

Determination of Mercury in Wastewater (ERM CA-713), EPA Method 245.7, M-8000 CVAFS, Performance Based

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INTRODUCTION

Mercury is a bio-accumulative, toxic element that can be found in wastewater. It occurs naturally and can also be released to the atmosphere, soil, and water from a variety of anthropogenic sources¹. With its high toxicity, ongoing mercury exposure in humans can lead to poor health outcomes such as tremors, muscle weakness, motor and speech impairment, and a decline of cognitive abilities. The general population is primarily exposed to mercury by ingesting contaminated food and water². Humans produce billions of gallons of wastewater and if left untreated the environment would be overwhelmed with contamination. Water must be treated before it is transferred back into the environment to protect ourselves and nature from pollution.

USEPA Method 245.7, *Mercury in Water by Cold Vapor Atomic Fluorescence Spectroscopy*, was developed to provide an analytical protocol capable of mercury determination at concentrations typically regulated under state water quality criteria. Method 245.7 is similar to USEPA Method 1631. These methods use the same underlying chemistry, and both require analyte detection using atomic fluorescence. Method 245.7 uses gas liquid separation for analyte isolation followed by continuous flow analysis, while Method 1631 employs gas liquid separation followed by gold trap amalgamation. It can be used for all water types including drinking water, surface and ground waters, marine water, and industrial and municipal wastewater.

With such a wide scope, Method 245.7 is performance based. Alternate procedures are allowed if they meet all performance requirements including all quality control tests to ensure reliable results. In this application, a performance-based method will be developed using EPA Method 245.7³ to quantitate mercury in wastewater at 100x the typical calibration range. Using the Teledyne Leeman Labs QuickTrace® M-8000 Mercury Analyzer ([Figure 1](#)), mercury concentration will be determined at low µg/L levels while maintaining quality control standards required for ng/L levels of analysis. The total elemental mercury (Hg⁰) in Institute for Reference Materials and Measurements (IRMM) certified reference material (CRM) ERM®-CA713 "Wastewater Effluent" will be determined.

INSTRUMENTATION

The QuickTrace® M-8000 is an independent stand-alone analyzer that uses Cold Vapor Atomic Fluorescence (CVAF) spectrometry for obtaining reliable quantitative data. The QuickTrace® M-8000 is accompanied with an autosampler which allows for hands-free sample batch analysis. The QuickTrace® M-8000 has a four-channel peristaltic pump that ensures consistent sample uptake into the analyzer and allows for online sample reduction in a closed system. The reduced sample then flows into the non-foaming Gas-Liquid Separator (GLS) and argon sweeps around the center post as elemental mercury is liberated.

Figure 1 QuickTrace® M-8000 CVAF Mercury Analyzer and CETAC ASX-560 Autosampler



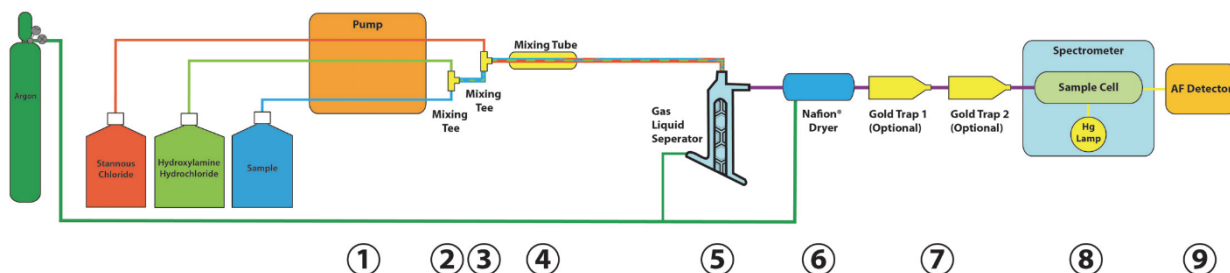


Figure 2 QuickTrace® M-8000 Process Diagram

The sample gas flow passes through a permeation dryer and then enters the system. The sample travels to a filtered photomultiplier fluorescence detector, and is measured at wavelength 253.7 nm, where it is recorded in a real-time chart recorder in the QuickTrace® software. [Figure 2](#) shows the basic instrument pathways. The working range for the QuickTrace® M-8000 Mercury Analyzer is from < 0.05 ng/L to > 400 µg/L. This dynamic quantitative range allows mercury concentrations to be determined in a broad range of sample substrates.

