 µL



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Calibration and Precision Study

Following the enhanced moisture control system validation, a calibration and precision study was performed. Initial results were less than desirable and indicated a need for improvement. After inspecting the system's internal components, water vapor was found to be collecting in a cold zone at the gold trap connection and absorbing elemental mercury at trace levels resulting in a degradation of precision. It was determined that optimization of instrument parameters and sample volumes would eliminate the formation of the liquid droplet at the gold trap interface. With the cool zone eliminated, higher deviations in signal affecting MDL and Limit of Quantitation (LOQ) were mitigated. Approximately 600 μ L was found to be the aqueous sample volume limit.

Nitric Acid and Nickel Reaction

A study was performed to minimize the reaction between the nitric acid standard preservative and the nickel of the sample boats, which through the liberation of hydrogen, assists in the removal of mercury from the passive sample. The nitric acid/nickel reaction is problematic when analyzing trace levels of mercury and can potentially affect the true mercury concentration of the samples.

100 μ L of previously prepared 0.03 % L-cysteine run in small batch tests showed promising results. The addition of diatomaceous earth added prior to the addition of the aqueous sample is also known to assist in the mitigation of the acid/nickel effect, but can be messy. Consequently, the clean and direct addition of L-cysteine was the additive of choice.

Calibration

The low concentration range returned an R-value of 0.9999246 using a weighted fit (Figure 11). The weighted fit was used to assist in trace values returning a lower deviation from theoretical calculated results, based on the curve values from 1 to 20 ng mass of mercury. The high concentration range returned an R-value of 0.9989464 using a quadratic fit (Figure 12). The quadratic fit was the only viable fit option because the linier function of absorbance values based on Beer's Law (the linear relationship between absorbance and concentration of an absorbing species) was exceeded.



Figure 11 Low Concentration Calibration Figures of Merit (High Sensitivity Cell; 0.1 – 20 ng)



Figure 12 High Concentration Calibration Figures of Merit (Low Sensitivity Cell; 50 - 1000 ng)



Table IV Calibration Figures of Merit					
Standard (ng Hg)	µabs Response	Calculated ng	Deviation ng	Detection Cell	
Blank	476	0.042	0.042	Low Range	
0.1 ng	916	0.087	-0.013	Low Range	
0.5 ng	4534	0.463	-0.037	Low Range	
1 ng	8992	0.925	-0.075	Low Range	
5 ng	49703	5.150	0.150	Low Range	
10 ng	97275	10.087	0.087	Low Range	
20 ng	191625	19.879	-0.121	Low Range	
50 ng	50104	57.603	7.603	High Range	
100 ng	97877	97.124	-2.876	High Range	
200 ng	197846	189.046	-10.954	High Range	
400 ng	389871	400.615	0.615	High Range	
600 ng	560370	627.054	27.054	High Range	
800 ng	658002	773.060	-26.940	High Range	
1000 ng	799331	1005.498	5.498	High Range	

Carryover Study

The carryover study using empty sampling positions between calibration standards showed favorable results as expected. The Hydra IIc is a complex, yet intuitive, analytical tool in the determination of mercury and the results of the carryover study confirmed the analyzer's ability to calibrate over a large dynamic range of 0.1 ng to 1000 ng with minimal "next sample" effects for values greater than 200 ng mass of mercury. The carryover effects are shown in Figure 13 with an exploded view of the low and high range calibration data. The displayed peaks are from the 0.1 % HNO₃ calibration blank and the highest calibration standard of 1000 ng.



