

# Mercury Determination in Bottled Water from World Sources

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**Measuring mercury in water and food is a crucial part of environmental monitoring. With a growing number of people relying solely on bottled water as their source of drinking water there is a concern that bottled water could be a source of mercury contamination. There is also a concern that the production process may be a source of contamination rather than the supplied water. In the production process contamination may come from bottle production or the process of filling and packaging the bottles. Mercury as a contaminant in water does not make water cloudy, give it a noticeable odour or change the taste but it may still be present.**



The United States Food and Drug Administration (FDA) and Environmental Protection Agency (EPA) are both responsible for the safety of drinking water in the United States. 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 US Federal Register; 70 FR 33694 June 9, 2005) sets the allowable levels of total mercury at less than 0.002mg/L. The allowable level is easily distinguished above background because today's instrumentation can easily detect levels 1000 times lower than the current allowable level.

Trace to ultra-trace mercury analysis can present many obstacles for the analyst. The major obstacles are background contamination, interferences, and ultra-trace sample preparation. Mercury is prevalent through point source contamination that often comes from industry and bio-accumulation. Commercially-purchased bottled water from around the world was obtained, fortified, and analysed using US EPA method 1631.

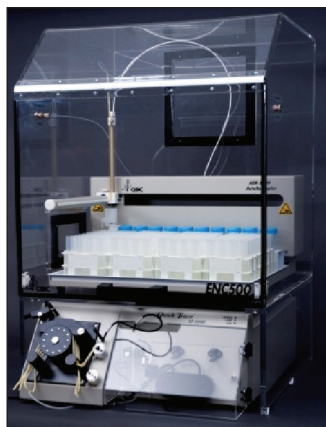


Figure 1: CETAC QuickTrace™ M-8000 Mercury Analyser

Sources of bottled water were collected from 11 countries from the global regions of Europe, South America, Australia, Africa, Asia, and the Middle East. Water sources included natural mineral water, spring water, and purified water. Analyses were performed on the CETAC QuickTrace™ M-8000 Cold Vapor Atomic Fluorescence Mercury Analyser in gold trap mode.

## Instrumentation and Principle of Operation

The working range for the QuickTrace™ M-8000 Mercury Analyser (see Figure 1) is from < 0.05ng/L (ppt) to > 400µg/L (ppb). The QuickTrace™ M-8000 is a stand-alone analyser that uses Cold Vapor Atomic Fluorescence (CVAF)

spectrometry for obtaining reliable quantitative data. The QuickTrace™ M-8000 is accompanied with an autosampler which enables unattended sample batch analysis. The QuickTrace™ M-8000 has a four-channel peristaltic pump that ensures consistent sample uptake into the analyser 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 gas is passed across a thin film of the sample as it flows down a frosted glass post within the GLS. Vapor-phase elemental mercury is liberated into the argon stream and enters into the analyser.

The elemental mercury may optionally be collected for a set time period on a gold amalgam trap composed of gold-coated glass beads. This has the effect of pre-concentrating the mercury, enhancing detection power. The gold trap is heated in an automated furnace, driving off the mercury which is carried by argon to the detector cell. The sample concentration measurement is carried out by a filtered photomultiplier tube in which the intensity of fluorescence from irradiation with a perpendicular mercury lamp is measured at a wavelength of 253.7nm.

Fluorescence intensity is recorded in real-time in the QuickTrace™ software. The measured intensity of fluorescence is proportional to the concentration of mercury in the sample. Software instrument controls include but are not limited to argon flow, lamp, photomultiplier automatic voltage select, pump control and smart rinse threshold. Adjusting these parameters enables increased or decreased sensitivity.

## Preparing for the Experiment

The bottled drinking water was digested in pre-cleaned 50mL polypropylene 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 (v/v; 0.1N potassium bromide / potassium bromate in DI water), and rinsed again in triplicate with ultrapure water.

The cleaned sample vials were stored in polyethylene zipper storage bags until use. Before each lot of pre-cleaned tubes was used, the lot was tested at a 10% rate to validate the tube cleaning process.

## Procedure



Figure 2: Washing of the sample bottles for contamination elimination

After logging, the samples were individually cleaned, bagged, and stored in an argon-purged enclosure. The bottles were cleaned by rinsing the outside of the bottle with 3% HCl followed by purged DI water (see Figure 2). Bottles were dried, labeled and logged, and stored in zipper storage bags until analysis.

The bottled water samples were digested in 40mL aliquots by pouring directly into pre-cleaned digestion tubes. The sample digestion was accomplished by the addition of 1.2mL of ultra-pure hydrochloric acid and 0.200mL of 0.1N potassium bromide / potassium bromate.

The vial was sealed and inverted to homogenise the sample and digested for 12 hours at room temperature, ensuring that the solution remained yellow. The oxidation process was followed by the addition of 0.060mL of 12% hydroxylamine hydrochloride solution to reduce the excess potassium bromide / potassium bromate which releases halogens, reducing the risk of gold trap destruction. The sample was then sealed and inverted, and allowed to sit for five minutes. Prior to concentration on the gold trap and subsequent measurement, the oxidised mercury in the calibration standards, quality control solutions, samples, spikes and duplicates was reduced to elemental mercury with online excess addition of 10% tin (II) chloride in 7% hydrochloric acid.