EXPERIMENTAL

The goal of this application is to optimize instrument parameters using EPA Method 245.7 for wastewater analysis to quantitate mercury at the low µg/L level using the Teledyne Leeman Labs QuickTrace® M-8000 Mercury Analyzer. The wastewater was digested in pre-cleaned 50 mL polypropylene co-polymer digestion tubes. The digestion tubes were pre-cleaned by soaking with 10% trace metal grade nitric acid then rinsed with ultrapure water in triplicate. Samples were preserved in the sample vials with hydrochloric acid and digested with 0.1 N potassium bromide / potassium bromate solution, followed by reduction with 10% hydroxylamine hydrochloride solution. Reduction of the inorganic mercury to elemental mercury was carried out by excess online addition of 10% stannous chloride, in 7% hydrochloric acid, at a rate of 3.6 mL/min at 100% pump speed. The wastewater samples were analyzed along with the appropriate quality control checks to validate the instrument. Total analysis time for each sample was approximately 80 seconds. A seven-point calibration curve was analyzed, which included five non-zero standards and two blanks.

The QuickTrace® software provides method specific control of the system and autosampler. Adjusting the gas flow, analyzer pump speed, sample uptake time, and photomultiplier tube (PMT) voltage allows parameter optimization for the quantitation of mercury in a dynamic range.

Figure 3 EPA Method 245.7 Autosampler and Analyzer Parameters shown in the QuickTrace® software

Autosampler		Analyzer	
Sample Probe depth (mm):	145		
ASX Rinse Pump Speed (%):	100		
Sample uptake time (s):	22.00		
Rinse time (s):	60.00		
Autosampler		Analyzer	
Gas Flow (ml/min)	High Flow		
Pump speed (%):	100		
Read delay time (s):	34.00		
Replicate read time (s):	1.00		
Replicates:	4		
<input checked="" type="checkbox"/> Auto adjust replicate read time			
<input checked="" type="checkbox"/> Baseline Drift Correction			
Start read (s):	10.00		
End read (s):	15.00		
<input checked="" type="checkbox"/> Two-point Baseline Correction			
Start read (s):	75.00		
End read (s):	80.00		
<input type="checkbox"/> Use Gold Trap #1			
Heater Start (s):	50.00		
Heater Stop (s):	70.00		
<input type="checkbox"/> Use Gold Trap #2			
Heater Start (s):	100.00		
Heater Stop (s):	120.00		
<input type="checkbox"/> Cut Enabled			
Cut Time:	40.00		

The PMT was manually adjusted down to attain a fluorescence response of ~4500 hF units for a 10 µg/L mercury solution in 3% hydrochloric acid diluent. The PMT voltage was lowered to ensure the calibration range was well within the linear range of the system. The parameters for this method are shown in [Figure 3](#).

The wastewater sample, ERM®-CA713, was collected from the effluent of a wastewater treatment works located in Flanders, Belgium. ERM®-CA713 is certified at 1.84 µg/L total mercury, with an uncertainty at 95% of ±0.11 µg/L⁴.

The outside of the ampoule was rinsed with deionized water to remove any contaminants, shaken for 2 minutes to ensure homogeneity, and then opened using a diamond tip cutter. According to USEPA Method 245.7, samples and standards use a working sample size of 100 mL. This was reduced to a 5mL volume, and all reagents were ratioed accordingly. Sample and standards were processed using 5 mL aliquots and total reagents added were 1.05 mL per digestion tube, for a final volume of 6.05 mL.

In USEPA Method 245.7, samples and standards are taken through the same preparation and digestion procedure using 50 mL polypropylene copolymer digestion tubes:

1. To each tube, 0.9 mL of 1:1 trace metal grade hydrochloric acid and then 0.1mL of 0.1 N potassium bromide / potassium bromate solution were added to acidify and reduce the aliquot addition.
2. A 5 mL aliquot (either calibration standard or sample) was added to each digestion tube.
3. The digestion tubes are capped and vortexed.
4. All tubes are digested at ambient temperature for 1 hour.
5. After digestion, the excess oxidants were neutralized with 0.050 mL 10% (w/v) hydroxylamine hydrochloride solution.
6. All tubes were left for 15 minutes with the caps on, swirled, and then left for 15 additional minutes with the caps off.
7. Reduction of the inorganic mercury (Hg²⁺) to elemental mercury (Hg⁰) was carried out by excess online addition of 10% (w/v) stannous chloride in 7% (v/v) hydrochloric acid.