Figure 13 Calibration Carryover Effects

n 2. 200 (400)	Туре	Sample ID	Conc [ng/g]	Hg [ng]	Weight [g]	% Moistu	μAbs.	Cal. Factor
and a second sec	S	Blank (1 % HNO3)	0.0000	0.00	0.50000	0.0000	476	LOW
Aqueous - Aqueous Calibration with L-Cysteine	U	MT	0.0188	0.02	1.00000	0.0000	22	LOW
The Brender Contract Pages Married Married Land Contract	S	1 ug/L	1.0000	0.10	0.10000	0.0000	916	LOW
9 90 0000 112 0000 12 12% 1 3 524 0000 13 0000 000 90 12%	U	MT	0.0187	0.02	1.00000	0.0000	22	LOW
5 (25. 100.) 113 (201.0 1130 458 129) 3 M	S	1 ug/L	1.0000	0.50	0.50000	0.0000	4534	LOW
agt 1000 10 1000 100 27 128	U	MT	0.0243	0.02	1.00000	0.0000	16	LOW
94 0022 110 0000 1100 0100 71 124 30-94 0000 110 0100 1100 079 134 97 0001 110 1000 1100 77 134	S	10 ug/L	10.0000	1.00	0.10000	0.0000	8992	LOW
20.42 20.001 21.01 20.00 11.00 12.28 12.87 30 0020 110 0020 11.00 13 12.57 30.57 0020 110 0020 11.00 13 12.57	U	MT	0.0307	0.03	1.00000	0.0000	21	LOW
w0er 09 Probes	S	10 ug/L	10.0000	5.00	0.50000	0.0000	49703	LOW
542 K	U	MT	0.0321	0.03	1.00000	0.0000	33	LOW
	S	100 ug/L	100.0000	10.00	0.10000	0.0000	97275	LOW
	U	MT	0.0308	0.03	1.00000	0.0000	55	LOW
-6.53	S	100 ug/L	100.0000	20.00	0.20000	0.0000	191625	LOW
The second se		A IT	0.0200	0.02	1 00000	0.0000	120	LOW
		MI	0.0300	0.05	1.00000	0.0000	130	LOW
	Type	M I Sample ID	Conc [ng/g]	Ha [na]	Weight [g]	% Moistu	u Abs.	Cal. Factor
	Type	Sample ID	Conc [ng/g]	Hg [ng]	Weight [g]	% Moistu	µ Abs.	Cal. Factor
	Type	Sample ID 100 ug/L	Conc [ng/g] 100.0000 0.0395	Hg [ng] 50.00	Weight [g] 0.50000 1.00000	% Moistu 0.0000 0.0000	μAbs. 50104 227	Cal. Factor HIGH
A De Calence A De Calence	Type S U S	MT Sample ID 100 ug/L MT 1000 ug/l	Conc [ng/g] 100.0000 0.0395 1000.0000	Hg [ng] 50.00 0.04 100.00	Weight [g] 0.50000 1.00000 0.10000	% Moistu 0.0000 0.0000 0.0000	μAbs. 50104 227 97877	Cal. Factor HIGH LOW HIGH
	Type S U S	MT Sample ID 100 ug/L MT 1000 ug/L MT	Conc [ng/g] 100.0000 0.0395 1000.0000 0.0562	Hg [ng] 50.00 0.04 100.00 0.06	Weight [g] 0.50000 1.00000 0.10000 1.00000	% Moistu 0.0000 0.0000 0.0000 0.0000	μAbs. 50104 227 97877 399	Cal. Factor HIGH LOW HIGH
	Type S U S U S	MT Sample ID 100 ug/L MT 1000 ug/L MT 1000 ug/L	Conc [ng/g] 100.0000 0.0395 1000.0000 0.0562 1000.0000	Hg [ng] 50.00 0.04 100.00 0.06 200.00	Weight [g] 0.50000 1.00000 0.10000 1.00000 0.20000	% Moistu 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000	μAbs. 50104 227 97877 399 197846	Cal. Factor HIGH LOW HIGH LOW
	U Type S U S U S	MT Sample ID 100 ug/L MT 1000 ug/L MT 1000 ug/L MT	Conc [ng/g] 100.0000 0.0395 1000.0000 0.0562 1000.0000 0.0942	Hg [ng] 50.00 0.04 100.00 0.06 200.00 0.09	Weight [g] 0.50000 1.00000 0.10000 1.00000 0.20000 1.00000	% Moistu 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000	μAbs. 50104 227 97877 399 197846 791	Cal. Factor HIGH LOW HIGH LOW HIGH
	Type S U S U S U S	MT Sample ID 100 ug/L MT 1000 ug/L MT 1000 ug/L MT 1000 ug/L MT 1000 ug/L MT	Conc [ng/g] 100.0000 0.0395 1000.0000 0.0562 1000.0000 0.0942 1000.0000	Hg [ng] 50.00 0.04 100.00 0.06 200.00 0.09 400.00	Weight [g] 0.50000 1.00000 0.10000 0.20000 1.00000 0.40000	% Moistu 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000	μAbs. 50104 227 97877 399 197846 791 389871	Cal. Factor HIGH LOW HIGH LOW HIGH
