

Ultra-Trace Mercury Determination in Bottled Water, EPA Method 1631, Using the CETAC QuickTrace™ M-8000 CVAFS

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INTRODUCTION

Mercury determination in water and foodstuffs is a crucial part of environmental monitoring. Toxicity of mercury and its compounds is well known. With the growing number of individuals drinking bottled water it is a concern not only that the water can be a source of contamination but that the process in which the products are produced may also be a source of contamination. Contamination may come from bottle production or the bottling process itself.

According to the International Bottled Water Association, bottled water was the second most popular beverage in the United States in 2008. That year Americans consumed more than 8.7 million gallons of bottled water averaging, an annual consumption of 28.5 gallons per person. In the United States, the only beverage that outsells bottled water is carbonated soft drinks.

The Food and Drug Administration (FDA) and the Environmental Protection Agency (EPA) of the United States are both responsible for the safety of drinking water. The EPA regulates public drinking water (tap water), while the FDA regulates bottled drinking water. The FDA samples and tests both the source water and the final product for contaminants. The FDA "Bottled Water Final Rule" (published in the Federal Register; 70 FR 33694 June 9, 2005) sets the allowable levels of total mercury at less than 0.002 mg/L. The allowable level is easily distinguished above background as today's instrumentation can easily detect levels 100 times lower than the current allowable level.

Ultra-trace mercury analysis can present many obstacles for the analyst. The major obstacles are contamination, interferences, and sample preparation. 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 for ultra-trace mercury analysis in single gold amalgamation mode. This was carried out by quantitation of mercury in bottled drinking water. The QuickTrace™ M-8000 Mercury Analyzer was validated by developing and passing all the quality control criteria for US EPA Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap and Cold Vapor Atomic Fluorescence Spectrometry.

Commercially-purchased bottled water from around the world was obtained, fortified, and analyzed using EPA method 1631. Sources of bottled water were collected from 11 countries from the global regions of Europe, South America, Australia, Africa, Asia, and the Middle East. Analyses were performed on the CETAC QuickTrace™ M-8000 Cold Vapor Atomic Fluorescence Mercury Analyzer in gold trap mode. Values for total mercury were low ppt to ultra-trace levels and concentration varied slightly among the sources which were natural mineral water, spring water, and purified water. Natural mineral water is considered to be microbiologically wholesome water which originates in an underground water table or deposit and emerges from a spring tapped at one or more natural or bore exits. Spring water is similar to mineral water, but needn't have a constant mineral composition and is usually cheaper. Purified water is taken from lakes, rivers, or underground springs and treated, all of which makes it almost identical to tap water.

INSTRUMENTATION

The working range for the QuickTrace™ M-8000 Mercury Analyzer is from < 0.05 ppt to > 400 ppb. These detection limits allow for extremely ultra-trace 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 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 sample/reagent reduction online in a closed system. The reduced sample then flows into the patented 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, photo multiplier automatic voltage select, pump control and smart rinse threshold. Optimizing these parameters allows for increased or decreased sensitivity.

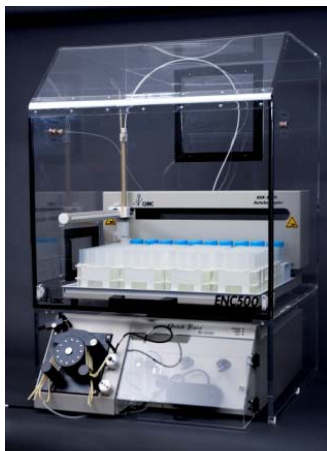


Figure 1. QuickTrace™ M-8000

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 ultra-trace detection range. The goal of this application is to optimize instrument parameters using EPA Method 1631 rev. E to quantitate mercury at the ultra-trace level.