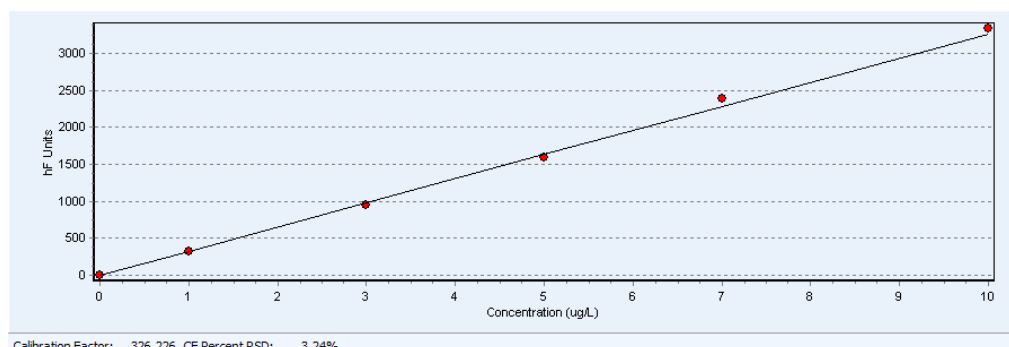
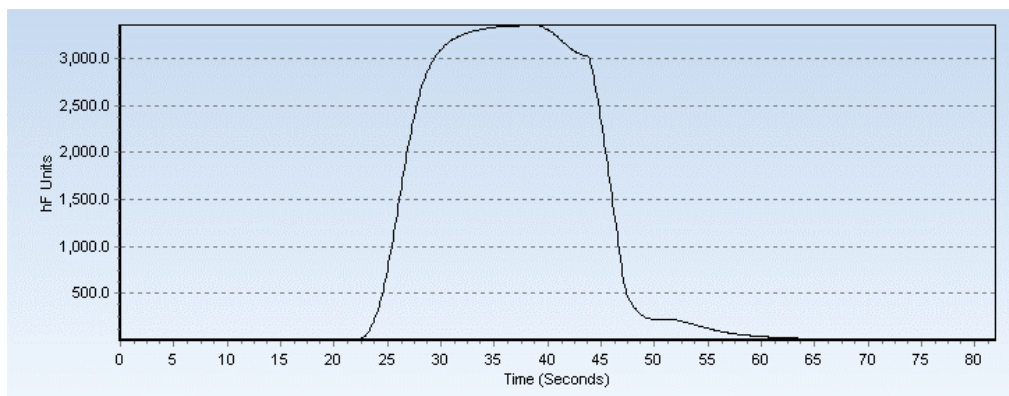
Seven replicates were analyzed along with the appropriate quality control checks to validate the instrument and calibration. Sample uptake was 22 seconds at 100% pump speed with 60 seconds of rinse at 100% pump speed, amounting to a total sample analysis time of 82 seconds using approximately 1.3 mL of sample. The integration mode was set to peak height utilizing 4 replicates at 1.00 second each. A seven-point calibration curve was analyzed, which included two blank and five non-zero standards. Total analysis time was approximately 40 minutes for 29 samples. At this rate, throughput would be ~44 sample tubes per hour.

Calibration Standardization

Calibration standards were prepared using the correct aliquots of a 100 µg/L working standard that was prepared from serial dilutions of a 1000 mg/L purchased stock standard. Working standard serial dilutions are summarized in [Table I](#) and calibration standard preparations are summarized in [Table II](#). Standards were prepared using a final volume of 100 mL. Calibration standards were prepared by aliquot volume additions of 1.0 mL, 3.0 mL, 5.0 mL, 7.0 mL, and 10.0mL of 100 µg/L working standard added to 100mL volumetric flasks containing 3% hydrochloric acid solution and brought to volume. Calibration standard concentrations were 1.0, 3.0, 5.0, 7.0, and 10.0 µg/L. Calibration standards were analyzed beginning with two matrix blanks and then proceeded from lowest concentration standard to the highest concentration standard. Each calibration peak was integrated for a total of 4 seconds. The final calibration curve and a 10 µg/L peak profile are shown in [Figures 4](#) and [5](#).

