

A Comparative Study of Groundwater, ERM® - CA615, EPA Method 245.7 and ISO Method 17852, using the Teledyne Leeman Lab's QuickTrace® M-8000 CVAFS

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INTRODUCTION

Groundwater analysis is a crucial part of environmental monitoring. Groundwater is one of the most vital natural resources. It is an essential source of drinking water; therefore its safety is critical. However, it can present many obstacles for the analyst. It is a powerful tool used to gather information regarding the ecosystem. Contamination, interferences and sample preparation are a few of the major obstacles that can arise when monitoring mercury at this level. Mercury is prevalent through point source contamination that often comes from industry and bio-accumulation.

The Teledyne Leeman Labs QuickTrace® M-8000 Cold Vapor Atomic Fluorescence Spectrometry Mercury Analyzer was used for a comparison between EPA method 245.7, Mercury in Water by Cold Vapor Atomic Fluorescence Spectroscopy Revision 2.0 and ISO Method 17852, Water quality - Determination of mercury – Method using atomic fluorescence spectrometry (AFS).

The standard reference material used was ERM®-CA615, Groundwater. These two methods are very similar in that they both use potassium bromate/bromide solution for the digest but use either hydroxylamine hydrochloride, EPA 245.7 or L-Ascorbic acid, ISO 17852, to reduce the excess bromine.

The ISO 17852 method mentions that hydroxylamine hydrochloride can generate dissolved nitrogen and this could cause quenching on atomic fluorescence instruments. Therefore we standardized the digest and only varied the reagent used to reduce excess potassium bromate/bromide solution.

INSTRUMENTATION

The QuickTrace® M-8000 is an independent, stand-alone analyzer that uses Cold Vapor Atomic Fluorescence (CVAF) spectrometry to obtain reliable quantitative data from simple to complex matrices. The working range for the QuickTrace® M-8000 Mercury Analyzer is from < 0.05 ng/L to > 400 µg/L. These detection limits allow for extremely low-level quantitation of total mercury. Minimal detector drift provides stability for larger sample batch analysis, which requires longer analysis run time. The QuickTrace® M-8000 is equipped 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 sample/reagent reduction online, in a closed system. The reduced sample then flows into the non-foaming Gas Liquid Separator (GLS), and argon is purged through the sample as elemental mercury is liberated and enters into the system. The sample then passes into 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. Software instrument controls include but are not limited to argon flow, lamp, photomultiplier automatic voltage select, pump control, smart rinse threshold, and over range protection. Optimizing these parameters allows for increased or decreased sensitivity.



EXPERIMENTAL

The QuickTrace® M-8000 is operated by the QuickTrace® software and provides method specific control of the system. Parameter optimization allows for the quantitation of mercury in the trace ng/L range. The goal of this application is to standardize instrument parameters and then compare ISO Method 17852 vs. EPA Method 245.7 to quantitate mercury at the trace ng/L level using the Teledyne Leeman Labs QuickTrace® M-8000 Mercury Analyzer. Groundwater samples were digested from standard reference material ERM®-CA615, groundwater, which was purchased from the Institute for Reference Materials and Measurements. The certified reference material was collected from a locked well located in Bree, North-East Limburg, Belgium. The reference material was stored in a 100 mL flame sealed borosilicate glass ampoule. The outside of the bottle was rinsed with mercury-free, ultra-pure deionized water to remove any contaminants that may have adhered to the outer surface. The samples were digested and analyzed in 50 mL polypropylene co-polymer centrifuge tubes. Samples were preserved in the sample vials with hydrochloric acid and digested with 0.1N potassium bromide/potassium bromate solution, followed by reduction with either 10% L-ascorbic acid or 12% hydroxylamine hydrochloride. 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. Seven replicates were analyzed along with the appropriate quality control checks to validate the instrument. Total analysis time was approximately 40 minutes with each sample analysis lasting approximately 105 seconds. By optimizing conditions the total sample volume was ~ 6 mL of sample per analysis. A seven-point calibration curve was analyzed, which included five non-zero standards and two blanks.

