

Mercury Determination in Soil, SRM 2710, EPA Method 245.5, using the CETAC QuickTrace™ M-8000 CVAFS

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INTRODUCTION

Mercury detection in soil plays a critical part in agriculture, human health, and overall environmental status. It allows for both long-term and short-term monitoring of each of these delicate systems, and gives information on specific sources of mercury contamination. Soil analysis gives quantitative data for crops, wildlife habitat, water quality, and air quality. Mercury concentration in soil is dependent on many variables including industry and human impact and mercury volatility conditions. The goal of this application note is to validate the QuickTrace™ Mercury Analyzer M-8000 Cold Vapor Atomic Fluorescence analyzer in the upper ppb range in non-gold trap mode. Total mercury in the standard reference material 2710, Montana Soil was quantitated using EPA method 245.5, Mercury in Sediment (Manual Cold Vapor Technique).

INSTRUMENTATION

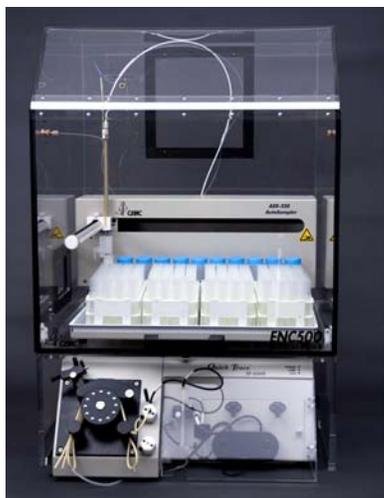


Figure 1. QuickTrace™ M-8000 Mercury Analyzer

Highly elevated trace element soil samples were digested from standard reference material 2710, Montana Soil, purchased from the National Institute of Standards and Technology, certified December 2007 through December 2011. The standard reference material was collected along Silver Bow Creek near Butte, Montana. Instrument method parameters were set for the ppb range with gas pressure set to 35 psi for non-gold trap analysis mode. Argon flow was set at high flow allowing approximately 220 mL/min of argon through the system. The standard reference material was stored in 50g sampling bottles. Prior to analysis the bottle was shaken for approximately five minutes to ensure sample homogeneity. The samples were digested and analyzed in 50 mL borosilicate digestion tubes. The tubes were pre-cleaned with a detergent wash, 30% nitric acid wash, and three ultra-pure deionized water rinses. Samples were digested and heated for two minutes with aqua regia then oxidized with potassium permanganate. The sample was then heated and digested for an additional thirty minutes. The potassium permanganate was then reduced by the addition of hydroxylamine. Liberated inorganic mercury was reduced to elemental mercury by excess online addition of 10% stannous chloride in 7% hydrochloric acid at a rate of 1.5 mL/min at 40% pump speed. Seven replicates of the standard reference material were analyzed along with appropriate quality control checks to validate the method. Total sample time was 1 hour 43 minutes with each sample analysis lasting 270 seconds.

The QuickTrace™ M-8000 is an independent stand-alone analyzer that uses cold vapor atomic fluorescence spectrometry for obtaining reliable quantitative data. The autosampler allows for hands-free sample batch analysis. The QuickTrace™ M-8000 is also accompanied with 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 where high purity 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, photon multiplier voltage select, pump control and smart rinse threshold. The QuickTrace™ Mercury Analyzer M-8000 is controlled using the QuickTrace™ software and allows for method development and parameter optimization. Optimizing these parameters allows for increased or decreased sensitivity depending on the working range of the sample batch. The instrument detection limit is < 0.05 ppt to > 400 ppb. Minimal instrument drift provides long-term stability for large sample batch analysis. Optimization of instrument parameters allows for quantitative analysis within this large range.

EXPERIMENTAL

Highly elevated trace element soil samples were digested from standard reference material 2710, Montana Soil, purchased from the National Institute of Standards and Technology, certified December 2007 through December 2011. The standard reference material was collected along Silver Bow Creek near Butte, Montana. Instrument method parameters were set for the ppb range with gas pressure set to 35 psi for non-gold trap analysis mode. Argon flow was set at high flow allowing approximately 220 mL/min of argon through the system. The standard reference material was stored in 50g sampling bottles. Prior to analysis the bottle was shaken for approximately five minutes to ensure sample homogeneity. The samples were digested and analyzed in 50 mL borosilicate digestion tubes. The tubes were pre-cleaned with a detergent wash, 30% nitric acid wash, and three ultra-pure deionized water rinses. Samples were digested and heated for two minutes with aqua regia then oxidized with potassium permanganate. The sample was then heated and digested for an additional thirty minutes. The potassium permanganate was then reduced by the addition of hydroxylamine. Liberated inorganic mercury was reduced to elemental mercury by excess online addition of 10% stannous chloride in 7% hydrochloric acid at a rate of 1.5 mL/min at 40% pump speed. Seven replicates of the standard reference material were analyzed along with appropriate quality control checks to validate the method. Total sample time was 1 hour 43 minutes with each sample analysis lasting 270 seconds.

Conditions	
GLS Gas Flow	High Flow
Pump speed (%)	40
Sipper depth (mm):	132
Sample uptake time (s):	20
Rinse time (s):	250
Peak start time (s):	128.75
Peak width (s):	102
Peak Area	0.00

Figure 2. Method Parameters

A calibration was analyzed and included seven non-zero standards and one blank. Initial calibration verification and initial calibration blank were analyzed immediately following the calibration and at the end of the sample batch to validate the calibration. Calibration standards were matrix-matched using the same reagents that were used in sample digestion and brought up to a final volume of 40 mL. Appropriate aliquots of 200 µg/L working standard were used to prepare a calibration curve that ranged from 1 to 150 µg/L. Standard reference material 2710, Montana Soil, was certified at 32.6 mg/kg, with an uncertainty of ±1.8 mg/kg.

