

Determination of Mercury in Wastewater (ERM CA-713), ISO Method 17852, M-8000 CVAFS

Sara Kennedy, Applications Chemist, Jeff Forsberg, Technical Product Manager; Teledyne Leeman Labs

Page | 1

INTRODUCTION

“Wastewater” is defined as all “used” water. Its composition ranges widely, from grey water produced in homes and businesses, to runoff into storm drains. It also includes sewage sludge and industrial process waste. Wastewater contains any number of substances, including chemicals, soaps, food scraps, oils, and human waste. These substances can have potentially harmful effects on ecosystems and human health.

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 contaminants. Water must be treated before it is transferred back into the environment to protect ourselves and nature from pollution.

On-going monitoring helps to control mercury movement through ecosystems and determine sources of contamination. Wastewater treatment assures mercury has been removed before releasing the water back into the environment. Many governments mandate the monitoring of mercury to ensure environmental and human health. International Standard Organization (ISO) method 17852:2006 provides guidance on “the determination of mercury in drinking, surface, ground and rainwater using atomic fluorescence spectrometry. It may be applied to industrial and municipal wastewater after an additional digestion step under appropriate conditions.”³

The goal of this application is to optimize instrument parameters using ISO Method 17852 to quantitate mercury in wastewater at low $\mu\text{g/L}$ levels using the Teledyne Leeman Labs QuickTrace® M-8000 Mercury Analyzer (Figure 1). The total elemental mercury (Hg^0) 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 that 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-



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

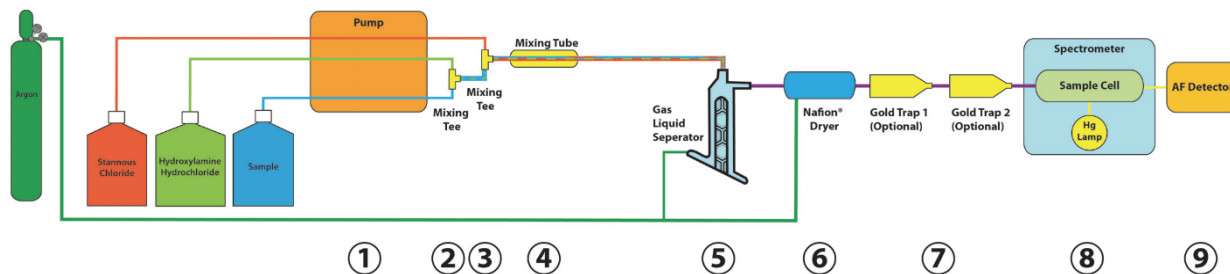


Figure 2: QuickTrace® M-8000 Process Diagram

foaming Gas-Liquid Separator (GLS) and argon sweeps around the center post as elemental mercury is liberated. 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 ISO method 17852 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% L-ascorbic acid. 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 six-point calibration curve was analyzed, which included five non-zero standards and one blank.

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. The PMT was manually adjusted down to attain a fluorescence response of ~2500 hF units for a 10 µg/L mercury solution in 3% hydrochloric acid diluent. The PMT voltage was

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		

Figure 3: ISO method 17852 Autosampler and Analyzer Parameters shown in the QuickTrace software.

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](#).

Wastewater samples were digested from ERM®-CA713. 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/L⁵.

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 ISO method 17852, 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 ISO method 17852, 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 were capped and vortexed.
4. All tubes were digested at ambient temperature for 1 hour.
5. After digestion, the excess oxidants were neutralized with 0.050 mL 10% (w/v) L-ascorbic acid 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 (Hg^{2+}) to elemental mercury (Hg^0) 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 four replicates at 1.00 second each. The calibration algorithm was set to force through the blank point. This subtracts the blank response from the calibration standards and samples, which helps with trace analysis in the MDL range. A six-point calibration curve was analyzed, which included one blank and five non-zero standards. Total analysis time was approximately 26 minutes for 19 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 one matrix blank 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	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

