

Application Note

Mercury Determination in Groundwater, ERM®- CA615, EPA Method 245.7 using the CETAC QuickTrace™ M-8000 CVAFS

Jeff Forsberg, Product Manager, Brian Cook, Mercury Product Specialist, Sarah Price, Laboratory Assistant, CETAC Technologies, Omaha, NE

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 purpose of this application note is to validate the capabilities of the CETAC QuickTrace™ M-8000 Cold Vapor Atomic Fluorescence Analyzer in the trace ng/L range. This was carried out by quantitation of mercury in groundwater. The QuickTrace™ M-8000 Mercury Analyzer was validated by developing a performance-based method following US EPA Method 245.7, Revision 2.0: Mercury in Water Cold Vapor Atomic Fluorescence Spectrometry. The standard reference material that was used was ERM®-CA615, groundwater.

INSTRUMENTATION

The QuickTrace™ M-8000 is an independent stand-alone analyzer that uses Cold Vapor Atomic Fluorescence (CVAF) spectrometry for obtaining 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 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 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.



Figure 1. CETAC QuickTrace™ M-8000 Cold Vapor Atomic Fluorescence Spectrometry Mercury Analyzer

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 optimize instrument parameters using EPA Method 245.7 to quantitate mercury at the trace ng/L level using the CETAC 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 12% (w/v) hydroxylamine hydrochloride and DI water. Reduction of the inorganic mercury to elemental mercury was carried out by excess online addition of 10% (w/v) stannous chloride and DI water, in 7% (v/v) hydrochloric acid and water, 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. Sample uptake was 37 seconds at 100% pump rate, utilizing approximately 6 mL of sample with 68 seconds of rinse time for a total sample analysis time of 105 seconds. The integration time was set to 4 seconds by integrating peak height for 4 replicates at 1.0 seconds per replicate. Total run analysis time was approximately 40 minutes. A seven-point calibration curve was analyzed, which included five non-zero standards and two blanks.

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 hydrox-

ylamine. Appropriate aliquots of 1000 ng/L working standard were used to prepare the calibration curve that consisted of two blanks 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.

Conditions	
GLS Gas Flow	Low Flow
Pump speed (%)	100
Sipper depth (mm):	155
ASX Rinse Pump Speed (%):	60
Sample uptake time (s):	37
Rinse time (s):	68
Read delay time (s):	52
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

Figure 2. Method Parameters

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 calibration standards were matrix-matched by the addition of 0.5 mL of 0.1N potassium bromide/potassium bromate solution and 0.05 mL of 12% (w/v) hydroxylamine hydrochloride and DI water on top of the 25 mL to give a final volume of 25.55 mL. Calibration

standards were analyzed beginning with two matrix blanks and then proceeded from lowest concentration standard to highest concentration standard. Each peak was integrated for a total of 4 seconds. The concentration and the calibration factor were calculated.

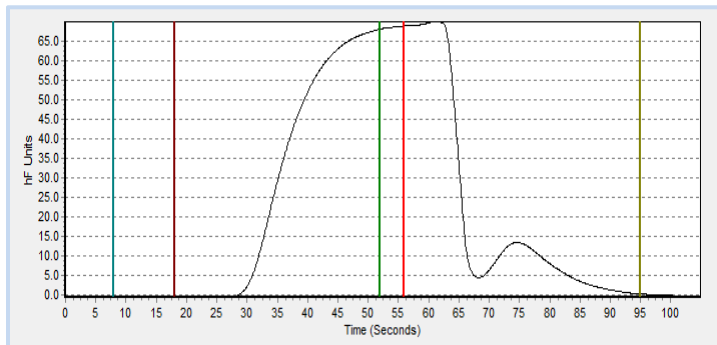


Figure 3. Peak Profile of 100 ng/L Standard

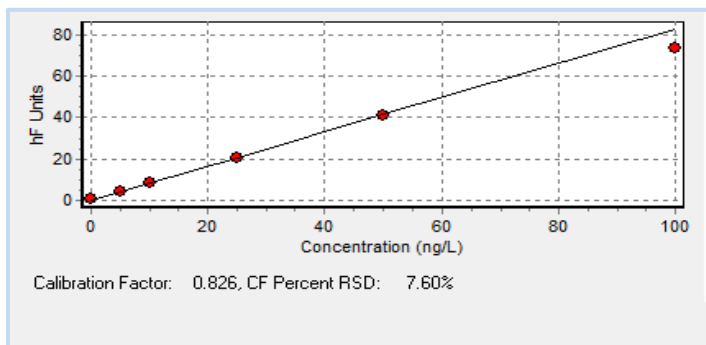


Figure 4. 245.7 Calibration

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 then diluted to 25 mL using deionized water. The samples were diluted due to limited volume, 100 mL, for seven replicates and two matrix spikes. 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 0.05 mL of 12% (w/v) hydroxylamine hydrochloride and DI water, sealed and inverted, and allowed to sit for five minutes. The sample vials were then placed on the autosampler

tray and analyzed. Inorganic mercury was reduced to elemental mercury with online excess addition of 10% (w/v) stannous chloride and DI water in 7% (v/v) hydrochloric acid and DI water at 3.6 mL/min at 100% pump speed. Peak height of each sample was integrated for 4 seconds. Initial calibration verification, initial calibration blank, initial precision and recovery, 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.

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 resulting in an ultra-trace MDL of 0.146 ng/L for the instrument settings associated with this application note. As a result, total mercury can be determined as accurately quantitated. Seven replicates of the digested standard reference material were analyzed and total mercury concentration was recorded and mean concentration and standard deviation were calculated. The results of $0.0371 \mu\text{g/L} \pm 0.0037$ are shown in figures 5 and 6.

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

tion 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.

REFERENCES

US EPA. Method 245.7, Mercury in Water by Cold Vapor Atomic Fluorescence Spectrometry

Figure 5. Results

ERM®-CA615 has a certified concentration of 0.0370 µg/L with an uncertainty of ±0.004 µg/L. The standard reference material value is the un-weighted 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%, and was 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.

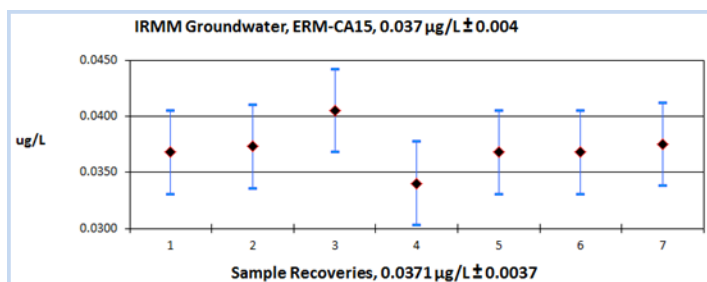


Figure 6. Results with Uncertainties

EPA 245.7 Quality Control		
Quality Control (ng/L)	% recovery	RPD%
OPR (10)	106-113	
CCV (25)	103-109	
ICV (25)	108	
LFB (10)	113	
MS (15)	97	
MSD (15)	100	3.38

Figure 7. EPA 245.7 Quality Control Chart.

Contamination at trace to ultra-trace levels can present many problems and can lead to inaccurate results. Therefore careful attention was given to minimize contamina-