The bottled drinking water 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, rinsed with ultrapure water in triplicate, soaked overnight in 0.5% bromine solution, and rinsed again in triplicate with ultrapure water. The cleaned sample vials were stored in polyethylene zipper storage bags until use. Prior to use of a lot of pre-cleaned tubes, each lot was tested at a 10% rate to validate the tube cleaning process

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% hydroxylamine. 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 3.8 mL/min at 100% pump speed. The bottled water samples were analyzed along with the appropriate quality control checks to validate the instrument. Total analysis time for each sample was approximately 7.5 minutes. An eight-point calibration curve was analyzed, which included five non-zero standards and three blanks.

Conditions	
Purge Gas Flow	Low Flow
Pump speed (%)	100
Sipper depth (mm):	145
Sample uptake time (s):	160
Rinse time (s):	290
Peak start time (s):	240
Peak width (s):	120
Peak Area	0.00

Figure 2. Method Parameters

<input checked="" type="checkbox"/> Gold Trap 1	Heater Start (s):	200
	Heater Stop (s):	380
<input checked="" type="checkbox"/> Gold Trap 2	Heater Start (s):	385
	Heater Stop (s):	445
<input checked="" type="checkbox"/> Cut Enabled	Cut Time	35
<input checked="" type="checkbox"/> Baseline drift correction		
Baseline Point #1		
Start read (s):	220	
End read (s):	230	
<input checked="" type="checkbox"/> Two-point baseline correction		
Baseline Point #2		
Start read (s):	364	
End read (s):	374	

Figure 3. Gold Trap Furnace Parameters

After a successful initial calibration (ICAL) and prior to the samples being analyzed, method detection limit (MDL) data was acquired in accordance to 40 CFR Ch.1 Part. 136, App B. 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, ultra-pure deionized water, and hydroxylamine. Appropriate aliquots of 200 ppt working standard were used to prepare the calibration curve that consisted of three blanks and five non-zero standards that ranged from 0.5 ppt to 100 ppt. Mercury is detected by a photo multiplier tube at wavelength 253.7 nm.