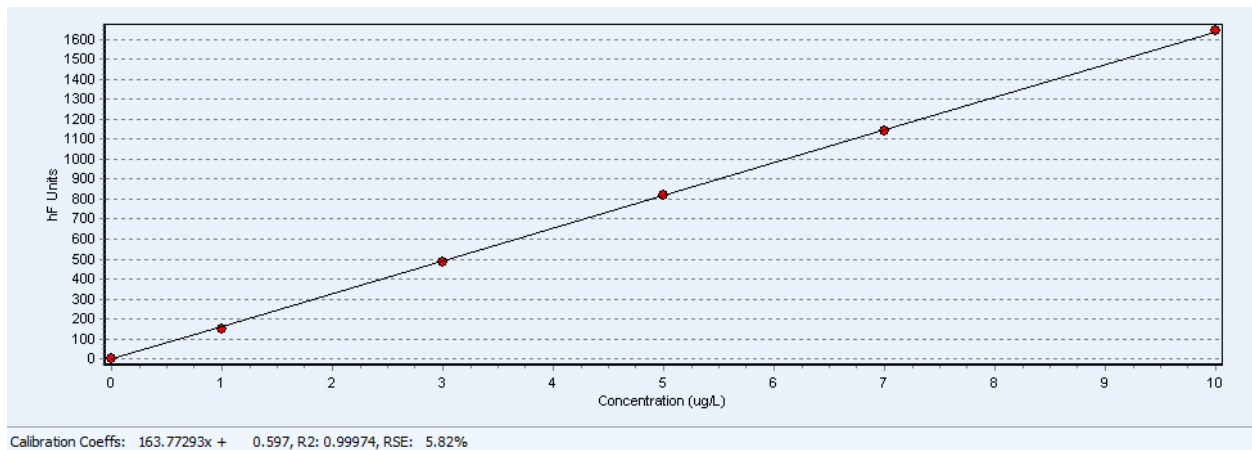


Figure 4: Calibration Curve

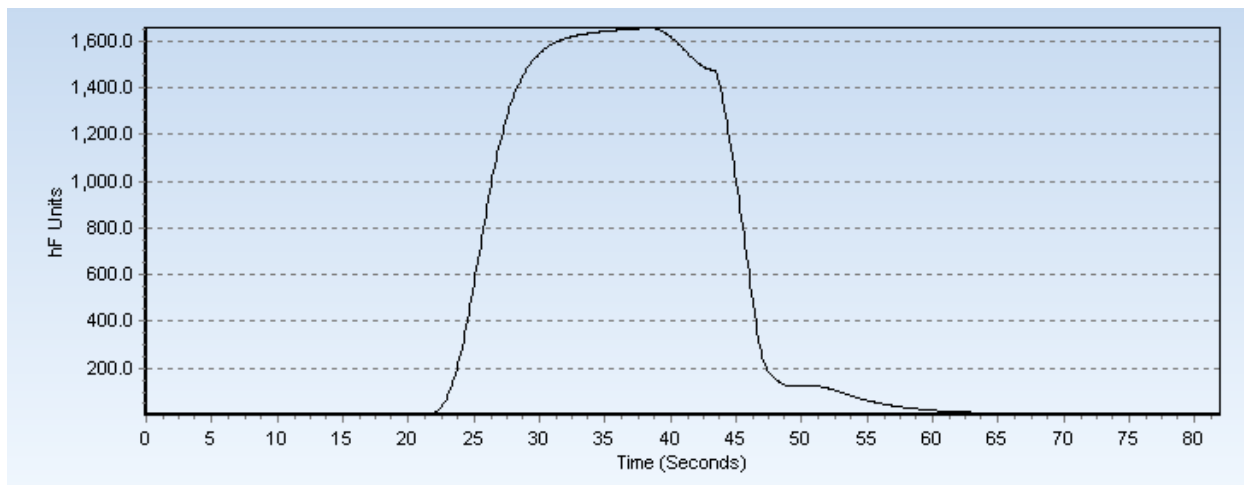


Figure 5: 10 µg/L Standard Peak Profile

RESULTS

MDL Study		Wastewater ISO 17852	
40 CFR Ch.1 (7-1-91) Part. 136, App B			
<u>Run 1 @ 0.0005 µg/L</u>		<u>Run 2 @ 0.0010 µg/L</u>	
	0.000618		0.001298
	0.000556		0.001112
	0.000618		0.001051
	0.000494		0.001298
	0.000556		0.001174
	0.000618		0.001112
	0.000433		0.001360
7.13575E-05 = Run 1 STDEV		1.17562E-04 = Run 2 STDEV	
5.09189E-09 = STDEV ²		1.38208E-08 = STDEV ²	
2.714 = F ratio			
1.89127E-08 Sum STDEV ² (Run 1 and 2)			
9.45637E-09 Sum STDEV ² / 2 ((Run 1 and 2) / 2)			
9.72439E-05 STDEV _{pooled}			
0.000261 = MDL			

Figure 6: Method Detection Limit Results and Calculations

After optimizing the method parameters, a Method Detection Limit (MDL) study was performed in accordance with CFR 40 Part 136 Appendix B before analyzing samples⁴. The study resulted in an MDL of 0.000261 µg/L using the parameters associated with this application. MDL results and calculations are shown in [Figure 6](#).

An initial calibration verification (ICV) was analyzed to validate calibration accuracy and method performance. The ICV was created using a 3.0 mL aliquot of 100 µg/L second source standard into a 100mL volumetric flask to give a concentration of 3.0 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 3.0 mL aliquot of 100 µg/L working standard into a 100mL volumetric flask to give a concentration of 3.0 µg/L. The CCB was a matrix matched blank using a 5mL aliquot of 3% hydrochloric acid.

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. A separate MDL study was performed in accordance with CFR 40 Part 136 Appendix B resulting in an MDL

of 0.000261 µg/L for the parameters associated with this application. Quality control check results are shown in [Figure 7](#). The mean concentration, standard deviation, and uncertainty at 95% are shown in [Figures 8](#) and [9](#).