	Type S U S U S U S U U S	MT Semple ID 100 ug/L MT 1000 ug/L MT 1000 ug/L MT 1000 ug/L MT 1000 ug/L MT	Conc [ng/g] 100.0000 0.0395 1000.0000 0.0562 1000.0000 0.0942 1000.0000 0.2273	Hg [ng] 50.00 0.04 100.00 0.06 200.00 0.09 400.00 0.23	Weight [g] 0.50000 1.00000 0.10000 0.20000 1.00000 0.20000 0.40000 1.00000	% Moistu 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000	μAbs. 50104 227 97877 399 197846 791 389871 2162	Cal. Factor HIGH LOW HIGH LOW HIGH LOW
	U Type S U S U S U S U S U S	M T Sample ID 100 ug/L MT 1000 ug/L MT 1000 ug/L MT 1000 ug/L MT 1000 ug/L	Conc [ng/g] 100.0000 0.0395 1000.0000 0.0562 1000.0000 0.0942 1000.0000 0.2273 10000.0001	Hg [ng] 50.00 0.04 100.00 0.06 200.00 0.09 400.00 0.23 600.00	Weight [g] 0.50000 1.00000 0.10000 0.20000 1.00000 0.20000 1.00000 0.40000 0.00000 0.00000	% Moistu 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000	μAbs. 50104 227 97877 399 197846 791 389871 2162 560320	Cal. Factor HIGH LOW HIGH LOW HIGH LOW HIGH
	U Type S U S U S U S U S	MT Sample ID 100 ug/L MT 1000 ug/L MT 1000 ug/L MT 1000 ug/L MT 10000 ug/L MT 10000 ug/L MT	Conc [ng/g] 100.0000 0.0395 1000.0000 0.0562 1000.0000 0.0942 1000.0000 0.2273 10000.0000 0.4561	Hg [ng] 50.00 0.04 100.00 0.06 200.00 0.09 400.00 0.23 600.00 0.46	Weight [g] 0.50000 1.00000 0.10000 0.20000 1.00000 0.20000 1.00000 0.40000 0.66000 1.00000	% Moistu 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000	μ Abs. 50104 227 97877 399 197846 791 389871 2162 560370 4518	Cal. Factor HIGH LOW HIGH LOW HIGH LOW HIGH LOW
	U Type S U S U S U S U S U S U S	M T Sample ID 100 ug/L MT 1000 ug/L MT 1000 ug/L MT 10000 ug/L MT 10000 ug/L MT 10000 ug/L	Conc [ng/g] 100.0000 0.0395 1000.0000 0.0562 1000.0000 0.0942 1000.0000 0.2273 1000.0000 0.4561 1000.0000	Hg [ng] 50.00 0.04 100.00 0.06 200.00 0.09 400.00 0.23 600.00 0.46 800.00	Weight [g] 0.50000 1.00000 0.10000 0.20000 1.00000 0.20000 1.00000 0.40000 1.00000 0.60000 0.66000 0.80000	% Moistu 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000	μAbs. 50104 227 97877 399 197846 791 389871 2162 560370 4518 658002	Cal. Factor HIGH LOW HIGH LOW HIGH LOW HIGH LOW HIGH
	U Type S U S U S U S U S U U S U U S U U	M T Semple ID 100 ug/L MT 1000 ug/L MT 1000 ug/L MT 1000 ug/L MT 10000 ug/L MT 10000 ug/L MT 10000 ug/L MT 10000 ug/L MT	Conc [ng/g] 100.0000 0.0395 1000.0000 0.0562 1000.0000 0.0562 1000.0000 0.2273 10000.0000 0.4561 10000.0000 0.7374	Hg [ng] 50.00 0.04 100.00 200.00 0.09 400.00 0.23 600.00 0.46 800.00 0.74	Weight [g] 0.50000 1.00000 0.10000 0.20000 1.00000 0.20000 1.00000 0.40000 0.60000 1.00000 0.60000 1.00000 0.66000 1.00000 0.68000 1.00000	% Moistu 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000	μAbs. 50104 227 97877 399 197846 791 389871 2162 560370 4518 658002 7416	Cal. Factor HIGH LOW HIGH LOW HIGH LOW HIGH LOW HIGH LOW
	U Type S U S U S U S U S U S U S U S U S S U S	M T Sample ID 100 ug/L MT 1000 ug/L MT 1000 ug/L MT 1000 ug/L MT 10000 ug/L MT 10000 ug/L MT 10000 ug/L	Conc [ng/g] 100.0000 0.0395 1000.0000 0.0562 1000.0000 0.0542 1000.0000 0.2273 1000.0000 0.4561 1000.0000 0.4561 1000.0000 0.7374 1000.0000	Hg [ng] 50.00 0.04 100.00 0.06 200.00 0.09 400.00 0.23 600.00 0.46 800.00 0.74 1000.00	Weight [g] 0.50000 1.00000 0.10000 0.20000 1.00000 0.20000 1.00000 0.40000 1.00000 0.66000 1.00000 0.06000 1.00000 0.08000 1.00000	% Moistu 0.0000	μAbs. 50104 227 97877 399 197846 791 389871 2162 560370 4518 658002 7416 79931	Cal, Factor HIGH LOW HIGH LOW HIGH LOW HIGH LOW HIGH LOW HIGH