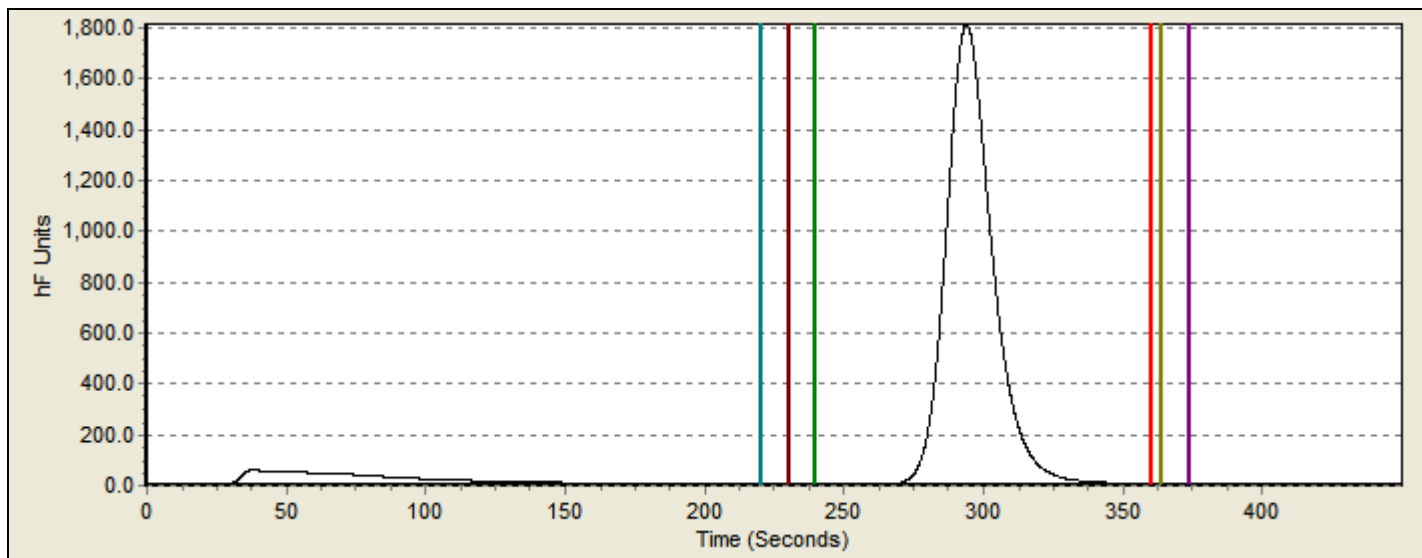


Figure 4. Peak Profile of 100 ppt Standard

Calibration standards were prepared using the correct aliquots of a 200 ppt working standard that was prepared from serial dilutions of a 1000 ppm Certified Standard. Standards were prepared using a final volume of 40 mL. Aliquot volumes of 0.1 mL, 1.0 mL, 5.0 mL, 10.0 mL, and 20.0 mL of 200 ng/L working standard were added to 15mL of ultra-pure purged deionized water. Calibration standard concentrations were 0.5, 5.0, 25.0, 50.0, and 100.0 ng/L. The calibration standards were matrix-matched to the digestion procedure by the addition of 1.2 mL of ultra-pure hydrochloric acid, 0.200 mL of 0.1N potassium bromide / potassium bromate solution, and 0.060 mL of 12% hydroxylamine. Calibration standards were analyzed beginning with three matrix blanks and then proceeded from lowest concentration standard to the highest concentration standard. Each calibration peak was integrated for a total of 120 seconds.

Analysis					
Tube	Sample Label	Conc ppt	hF Units	Flag	%RSD Abs
S:1	Calibration Blank	0.0	1293.8		0.0
S:2	Calibration Blank	0.0	1359.7		0.0
S:3	Calibration Blank	0.0	1162.0		0.0
S:4	Standard #1 (0.5 ppt)	0.5	2894.9		0.0
S:5	Standard #2 (5.0 ppt)	5.0	18798.7		0.0
S:6	Standard #3 (25.0 ppt)	25.0	88922.5		0.0
S:7	Standard #4 (50.0 ppt)	50.0	176521.5		0.0
S:8	Standard #5 (100.0 ppt)	100.0	349337.7		0.0

Figure 5. Calibration Standards with Response

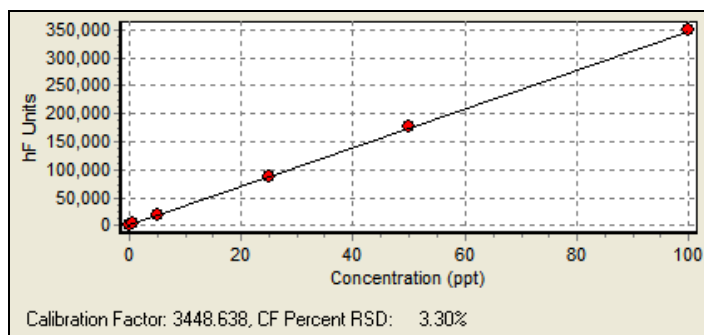


Figure 6. 1631 Calibration Graph

PROCEDURE

The bottled water samples were received and a sample log was created for each sample. After logging, the samples were individually cleaned, bagged, and stored in an argon purged enclosure.



Figure 7. Sample Storage

The Bottled Water bottles were cleaned by rinsing the outside of the bottle with 3% HCl followed by purged DI water, dried, labeled and logged, and stored in zipper storage bags until analysis. With the enclosure located in the clean zone for digestion and sample preparation access to the samples could be accomplished with minimal risk of contamination. The bottled water samples were digested in 40 mL aliquots by pouring directly into pre-cleaned digestion tubes. The sample digestion was accomplished by the addition of 1.2 mL of ultra-pure hydrochloric acid and 0.200 mL of 0.1N potassium bromide / potassium bromate. The vial was sealed and inverted to homogenize the sample and allowed to digest 12 hours at room temperature, ensuring that the solution remained yellow. Prior to analysis 0.060 mL of 12% hydroxylamine was added to reduce the excess potassium bromide / potassium bromate solution. The sample was then 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% stannous chloride in 7% hydrochloric acid at 3.8 mL/min at 100% pump speed. Initial calibration verification, ongoing precision recovery, method blanks, matrix spike, and matrix spike duplicates were analyzed to validate the instrument. The ICV was prepared with a 0.5 mL aliquot of the 200 ng/L second source standard into a matrix-matched solution to give a concentration of 5 ng/L. The OPR was prepared with a 0.5 mL aliquot of the 200 ng/L working standard into a matrix-matched solution to give a concentration of 5 ng/L. Each matrix spike and matrix spike duplicate was prepared by the addition of 0.1 ml of the 200 ng/L working standard into a 40 mL sample aliquot follow by digestion with 1.2 mL of ultra-pure hydrochloric acid and potassium bromide / potassium bromate solution.



Figure 8. Washing of Samples



Figure 9. Bagging Samples for Storage

RESULTS AND DISCUSSION

Low-level contamination can present many problems and can lead to inaccurate results. Therefore 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 ultra-trace level with minimal reagents and time while giving reliable quantitative data. The ICAL passed all data validation criteria easily: the calibration factor RSD was 3.3%, the 0.5 ppt standard was recovered at 0.47 ppt (94%), and the blank concentration was reported as 0.37 ppt with a standard deviation of 0.029 ppt. The method limits for percent recovery of the low standard must fall within 75 to 125 percent. The standard deviation for the blanks and blank concentration without correction must be less than 0.1 ppt and 0.5 ppt.

Analysis					
Tube	Sample Label	Conc ppt	hF Units	Flag	%RSD Abs
S:9	OPR	5.30	19549.9		0.0
1:1	MDL 1 - 1.0 ppt	1.04	4863.0		0.0
1:2	MDL 1 - 1.0 ppt	1.03	4817.6		0.0
1:3	MDL 1 - 1.0 ppt	1.02	4801.8		0.0
1:4	MDL 1 - 1.0 ppt	1.01	4765.7		0.0
1:5	MDL 1 - 1.0 ppt	1.01	4767.4		0.0
1:6	MDL 1 - 1.0 ppt	1.05	4899.2		0.0
1:7	MDL 1 - 1.0 ppt	1.05	4902.9		0.0
S:10	OPR	5.18	19139.1		0.0

Figure 10. Primary 1 ppt MDL Data

Analysis					
Tube	Sample Label	Conc ppt	hF Units	Flag	%RSD Abs
S:9	OPR	5.17	19091.1		0.0
1:1	MDL 2 - 0.25 ppt	0.26	2183.0		0.0
1:2	MDL 2 - 0.25 ppt	0.24	2104.9		0.0
1:3	MDL 2 - 0.25 ppt	0.22	2043.7		0.0
1:4	MDL 2 - 0.25 ppt	0.23	2076.0		0.0
1:5	MDL 2 - 0.25 ppt	0.26	2179.2		0.0
1:6	MDL 2 - 0.25 ppt	0.27	2207.4		0.0
1:7	MDL 2 - 0.25 ppt	0.28	2235.4		0.0
S:10	OPR	5.17	19096.1		0.0

Figure 11. Secondary 0.25 ppt MDL Data

Prior to analysis of samples an MDL and IPR study must be performed to validate the sensitivity and stability of the QuickTrace™ M-8000 Mercury Analyzer. The MDL study yielded an MDL of 0.053 ppt while the IPR study returned a value of 103.2%, which is in the acceptable range of 79–121%.