ISO 17852 Quality Control	
Quality Control	% Recovery
ICV (3 µg/L)	104.3
CCV (3 µg/L)	99.9-103.7

Figure 7: Quality Control Results

ERM Wastewater, CA-713, 1.84 µg/L ± 0.11	
Digest	µg/L
1	1.90
2	1.92
3	1.91
4	1.93
5	1.94
6	1.95
7	1.96
Mean = 1.93	
Uncertainty = 0.02 @ 95 % Confidence	
n = 7 Replicates	STDEV = 0.022 RSD% = 1.119

Figure 8: Results

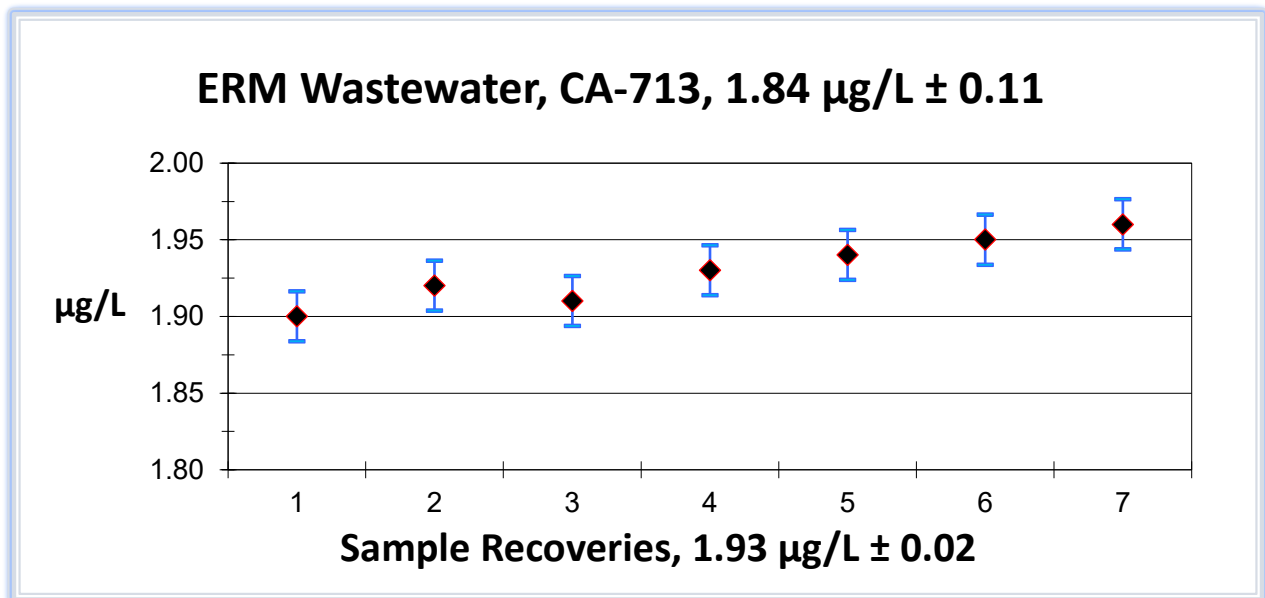


Figure 9: Graphed results with confidence interval

DISCUSSION

Monitoring for mercury contamination in wastewaters is necessary to keep the environment and people healthy. 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 1.93 ± 0.02 µg/L. This is an average recovery of 104.9%.

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/>

1. World Health Organization (WHO). Mercury and Health Fact Sheet. January 2016 [Online] <https://www.who.int/en/news-room/fact-sheets/detail/mercury-and-health> (accessed May 30, 2023).
2. U.S. Department of Health and Human Services Public Health Service Agency for Toxic Substances and Disease Registry (ASTDR CDC). ToxGuide™ for Mercury. April 2022 [Online] <https://www.atsdr.cdc.gov/toxguides/toxguide-46.pdf> (accessed May 30, 2023).
3. International Organization for Standardization (ISO). Water quality — Determination of mercury — Method using atomic fluorescence spectrometry. (ISO 17852:2006). [online] <https://www.iso.org/standard/38502.html> (accessed May 30, 2023)
4. Office of the Federal Register, National Archives and Records Administration. 40 CFR Appendix B to Part 136 - Definition and Procedure for the Determination of the Method Detection Limit- Revision 2. Office of the Federal Register, National Archives and Records Administration. July 1, 2016. [Online] <https://www.govinfo.gov/app/details/CFR-2016-title40-vol25/CFR-2016-title40-vol25-part136-appB> (accessed May 30, 2023)
5. Joint Research Centre, Institute for Reference Materials and Measurements, Oostru, A., Vos, E., Bacquart, T. et al. (2013) The certification of the mass concentration of arsenic, cadmium, chromium, copper, iron, manganese, mercury, lead, nickel and selenium in wastewater – ERM-CA713. Publications Office. <https://data.europa.eu/doi/10.2787/76888> (accessed May 30, 2023)