

Application Note

Performance-Based Ultra-Trace Mercury Determination in Coastal Seawater, BCR-579, EPA Method 245.7, using the CETAC QuickTrace™ M-7600 CVAAS

Jeff Forsberg, Product Manager, Brian Cook, Mercury Product Specialist, Teledyne CETAC Technologies, Omaha, NE

INTRODUCTION

Seawater analysis is a crucial part of environmental monitoring. 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-7600 Cold Vapor Atomic Absorbance Analyzer in the ultra-trace ng/L range. This was carried out by quantitation of mercury in coastal seawater. The QuickTrace™ M-7600 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 BCR-579, Coastal Seawater.

INSTRUMENTATION

The QuickTrace™ M-7600 is an independent stand-alone analyzer that uses Cold Vapor Atomic Absorbance (CVAAS) spectrometry for obtaining reliable quantitative data from simple to complex matrices. The working range for the QuickTrace™ M-7600 Mercury Analyzer is from < 0.5 ng/L to > 500 µg/L. This dynamic quantitative range allows mercury concentrations to be determined in broad range of sample substrates without dilution or pre-concentration. The QuickTrace™ M-7600 is accompanied with an autosampler that allows for hands-free sample batch analysis. The QuickTrace™ M-7600 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 mercury is then passed through the Perma Pure® drying cartridge and into the sample cell where it is measured at 253.7 nm. Software instrument controls include, but are not limited to, argon flow, lamp, pump control, smart rinse threshold, and over range protection. Optimizing these parameters allows for increased or decreased sensitivity.



Figure 1. CETAC QuickTrace™ M-7600 Cold Vapor Atomic Absorbance Spectrometry Mercury Analyzer

EXPERIMENTAL

The QuickTrace™ M-7600 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 ng/L range. The goal of this application is to optimize instrument parameters using EPA Method 245.7 rev. 2.0 to quantitate mercury at the ultra-trace ng/L level using the CETAC QuickTrace™ M-7600 Mercury Analyzer. Coastal seawater samples were digested from standard reference material BCR-579, coastal seawater, which was purchased from the Institute for Reference Materials and Measurements. The certified reference material was collected from the Royal Netherlands Navy's Chemical Laboratory in a nearby tidal channel (Marsdiep) at 10M depth. The reference material was stored in a 1L glass bottle and shaken for approximately one minute to re-homogenize the sample prior to sample preparation. The outside of the bottle was rinsed with mercury-free ultra-pure deionized water to remove any salt particles that may have adhered to the outer surface. The samples were digested and analyzed in 50 mL polypropylene co-polymer centrifuge tubes. Potassium bromate / potassium bromide solution was prepared by diluting purchased and precleaned 1N Br / 1N BrO₃ solution with 90 mL of double distilled HCl to make a 0.1N bromine monochloride (BrCl) solution. Samples were preserved in the sample vials with hydrochloric acid and digested with 0.1N BrCl 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 6.0 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 70 minutes, with each sample analysis lasting approximately 165 seconds. Since we were optimizing conditions for high sensitivity we used about 16 mL of sample per analysis. 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 using 1:1 hydrochloric acid (v/v), BrCl solution, ultra-pure deionized water, and hydroxylamine. 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. BCR-579 total mercury is certified at 1.9 ng/kg with an uncertainty of ± 0.5 ng/kg.

Conditions	
Gas Flow (ml/min)	40
Pump speed (%)	100
Sipper depth (mm):	145
ASX Rinse Pump Speed (%):	100
Sample uptake time (s):	65
Rinse time (s):	100
Read delay time (s):	70
Replicate read time (s):	2.5
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:	14000 μ Abs

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 volume of 50 mL. Aliquot volumes of 0.25 mL, 0.5 mL, 1.25 mL, 2.5 mL, and 5.0 mL of 1000 ng/L working standard were added to the ultra-pure deionized water with 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 addi-

tion of 0.5 mL of 0.1N BrCl solution and 0.05 mL of 12% hydroxylamine. Calibration standards were analyzed beginning with two matrix blanks and then proceeded from lowest concentration standard to the highest concentration standard. Each peak was integrated for a total of 10 seconds. The concentration and the calibration factor were calculated.