Table I Working Standard Preparation				
Standard Concentration	Stock 1000 mg/L	Working 10 mg/L	Working 1000 µg/L	Working 100 µg/L
3% HCl		99 mL	90 mL	90 mL
Standard Added		1 mL Stock, 1000 mg/L	10 mL 10 mg/L	10 mL 1000 µg/L
Total Volume		100 mL	100 mL	100 mL

Table II Calibration Standard Preparation					
Standard Concentration	Calibration 1 µg/L	Calibration 3 µg/L	Calibration 5 µg/L	Calibration 7 µg/L	Calibration 10 µg/L
3% HCl Added	99 mL	97 mL	95 mL	93 mL	90 mL
Standard Added	1 mL 100 µg/L	3 mL 100 µg/L	5 mL 100 µg/L	7 mL 100 µg/L	10 mL 100 µg/L
Total Volume	100 mL	100 mL	100 mL	100 mL	100 mL

Figure 4 Calibration Curve

Figure 5 10 µg/L Standard Peak Profile


RESULTS

Because the calibration range is extended 100x higher than the original method, the quality control standards were adjusted to the same ratio utilized in the original methodology. For example, the original method has quality control checks at 10% of the full calibration range (10 ng/L), so the quality control checks used in this application were 10% of the full scale (1 µg/L).

The initial calibration (ICAL) passed all data validation criteria easily: the calibration factor RSD was 3.24%, the 1 µg/L standard was recovered at 0.99 µg/L (99%), and the average blank concentration was reported as 0.00147 µg/L with a standard deviation of 0.00013 µg/L. The standard deviation for the blanks and blank concentration without correction must be less than 0.0005 µg/L and 0.0018 µg/L.

After a successful initial calibration (ICAL) and prior to the analysis of samples, a method detection limit (MDL) must be performed to validate the sensitivity and stability of the QuickTrace® M-8000 Mercury Analyzer. The MDL was acquired in accordance to 40 CFR Ch.1 Part. 136, App B⁵. The MDL study yielded a result of 0.00040 µg/L, or 0.4 ng/L. MDL results and calculations are shown in [Figure 6](#).

This was followed by initial precision recovery (IPR) tests to further validate the system for ultra-trace mercury analysis. Initial calibration verification (ICV), ongoing precision recovery (OPR) and method blanks were analyzed with each sample batch to validate the accuracy and stability of the ICAL. Calibration standards and control standards were prepared in hydrochloric acid, potassium bromide / potassium bromate solution, ultrapure deionized water, and hydroxylamine hydrochloride solution. The IPR study returned an average recovery of 98.4%, which is in the acceptable range of 78–108%. An initial calibration verification (ICV) was analyzed to validate calibration accuracy and method performance. The ICV was created using a 1.0 mL aliquot of 100 µg/L second source standard into a 100mL volumetric flask to give a concentration of 1.0 µg/L. A continuing calibration verification (CCV) and continuing calibration blank (CCB) were analyzed to evaluate instrument drift and carryover. The CCV was created using a 1.0 mL aliquot of 100 µg/L working standard into a 100mL volumetric flask to give a concentration of 1.0 µg/L. The CCB was a matrix matched blank using a 5mL aliquot of 3% hydrochloric acid.

The OPR samples returned a mercury concentration recovery of 99.0% and 99.4%. The method blanks ranged from 0.00009 to 0.0003 µg/L while the ICV samples returned recovery value was 101.7%. The spike and spike duplicates were 82.7% and 82.9% respectively with a relative percent difference of 0.14. The matrix spike recoveries must be within 76-111% with an RPD <18%.

Seven replicates of the digested CRM were analyzed and the total mercury concentration in µg/L was recorded. ERM®-CA713 is certified at 1.84 µg/L total mercury, with an uncertainty at 95% of ± 0.11 µg/L. Our analysis calculated the sample concentration to be 1.85 ± 0.005 µg/L. QC check results are shown in [Figure 7](#). The mean concentration, standard deviation, and uncertainty at 95% are shown in [Figures 8](#) and [9](#).

