

Mercury Determination in Coastal Seawater, BCR-579, EPA Method 1631, using the CETAC QuickTrace™ M-8000 CVAFS

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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 the low levels present in seawater. Mercury is prevalent through point source contamination that often comes from industry and bio-accumulation.

The purpose of this study is to validate the capabilities of the CETAC QuickTrace™ M-8000 Cold Vapor Atomic Fluorescence Analyzer in the sub-ppt range in single amalgamation mode. This was carried out by quantitation of mercury in coastal seawater. The QuickTrace™ M-8000 Mercury Analyzer was validated by developing a performance-based method following US EPA Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap and Cold Vapor Atomic Fluorescence Spectrometry.

INSTRUMENTATION

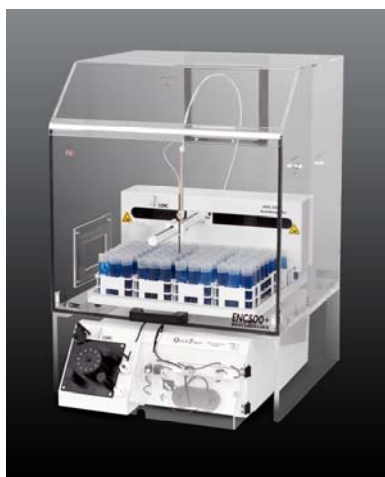


Figure 1. QuickTrace™ M-8000 Mercury Analyzer

is accompanied by 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 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 onto a gold trap where it forms an amalgam. The gold trap is then heated to release mercury from the amalgam. The sample then passes into a filtered photomultiplier fluorescence detector, and is measured at wavelength 253.7nm, 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.

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 sub-ppt range. The goal of this application is to optimize instrument parameters using EPA Method 1631 rev. E to quantitate mercury at the sub-ppt level using the CETAC QuickTrace™ M-8000 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 10 m depth. The reference material was stored in a 1 L 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 de-ionized water to remove any salt particles that may have adhered to the outer surface.

The digestion tubes were pre-cleaned using a detergent wash, a 20% nitric acid wash, and two ultra-pure de-ionized water rinses. 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 0.1 N 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.

Seven replicates were analyzed along with the appropriate quality control checks to validate the instrument. Total

analysis time was approximately 203 minutes, with each sample analysis lasting approximately 450 seconds. A nine-point calibration curve was analyzed, which included six 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): 110

Peak Area: 0.00

Gold Trap 1 Heater Start (s): 200
Heater Stop (s): 380

Gold Trap 2 Heater Start (s): 385
Heater Stop (s): 445

Cut Enabled Cut Time: 40

Baseline drift correction

Baseline Point #1

Start read (s): 220

End read (s): 230

Two-point baseline correction

Baseline Point #2

Start read (s): 360

End read (s): 370

Figure 2. Method Parameters

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. Appropriate aliquots of 200 ng/L working standard were used to prepare the calibration curve that consisted of three blanks and six non-zero standards that ranged from 0.5 ng/L to 20 ng/L. Mercury is detected by a photo multiplier tube at wavelength 253.7 nm. BCR-579 total mercury is certified at 1.9 ng/kg with an uncertainty of ± 0.5 ng/kg.

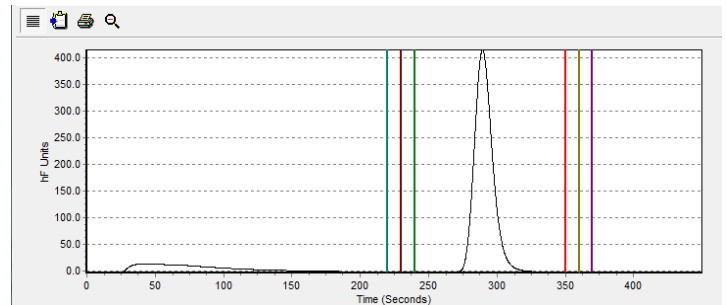


Figure 3. Peak Profile of 10 ppt Standard

CALIBRATION STANDARDIZATION

Calibration standards were prepared using the correct aliquots of a 200 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 40 mL. Aliquot volumes of 0.1 mL, 0.2 mL, 0.5 mL, 1.0 mL, 2.0, and 4.0 mL of 200 ng/L working standard were added to 40 mL of ultra-pure deionized water. Calibration standard concentrations were 0.5, 1.0, 2.5, 5.0, 10.0, and 20.0 ng/L. The calibration standards were matrix-matched by the addition of 0.20 mL of trace metal grade hydrochloric acid, 0.20 mL of 0.1 N potassium bromide/potassium bromate solution, and 0.050 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 peak was integrated for a total of 110 seconds. The concentration and the calibration factor were calculated.