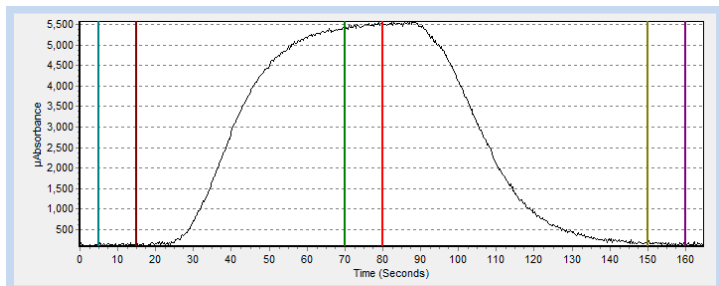


Figure 3. Peak Profile of 100 ng/L Standard

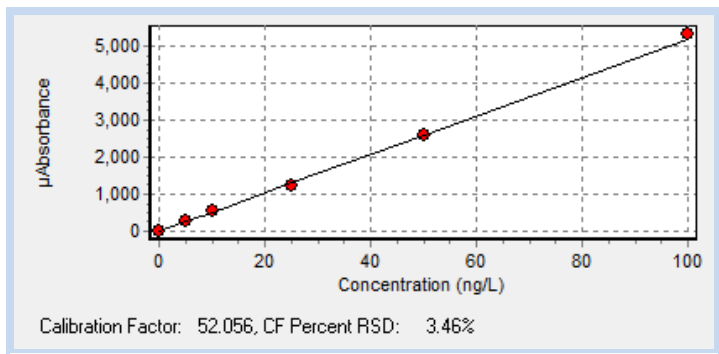


Figure 4. 245.7 Calibration

PROCEDURE

After thoroughly shaking the 1L sample bottle, 50 mL of BCR-579, coastal seawater was pipetted directly into a 50 mL polypropylene centrifuge tube that contained 5.0 mL of 1:1 trace metal grade hydrochloric acid to preserve the sample. The sample was then oxidized using 0.5 mL of 0.1N BrCl 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% hydroxylamine, sealed and inverted, and allowed to sit for five minutes. Since the coastal seawater had a final volume with HCl of 55 mL the values shown were dilution corrected. This could be avoided by adding an additional 5 mL of deionized water to the 50 mL standards and quality

control to ensure uniform final volume. 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 6.0 mL/min at 100% pump speed. Peak height of each sample was integrated for 10 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 0.5 mL aliquot of the 1000 ng/L working standard into a matrix-matched solution to give a concentration of 10 ng/L. Each quality control was prepared in the same manner. Initial precision and recovery had a range of recoveries from 104.8% to 107.3% with an RSD of 0.9%. The ongoing precision and recovery had recoveries from 105.6% to 106.9%. Matrix spike and matrix spike duplicate were all prepared with 0.5 mL aliquots of 1000 ng/L working standard to give a concentration of 10 ng/L. (Recoveries were MS = 106.8%; MSD = 101.3% with RPD at 5.3%).

RESULTS

Using the QuickTrace™ M-7600 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 coastal seawater at trace ng/L levels was easily recovered by utilizing the various instrument settings of the QuickTrace™ M-7600 Mercury Analyzer. Method development using QuickTrace™ software included calibration, quality controls, and spike recovery. A separate MDL study was performed in accordance to 40 CFR Part 136 Appendix B, resulting in an ultra-trace MDL of 0.25 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 $2.04 \text{ ng/kg} \pm 0.2$ are shown in Figures 5 and 6.

IRMM Coastal Seawater, BCR 579, $1.9 \text{ ng/Kg} \pm 0.5$

Digest	ng/Kg
1	2.08
2	1.97
3	1.92
4	2.21
5	1.95
6	1.96
7	2.18
Mean = 2.04	
Uncertainty = 0.232	
n = 7 Replicates	STDEV = 0.118 RSD% = 5.800

Figure 5. Results

BCR-579 has a certified concentration of 1.9 ng/kg with an uncertainty of $\pm 0.5 \text{ ng/kg}$. The standard reference material value is the un-weighted mean of six values, with each value being the mean of a set of results obtained from a different laboratory or method. 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-7600 using four peak height replicate readings for each of the 7 samples.

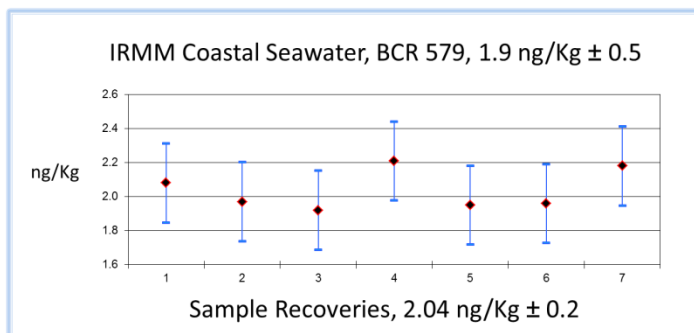


Figure 6. Results with Uncertainties

Contamination at trace to ultra-trace levels 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-7600 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