Analysis					
Tube	Sample Label	Conc ppt	hF Units	Flag	%RSD Abs
1:1	IPR	5.15	19040.9		0.0
1:2	IPR	5.15	19048.9		0.0
1:3	IPR	5.15	19022.8		0.0
1:4	IPR	5.18	19128.4		0.0

Figure 12. Initial Precision Recovery Data

All OPR samples returned a mercury concentration recovery between 98% and 106%. The method blanks ranged from 0.15 to 0.48 ppt while the ICV samples returned recovery values of 100–108%. The spike and spike duplicates ranged from a low of 94% recovery to a high of 103% recovery.

Country	Brand	Log ID	[Hg]	Log ID	[Hg]	Log ID	[Hg]	Average [Hg]
United Kingdom	Strathmore	US1	0.1	US2	0.4	US3	0.2	0.23
Canada	Custom Water LTD.	CC1	0.2	CC2	0.4	CC3	0.1	0.23
Germany	Vittel	GV1	0.1	GV2	0.4	GV3	0.1	0.20
France	Evian	FE1	0.1	FE2	0.4	FE3	0.2	0.23
China	Nongfu Spring	CN1	0.2	CN2	0.5	CN3	0.2	0.30
Brazil	Minalba	BM1	0.2	BM2	0.4	BM3	0.2	0.27
South Africa	Valpre Spring Water	SV1	0.2	SV2	0.4	SV3	0.1	0.23
India	Bisleri	IB1	0.2	IB2	0.5	IB3	0.3	0.33
US	Deer Park	UD1	0.3	UD2	0.5	UD3	0.3	0.37
Australia	Coles Natural Spring Water	AC1	1.6	AC2	2	AC3	1.7	1.77
Israel	Eden Mineral Water	IE1	0.4	IE2	0.5	IE3	0.4	0.43

Figure 13. Average Mercury Concentration In Bottled Water Samples

Mercury levels in each of the bottled water samples do not pose a significant threat to human health. Each sample with the exception of the Australian sample returned values at or below the method blank value and would be considered to have essentially zero mercury content. The bottled water from Australia showed the highest concentration with average mercury content of 1.77 ppt. The Australian sample was the only natural source that was tested; all other samples were either filtered spring water or water from a treated source.

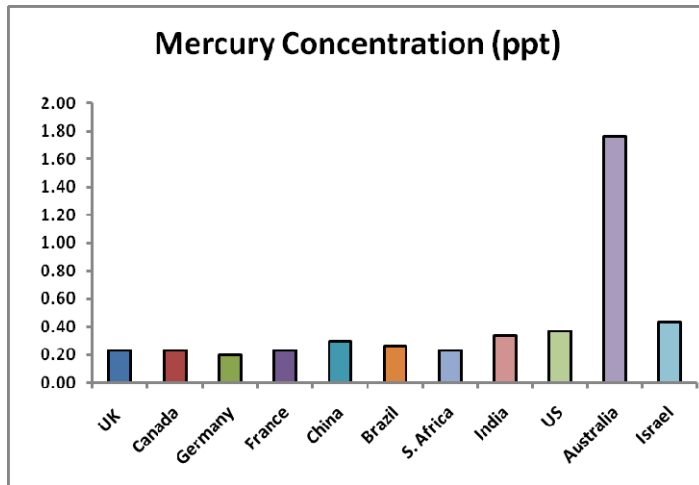


Figure 14. Average Concentration In Graphical View By Country Of Origin

The Cetac QuickTrace™ M-8000 CVAFS mercury analyzer is suitable for ultra-trace analysis although detailed care must be taken and stringent clean practices followed for ultra-trace levels of detection. Using the QuickTrace™ M-8000 analyzer for measurement of ultra-trace mercury 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. Method development using QuickTrace™ software included calibration, quality controls, and spike recovery. As a result, total mercury was accurately quantitated in bottled water at the ultra-trace level utilizing the various instrument settings of the QuickTrace™ M-8000 Mercury Analyzer.

REFERENCES

- Bottled Water. Code of Federal Regulations, Part 21, Title 165, Section 110, 2006. (Published in the Federal Register; 70 FR 33694 June 9, 2005, Volume 70, Number 110.)*
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