Figure 1 Method Parameters

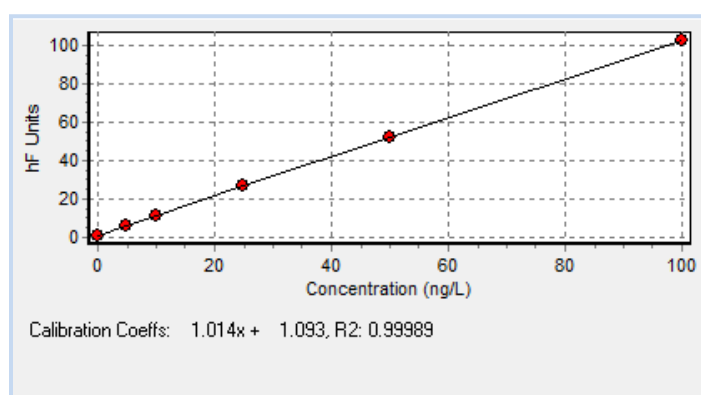
Conditions	
GLS Gas Flow	Low Flow
Pump speed (%)	100
Sipper depth (mm):	150
ASX Rinse Pump Speed (%):	60
Sample uptake time (s):	37
Rinse time (s):	68
Read delay time (s):	53
Replicate read time (s):	1
Replicates:	4
<input checked="" type="checkbox"/> Auto adjust replicate read time	
Profile Replicate %RSD:	0.00%
<input type="checkbox"/> Abort on Over Range	
Over Range Abort Threshold:	1000 hF

Initial calibration verification and initial calibration blank were analyzed to validate the accuracy of the calibration. Calibration standards and control standards were prepared in hydrochloric acid, potassium bromide/potassium bromate solution, ultra-pure deionized water, and hydroxylamine hydrochloride or L-ascorbic acid, depending on the method. Appropriate aliquots of 1000 ng/L working standard were used to prepare the calibration curve that consisted of two blanks, EPA 245.7, or one blank, ISO 17852, and five non-zero standards that ranged from 5 ng/L to 100 ng/L. Mercury is detected at wavelength 253.7 nm. ERM®-CA615 total mercury is certified at 0.037 µg/L with an uncertainty of ± 0.004 µg/L.

CALIBRATION STANDARDIZATION

Calibration standards were prepared with aliquots of a 1000 ng/L working standard that was prepared from serial dilutions of a 1000 mg/L certified standard. Standards were prepared using a final calculated volume of 25 mL. Aliquot volumes of 0.125 mL, 0.25 mL, 0.625 mL, 1.25 mL, and 2.50 mL of 1000 ng/L working standard were added to the ultra-pure deionized water with 2.5 mL 1:1 trace metal grade hydrochloric acid already added. Calibration standard concentrations were 5.0, 10.0, 25.0, 50.0, and 100.0 ng/L. The standards were then brought up to 25 mL volume. Then the calibration standards were matrix-matched by the addition of 0.5 mL of 0.1N potassium bromide/potassium bromate solution, and either 0.25 mL of 10% L-ascorbic acid or 0.05 ml 12% hydroxylamine hydrochloride, for a total volume of 25.75 mL or 25.55 mL. Calibration standards were analyzed beginning with two matrix blanks for EPA 245.7 and one blank for ISO 17852 and then proceeded from lowest concentration standard to highest concentration standard. Each peak was integrated for a total of four seconds. The concentration and the calibration factor or linear regression was calculated.

Figure 2 Calibration for ISO 17852 Method

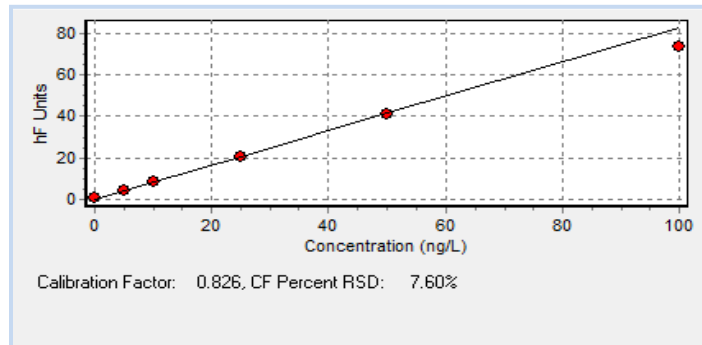


PROCEDURE

10 mL of ERM®-CA615 groundwater was pipetted directly into a 50 mL polypropylene centrifuge tube that contained 2.5 mL of deionized water and 2.5 mL of 1:1 trace metal grade hydrochloric acid to preserve the sample. The sample was diluted to 25 mL using deionized water. This was done due to the limited sample volume, 100 mL, for seven replicates and two matrix spikes. The samples read about 14.8 ng/L, 0.0148µ g/L, in solution the sample was then oxidized using 0.5 mL of 0.1N potassium bromide/potassium bromate solution. The vial was sealed and inverted to homogenize the sample and allowed to sit for approximately 30 minutes, ensuring that the solution remained yellow and that all organics were oxidized. The sample was then reduced by manually adding 0.25 mL of 10% L-ascorbic acid or 0.05 mL 12% hydroxylamine hydrochloride, sealed and inverted and allowed to sit for 5 minutes. The sample vials were placed on the autosampler tray and analyzed. Inorganic mercury was reduced to elemental mercury with online excess addition of 10% stannous chloride in 7% hydrochloric acid at 3.6 mL/min at 100% pump speed. Peak height of each sample was integrated for 4 seconds. Depending on the digest method requirements, initial calibration verification, initial calibration blank, ongoing precision and recovery, continuing calibration verification, lab fortified blank, lab reagent blank, matrix spike, and matrix spike duplicate were analyzed to validate the instrument stability and to identify any method inconsistencies. Initial calibration verification was prepared with a 0.625 mL aliquot of a second source 1000 ng/L working standard into a matrix-matched solution to give a concentration of 25 ng/L.