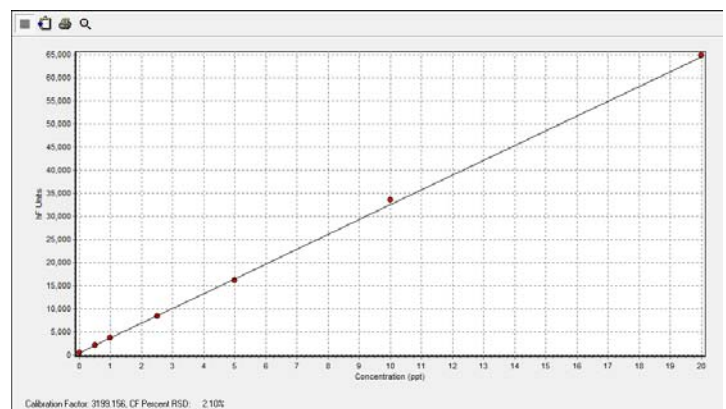


Figure 4. 1631 Calibration

PROCEDURE

After thoroughly shaking the 1 L sample bottle, 40 mL of BCR-579, coastal seawater was pipetted directly into a 50 mL polypropylene centrifuge tube that contained 0.2 mL of trace metal grade hydrochloric acid to preserve the sample. The sample was then oxidized using 0.20 mL of 0.1 N potassium bromide/potassium bromate solution. The vial was sealed and inverted to homogenize the sample and allowed to sit for approximately 12 hours, ensuring that the solution remained yellow and that all organics were oxidized. The sample was then reduced by manually adding 0.050 mL of 12% hydroxylamine, sealed and inverted, and allowed to sit for five minutes. The sample vials were then placed on the auto-sampler 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. Peak area of each sample was integrated for 110 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. Initial calibration verification 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 quality control was prepared in the same manor. Initial precision and recovery had a range of recoveries from 96.8% to 97.8% with an RSD of 0.5%. The ongoing precision and recovery had recoveries from 93.8% to 100.1%. Matrix spike and matrix spike duplicate were all prepared with 0.4 mL aliquots of 200 ng/L working standard to give a concentration of 2 ppt (recoveries were MS = 97%; MSD = 99%; with RPD at 0.92%).

RESULTS

Using the QuickTrace™ M-8000 for measurement of low-level 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. 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 the sub-ppt 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. As a result, total mercury was 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 $2.35 \text{ ng/kg} \pm 0.07$ are shown in figures 5 and 6.

Mercury In Coastal Seawater, BCR 579, $1.9 \text{ ng/kg} \pm 0.5$		
Digest	ng/kg	
1	2.34	
2	2.41	
3	2.35	
4	2.32	
5	2.31	
6	2.37	
7	2.37	
	Mean =	2.35
	Uncertainty =	0.067
	n = 7 Replicates	STD = 0.0340 RSD% = 1.446

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. The uncertainty value corresponds to a 95% level of confidence, and was calculated for seven replicates of the standard reference material that were analyzed on the QuickTrace™ M-8000.

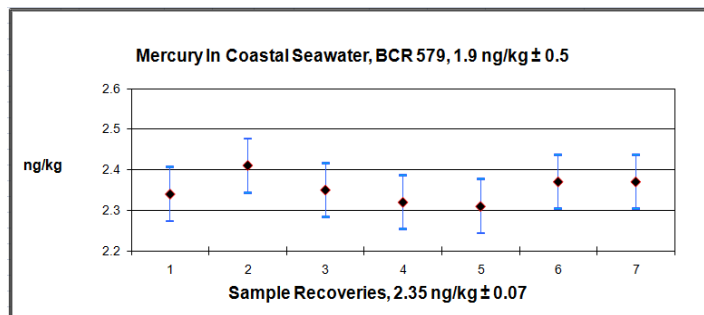


Figure 6. Results with Uncertainties

Contamination at the low level 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 sub-ppt level giving reliable quantitative data.

REFERENCES

US EPA. Method 1631, Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry