

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 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 sub-ppt range in non-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 US EPA Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap and Cold Vapor Atomic Fluorescence Spectrometry. The standard reference material that was used was BCR-579, Coastal Seawater, purchased from the Community Bureau of Reference.

INSTRUMENTATION

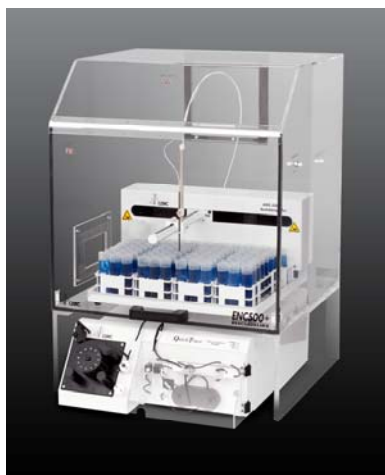


Figure 1. QuickTrace™ M-8000 Mercury Analyzer

The working range for the QuickTrace™ M-8000 Mercury Analyzer is from < 0.05 ppt to > 400 ppb. 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 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

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 253.7nm, 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 Community Bureau of Reference. 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 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 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, 30% nitric acid wash and three ultra-pure de-ionized water rinses. The samples were digested and analyzed in 50mL polypropylene co-polymer centrifuge tubes. Samples were preserved in the sample vials with 1:1 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. Seven replicates were analyzed along with the appropriate quality control checks to validate the instrument. Total analysis time was approximately 76 minutes, with each sample analysis lasting approximately 200 seconds. An eight-point calibration curve was analyzed, which included five non-zero standards and three blanks.

Conditions

GLS Gas Flow: Low Flow

Pump speed (%): 100

Sipper depth (mm): 145

Sample uptake time (s): 60

Rinse time (s): 140

Read delay time (s): 62

Replicate read time (s): 2

Replicates: 4

Auto adjust replicate read time

Profile Replicate %RSD: 0.00%

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 1:1 hydrochloric, 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 10 ppt. 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.

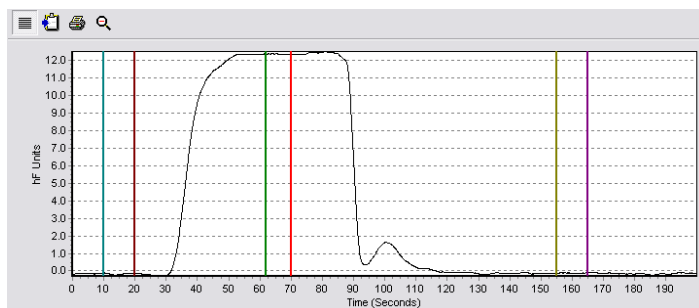


Figure 3. Peak Profile of 10 ppt Standard

CALIBRATION STANDARDIZATION

Calibration standards were prepared using the correct aliquots of a 200 ppt working standard that was prepared from serial dilutions of a 1000 ppm Certified Standard. Standards were prepared using a final volume of 20 mL. Aliquot volumes of 0.05 mL, 0.1 mL, 0.3 mL, 0.5 mL, and 1 mL of 200 ng/L working standard were added to 20 mL of 3% HCl. Calibration standard concentrations were 0.5, 1.0, 3.0, 5.0, and 10.0 ng/L. The calibration standards were matrix-matched by the addition of 0.25 mL of 1:1 trace metal grade hydrochloric acid, 0.25 mL of 0.1N potassium bromide/potassium bromate solution and 0.025 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 8 seconds. The mean concentration %RSD and the calibration factor were calculated.

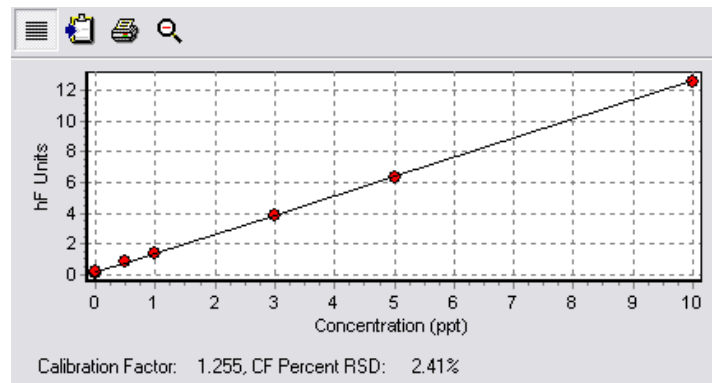


Figure 4. 1631 Calibration

PROCEDURE

After thoroughly shaking the 1L sample bottle, 20 mL of BCR-579, coastal seawater was poured directly into a 50 mL polypropylene centrifuge tube that contained 0.25 mL of 1:1 trace metal grade hydrochloric acid to preserve the sample. The sample was then oxidized using 0.25 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 0.025 mL of 12% hydroxylamine, 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. Peak height of each sample was integrated for two seconds with four replicates. The %RSD was then calculated based on standard deviation and mean concentration. Initial calibration verification, initial calibration blank, quality control spike, 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 manner. Quality control spike, matrix spike and matrix spike duplicate were all prepared with 0.2 mL aliquots of 200 ng/L working standard to give a concentration of 2 ppt. (QCS Recovery = 98%; MS = 104%; MSD = 95%).

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. Based on the concentration range, four replicates of each sample were integrated to give the mean concentration and standard deviation. The results of $1.7 \text{ ng/kg} \pm 0.2$ 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	1.77	
2	1.62	
3	1.62	
4	1.65	
5	1.81	
6	1.74	
7	1.76	
Mean =	1.71	
Uncertainty =	0.153	
n = 7 Replicates	STD = 0.0783	RSD% = 4.580

Figure 5. Results

BCR-579 is 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-8000.

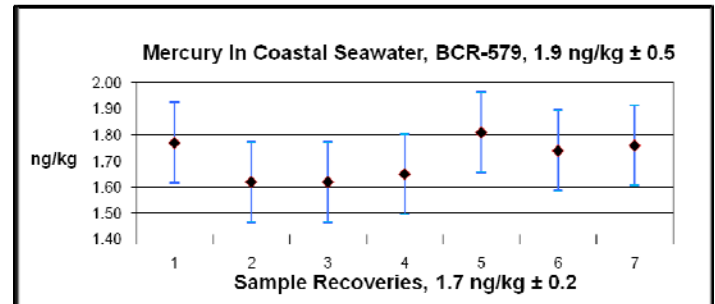


Figure 6. Results with Uncertainties

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. Short sample uptake time allows for greater batch analysis while minimizing costs for the analytical laboratory. Through method development, parameter optimization, and sample preparation, the QuickTrace™ M-8000 Mercury Analyzer quantitates total mercury at the sub-ppt level with minimal reagents and time while giving reliable quantitative data.

REFERENCES

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