Figure 6 Method Detection Limit Results and Calculations

MDL Study	Wastewater USEPA 245.7
40 CFR Ch.1 (7-1-91) Part. 136, App B	
Run 1 @ 0.0035 µg/L	Run 2 @ 0.0055 µg/L
0.00314	0.00506
0.00347	0.00523
0.00331	0.00526
0.00341	0.00500
0.00341	0.00506
0.00328	0.00536
0.00338	0.00549
1.10E-04 = Run 1 STDEV	1.80E-04 = Run 2 STDEV
1.20E-08 = STDEV ²	3.24E-08 = STDEV ²
2.693 = F ratio	
0.000000 Sum STDEV ² (Run 1 and 2)	
2.2238E-08 Sum STDEV ² / 2 ((Run 1 and 2) / 2)	
0.00014912 STDEV _{Pooled}	
0.00040 = MDL	

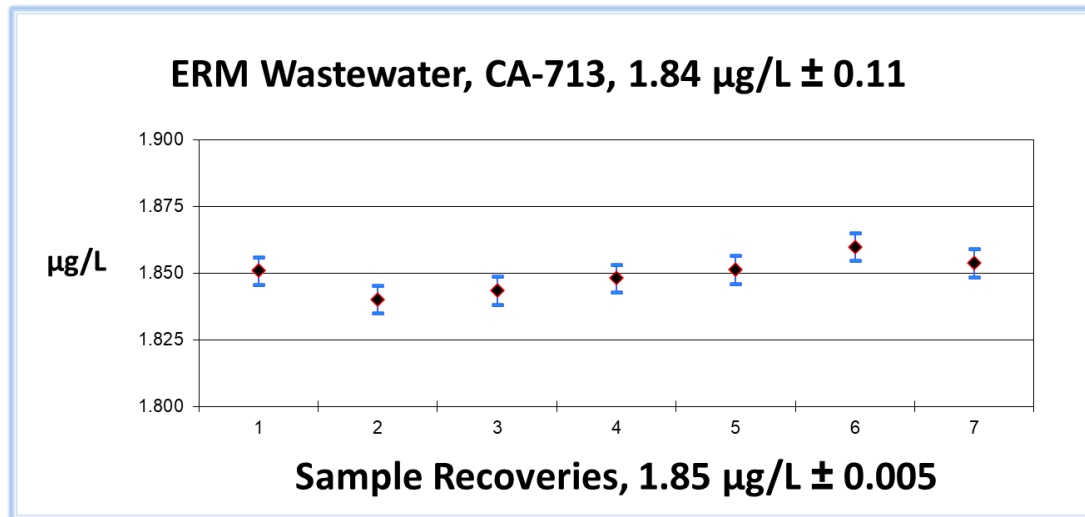
Figure 7 Quality Control Results

EPA 245.7 Quality Control		
Quality Control	% Recovery	RPD%
IPR (1 µg/L)	97.9-99.0	
OPR (1 µg/L)	99.0-99.4	
ICV/QCS (1 µg/L)	101.7	
CCV (1 µg/L)	99.1-100.0	
MS (3.5 µg/L)	82.7	
MSD (3.5 µg/L)	82.9	0.14

Figure 8 Results

ERM Wastewater, CA-713, 1.84 µg/L ± 0.11	
Digest	µg/L
1	1.85
2	1.84
3	1.84
4	1.85
5	1.85
6	1.86
7	1.85
Mean = 1.85	
Uncertainty = 0.005 @ 95 % Confidence	
n = 7 Replicates	STDEV = 0.007 RSD% = 0.373

Figure 9 Graphed Results with Confidence Interval



DISCUSSION

With a calibration range extended 100x higher than the original method, this application was still able to meet the quality control acceptance criteria for performance tests and well as exceed the method detection limit listed in Method 245.7. This method range spans multiple orders of magnitude while still meeting the lowest water quality criterion set for the Great Lakes Systems, 1.3 ng/L.

Total mercury in wastewater ERM® CA-713 was accurately quantitated in wastewater utilizing the various instrument settings of the QuickTrace® M-8000 Mercury Analyzer. The certified value for ERM®-CA-713 is 1.84 ± 0.11 µg/L. The average recovery for the sample replicates was calculated to be 1.85 ± 0.005 µg/L. This is an average recovery of 100.5%.

Optimizing carrier gas flow, pump speed, sample uptake, and PMT voltage allows for analysis of calibrations, quality controls, and samples over a broad dynamic range. Using the QuickTrace® M-8000 analyzer for measurement of low µg/L mercury is an effective analytical technique used for obtaining reliable quantitative data.

REFERENCES

Please visit our website for complete access to application notes, technical notes, and other resources. Go to: <https://www.teledyneleemanlabs.com/>

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