The theoretical positive biases from unknowns following samples that range in Hg mass of 200 to 1000 ng mercury are calculated in Table V based on 500 μ L of sample.

Table V Carryover Response Bias	e V Carryover Response Bias Results					
ng Mercury	Response in ng Hg (Low Range Cell)	Theoretical Concentration				
200	~ 800 µabs	0.2 µg/L				
400	~ 2000 µabs	0.4 µg/L				
600	~ 4500 µabs	1 µg/L				
800	~ 7500 µabs	1.5 µg/L				
1000	~ 9000 µabs	2 µg/L				

Sample Vessel/Media Bias Study

A sample vessel and media bias study was performed to evaluate their effects on trace analysis. A 0.05 ng standard was used to measure any resulting bias at trace concentrations of mercury. Seven boats were loaded with a volume of mercury standard that would equate to 0.05 ng total mass mercury. The study included nickel boats with diatomaceous earth, quartz boats without a modifier, and nickel boats with L-cysteine solution. The control group consisted of seven pre-blanked empty nickel boats.

The results shown in Table VI indicate that nickel boats with L-cysteine is an acceptable and reliable sample vessel for determination of mercury in aqueous samples. Pristine quartz sample boats showed the least amount of bias, but as the most expensive sample vessel option, the reduction in bias does not outweigh their expense.