Each quality control was prepared in the same manner. Matrix spike and matrix spike duplicate were all prepared with 0.375 mL aliquots of 1000 ng/L working standard to give a concentration of 15 ng/L.

Figure 3 Calibration for EPA 245.7 Method



RESULTS

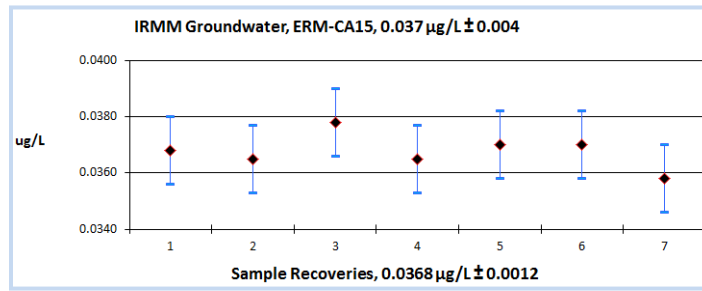
Using the QuickTrace® M-8000 for measurement of mercury at trace levels is an effective analytical technique used for obtaining reliable quantitative data. Optimizing carrier gas flow, pump speed, sample uptake and rinse time allows for analysis of a calibration, quality controls, and samples over a broad dynamic range. Minimal sample analysis time reduces laboratory costs, analyst time and effort along with minimizing instrument maintenance, while giving reliable quantitative data. Total mercury in groundwater at trace ng/L level was easily recovered by utilizing the various instrument settings of the QuickTrace® M-8000 Mercury Analyzer. Method development using QuickTrace® Software included calibration, quality controls, and spike recovery.

A separate MDL study was performed in accordance to CFR 40 Part 136 Appendix B for each of the digests. The ISO 17852 method resulted in an ultra-trace MDL of 0.084 ng/L with the above settings. As a result, total mercury can be determined and accurately quantitated. Seven replicates of the digested standard reference material were analyzed. The total mercury concentration was recorded, and the mean concentration and standard deviation were calculated. The results of 0.0368 µg/L ± 0.0012 are shown in figures [Figure 4](#) and [Figure 5](#).

Figure 4 ISO 17852 Results

IRMM Groundwater, ERM®-CA615, 0.037 µg/l ± 0.004		
Digest	µg/L	
1	0.0368	
2	0.0365	
3	0.0378	
4	0.0365	
5	0.0370	
6	0.0370	
7	0.0358	
	Mean = 0.0368	
	Uncertainty = 0.0012	
n = 7 Replicates	STDEV = 0.001	RSD% = 1.667

Figure 5 ISO 17852 Results with Uncertainties

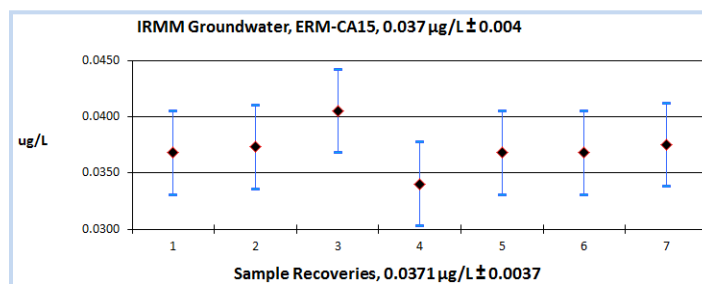


The MDL for EPA 245.7 in an ultra-trace mode was 0.146 ng/L using the stated settings. As a result, total mercury can be determined as accurately quantitated. Seven replicates of the digested standard reference material were analyzed. Total mercury concentration was recorded and mean concentration and standard deviation were calculated. The results of 0.0371 µg/L ± 0.0037 are shown in Figure 6 and Figure 7.

Figure 6 EPA 245.7 Results

IRMM Groundwater, ERM®-CA615, 0.037 µg/l ± 0.004	
Digest	µg/L
1	0.0368
2	0.0373
3	0.0405
4	0.0340
5	0.0368
6	0.0368
7	0.0375
Mean = 0.0371	
Uncertainty = 0.0037	
n = 7 Replicates	STDEV = 0.002 RSD% = 5.119

Figure 7 EPA 245.7 Results with Uncertainties



ERM®-CA615 has a certified concentration of 0.037 µg/L with an uncertainty of ±0.004 µg/L. The standard reference material value is the unweighted mean of accepted sets of data values, with each data value being the mean of a set of results obtained from a different laboratory and/or instrument. Uncertainty values for the standard reference material were calculated with a confidence level of 95%. The calculated results and uncertainty values correspond to a level of confidence at 95%. They were calculated for seven replicates of the standard reference material that were analyzed on the QuickTrace® M-8000 using four peak height replicate readings for each of the 7 samples.