An eight-point calibration curve was prepared, which included five non-zero standards and three blanks. Calibration and control standards were prepared in the same manner as unknowns with an appropriate aliquot of a 200ng/L (ppt) working standard to prepare the calibration curve that ranged from 0.5ng/L to 100ng/L.

After a successful initial calibration (ICAL) and prior to the samples being analysed, method detection limit (MDL) data was acquired in accordance to 40 CFR Chapter 1 Part 136, Appendix B (see data from software screen shot in Figure 3). 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 analysed with each sample batch to validate the accuracy and stability of the ICAL.

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 3: Software screenshot showing results of MDL characterisation with 0.25ng/L solution

The ICV was prepared with a 0.5mL aliquot of the 200ng/L second source standard into a matrix-matched solution to give a concentration of 5ng/L. The OPR was prepared with a 0.5mL aliquot of the 200ng/L working standard into a matrix-matched solution to give a concentration of 5ng/L. Each matrix spike and matrix spike duplicate was prepared by the addition of 0.1 mL of the 200ng/L working standard into a 40mL sample aliquot followed by digestion with 1.2mL of ultrapure hydrochloric acid and potassium bromide / potassium bromate solution.

## Results and Discussion

Careful attention was given to minimise contamination in reagents, acids, and deionised water as contamination at ultra-trace analysis can present many problems and can lead to inaccurate results.

Through method development, parameter optimisation, and sample preparation, the QuickTrace™ M-8000 successfully quantified 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 0.5ng/L standard was recovered at 0.47ng/L (94%), and the blank concentration

was reported as 0.37ng/L with a standard deviation of 0.029ng/L. 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 0.1ng/L and 0.5ng/L.

Before analysing samples, a MDL and IPR study must be performed to validate the sensitivity and stability of the mercury analyser. The MDL study yielded an MDL of 0.053ng/L while the IPR study returned a value of 103.2%, which is in the acceptable range of 79–121%.

All OPR samples returned a mercury concentration recovery between 98% and 106%. The method blanks ranged from 0.15 to 0.48ng/L while the ICV samples returned recovery values of 100–108%. The spike and spike duplicates at levels of 0.5 and 1ng/L ranged from a low of 94% recovery to a high of 103% recovery.

Analysis					
Tube	Sample Label	Conc ppt	hF Units	Flag	%RSD Abs
1:8	IB2	0.47	2903.7		0.0
1:9	UD2	0.51	3037.5		0.0
1:10	AC2	2.03	8276.0		0.0

Figure 4: One of three Australian bottled water results showing elevated results above 1 ppt

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 1.77ng/L (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.

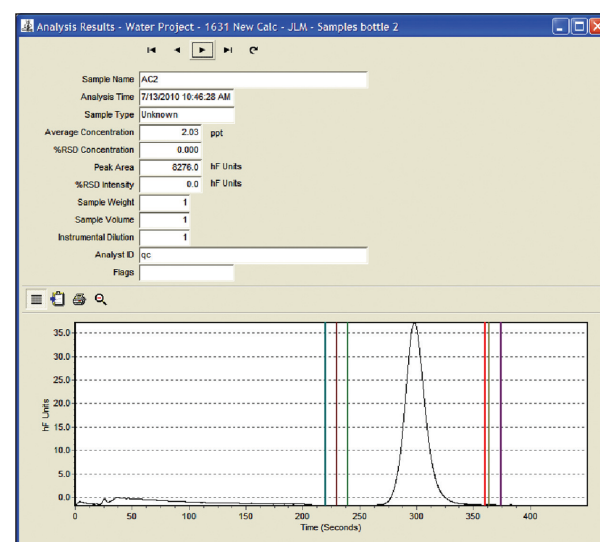


Figure 5: Graphical peak view of results from the Australian bottled water

## Conclusions

Mercury levels in each of the bottled water samples pose little or no significant threat to human health. The CETAC QuickTrace™ M-8000 mercury analyser offers phenomenal detection power, giving a method detection limit in this study of about 0.05ng/L (ppt). Accurate and precise results were obtained even at single figure ng/L levels, demonstrating the ability of the system to produce high quality quantitative data at ultra-trace levels.

Even though the Cetac QuickTrace™ M-8000 CVAFS mercury analyser exceeds the requirements for ultra-trace mercury analysis detailed care must be taken with stringent clean practices followed for accurate ultra-trace levels of detection. Optimising carrier gas flow, pump speed, sample uptake, and rinse time allows for analysis of a calibration, quality controls, and samples at ultra-trace levels or over a broad dynamic range. As a result, total mercury was accurately quantified in bottled water at the ultra-trace level utilising the various instrument settings of the QuickTrace™ M-8000 Mercury Analyser.

Researchers at CETAC Technologies have validated the QuickTrace™ M-8000 Mercury Analyser 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. What were the results for bottled water from your region of the world? For complete results of the study, go to [www.cetac.com](http://www.cetac.com) and download the free application note "Ultra-Trace Mercury Determination in Bottled Water, EPA Method 1631, Using the CETAC QuickTrace™ M-8000 CVAFS."

For more information on this application and on the CETAC QuickTrace™ M-8000 mercury analyser, visit [www.cetac.com/mercury\\_analyzers](http://www.cetac.com/mercury_analyzers)

## References

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