Table VI Matrix Bias Test Results					
Sample Vessel With 0.05 ng Hg	Average Response	Response STDEV			
Nickel Boat W/Diatomaceous Earth	373 µabs	100 µabs			
Quartz Boat	208 µabs	62 µabs			
Nickel Boat W/L-cysteine	319 µabs	71 µabs			
Empty Nickel Boat	46 µabs	47 µabs			

Precision Study

A 30-sample, 1 μ g/L precision study was performed to evaluate the overall stability of the system with the enhanced moisture control system. The results of this study are shown in Figure 14 where the average concentration was 0.87 ± 0.081 μ g/L.

Figure 14 1.0 µg/L Precision Study



Method Detection Limit (MDL)

The final study performed a Method Detection Limit (MDL) on the modified system. Figure 15 shows the results for the MDL at ~ 0.1 μ g/L. While a small amount of contamination occurred during the MDL study, it was minimal in relation to the theoretical value. Consequently, the MDL was calculated "as is" and represents the analytical challenges faced by analysts in a typical laboratory setting.



Figure 15 Method Limit Study

MDL Study	udy Aqueous MDL Study (Hydra II _c)				
40 CFR Ch.1 (7-1-91) Part. 136, App B					
Rur	n 1 @ 0.1 µg/L	Run 2 @ 0.05 µg/L			
	0.3194	0.1674			
	0.2442	0.1236			
	0.327	0.1292			
	0.254	0.113			
	0.2527	0.0904			
	0.2237	0.056			
	0.2893	0.0697			
0.03951 = 0.001561 =	= Run 1 STDEV = STDEV ²	0.03812 = Run 2 STDEV 0.001453 = STDEV ²			
0.931 =	= F ratio				
0.003015 0.001507 0.038824	Sum STDEV ² (Ru Sum STDEV ² / 2 (STDEV _{Pooled}	in 1 and 2) ((Run 1 and 2) / 2)			
0.104 เ	ua/L = MDL				

CONCLUSIONS

The Hydra IIc, CVAA Combustion Mercury Analyzer is an effective analytical tool that is capable of obtaining reliable quantitative data in virtually any sample matrix including large quantities of aqueous samples. The addition of an external dryer tube filled with magnesium perchlorate Mg(CIO₄)₂, in conjunction with optimization of carrier gas flow, drying, decomposition, integration and amalgamation temperature/time, permitted analysis of calibration standards, quality control checks, and samples in aqueous form for USEPA Method 7473 without issue. The sample analysis time for direct combustion of aqueous samples was ~ 8 minutes and 30 seconds from boat pick up to drop off.

 $Mg(CIO_4)_2$ was used in the external dryer tube because it is both hygroscopic and free of mercury, making it ideally suited for the task of water vapor removal from the system. The chemical dryer needs to be maintained for optimal performance and it is recommended that the dyer should be inspected after 40 samples for degradation of the $Mg(CIO_4)_2$. Figure 16 shows a magnified view of fresh, free-flowing granular $Mg(CIO_4)_2$ compared to $Mg(CIO_4)_2$ in a drying tube that has been used/consumed and needs to be recharged. To recharge the chemical dyer use a clean utensil to gently remove any spent material until the $Mg(CIO_4)_2$ is free flowing. Add additional sieved $Mg(CIO_4)_2$ to ready the dryer for a further analysis.

Figure 16 Chemical Dryer Before and After Analysis



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The Hydra II_C, CVAA Combustion Mercury Analyzer was capable of analyzing aqueous samples in trace to mg/L concentration without dilution or digestion. The system demonstrated its ability to easily analyze aqueous samples with the addition of an enhanced moisture control system using Mg(ClO₄)₂ in an external dryer tube, and optimized method parameters. Preparation of the system for analysis and routine maintenance of the chemical dryer were not cumbersome, nor time consuming. The typical analytical range with 0.5 mL of sample is 0.1 µg/L to 2 mg/L. Using a reduced sample size of 0.1 mL the analytical range would be ~ 0.5 µg/L to 10 mg/L without dilution or sample preparation steps such as digestion.



Figure 17 Hydra II_C Direct Combustion Mercury Analyzer in a Typical Laboratory Setting

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