Contamination at trace to ultra-trace levels can present many problems and can lead to inaccurate results. Thus, careful attention was given to minimize contamination in reagents, acids and deionized water. Through method development, parameter optimization and sample preparation, the QuickTrace® M-8000 Mercury Analyzer quantitates total mercury at the trace ng/L level giving reliable quantitative data.

Conclusions

There seems to be decreased response with the standards and samples in EPA method 245.7 when only allowing five minutes after addition of hydroxylamine hydrochloride. Figure 8 and Figure 9 show the response of the 100 ng/L standards for both calibrations. The ISO 17852 method 100 ng/L standard had a response of 100 hF units and the EPA 245.7 100 ng/L standard had a response of 66 hF units. This would seem to indicate that there is some quenching since the quality control and the reference material passed for both methods, but the responses were lower for the EPA 245.7 method. This could create problems in long runs as the later samples could possibly be biased high with the dissolved gases leaving solution and not demonstrating the quenching that is suspected.

Figure 8 Peak Profile of 100 ng/L Standard Using ISO 17852

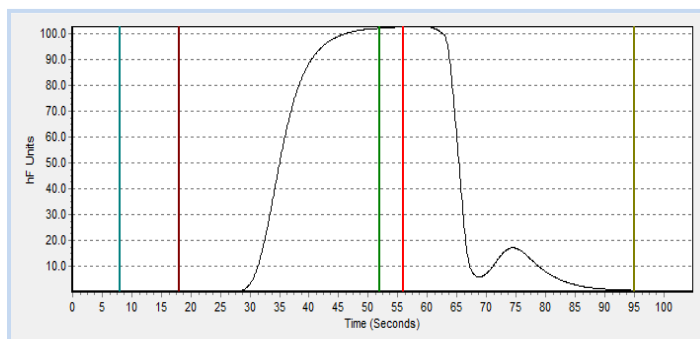
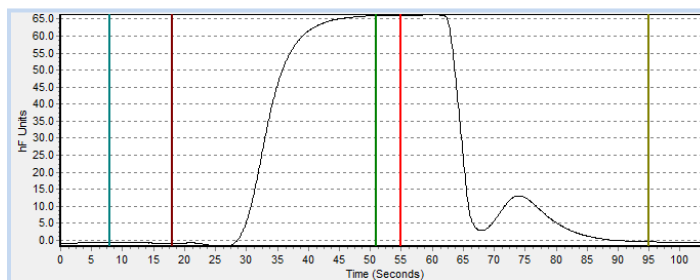


Figure 9 Peak Profile of 100 ng/L Standard Using EPA 245.7



This may also explain the higher MDL for EPA 245.7. 1631 MDL studies have been conducted on this instrument under similar conditions and MDL was 0.08 ng/L. The quality control also exhibited more variability in EPA method 245.7 as compared to ISO method 17852. The response values increased when the standards and samples were rerun after about an hour. More testing needs to be done to determine when the samples stabilize and dissolved nitrogen gas is no longer being released. This problem would not present itself in gold trap mode as the mercury is pre-concentrated on a gold trap and then desorbed under argon flow. The dissolved nitrogen gas would be passed over the gold trap and directly to waste during the loading step.

Figure 10 ISO 17852 Quality Control Chart

ISO 17852 Quality Control		
Quality Control (ng/L)	% recovery	RPD %
OPR (10)	NA	
CCV (25)	101-101	
ICV (25)	101.00	
LFB (10)	100.50	
MS (15)	103.30	
MSD (15)	99.30	3.94

Figure 11 EPA 245.7 Quality Control Chart

EPA 245.7 Quality Control		
Quality Control (ng/L)	% recovery	RPD%
OPR (10)	106-113	
CCV (25)	103-109	
ICV (25)	108.60	
LFB (10)	112.50	
MS (15)	96.70	
MSD (15)	100.00	3.38

REFERENCES

1. ISO. Method 17852, Water quality- Determination of mercury- Method using atomic fluorescence spectrometry
2. US EPA. Method 245.7, Mercury in Water by Cold Vapor Atomic Fluorescence Spectrometry
3. Teledyne Leeman Labs. Performance-Based EPA Method 1631 MDL Study in 90s Using Teledyne Leeman Lab's QuickTrace M-8000 CVAFS