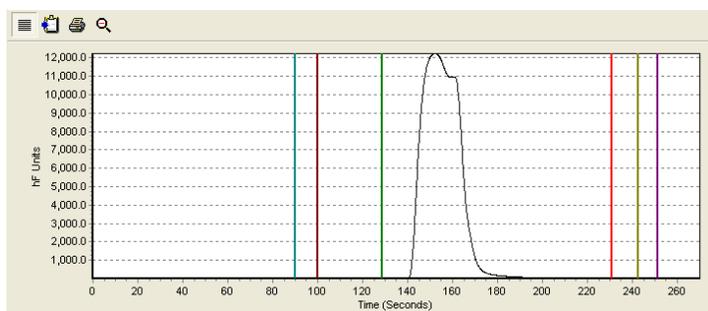


Figure 3. Standard Peak Integration

CALIBRATION STANDARDIZATION

Calibration standards were prepared using appropriate aliquots of 200 µg/L working mercury standard. The working standard was prepared from dilutions of a 1000 ppm mercury standard. Standards were prepared with a final volume of 40 mL. Aliquot volumes of 0.2 mL, 1 mL, 2 mL, 5 mL, 10 mL, 20 mL, and 30 mL of 200 µg/L working standard were added to 1.5 mL of ultra-pure mercury-free deionized water, 1.5 mL of freshly prepared aqua regia, 4.4 mL of 5% potassium permanganate, 1.7 mL of 12% hydroxylamine, and brought up to volume with the appropriate amount of deionized water for a

final volume of 40 mL. Calibration standard concentrations were 1, 5, 10, 25, 50, 100, and 150 µg/L respectively. The calibration was analyzed beginning with a calibration blank and then from lowest to highest concentrations. Peak area was integrated.

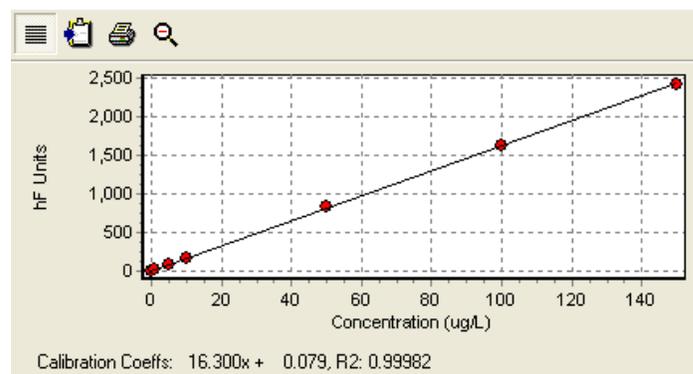


Figure 4. Calibration Curve

PROCEDURE

Standard reference material 2710, Montana Soil, was digested and analyzed to quantitate the total mercury using the QuickTrace™ Mercury Analyzer M-8000. The standard reference material was shaken for approximately five minutes to re-homogenize the sample. An excess amount was tapped into a 50 mL pre-cleaned polystyrene beaker to minimize contamination of the standard reference source. From this beaker, ~ 0.1g of sample was taken and measured into a tared 50 mL borosilicate digestion tube and 1.5 mL of ultra-pure mercury-free de-ionized water and 1.5 mL freshly prepared aqua regia were added. The sample was digested in a Fisher® Dry Block Incubator at 95 °C for two minutes. The sample was allowed to cool to ambient temperature and 14.5 mL of ultra-pure mercury-free deionized water and 4.4 mL of 5% potassium permanganate was added to the vial. The vessel was sealed and inverted and the sample was digested in a Fisher® Dry Block at 95 °C for thirty minutes. The sample was allowed to cool to ambient temperature. The potassium permanganate was reduced with the addition of 1.7 mL of 12% hydroxylamine. The sample was brought up to final volume of 40 mL with 16.4 mL of ultra-pure mercury-free deionized water. The expected concentration in solution is ~ 81 µg/L. The sample vials were placed directly onto the autosampler rack for analysis. Inorganic mercury was reduced to elemental mercury by the excess online addition of 10% stannous chloride in 7% hydrochloric acid at a rate of 1.5 mL/min at 40% pump speed. Due to the high concentration and small volume sampled, peak area was used to measure and quantitate each sample.

Initial calibration verification, initial calibration blank, quality control spike, matrix spike, and matrix spike duplicate were analyzed to validate the method. The initial calibration verification was prepared by adding 16 mL of the 200 µg/L working standard to 1.5 mL of ultra-pure mercury-free deionized water and 1.5 mL freshly prepared aqua regia, 4.4 mL of 5% potassium permanganate and 1.7 mL of 12% hydroxylamine were added to the vial. The initial calibration verification was brought up to a final volume of 40 mL with ultra-pure mercury-

free deionized water. The matrix spike and the matrix spike duplicate were spiked pre-digest with 10 mL of a 200 µg/L mercury standard into 1.5 mL ultra-pure deionized water and 1.5 mL aqua regia. The matrix includes 4.4 mL of 5% potassium permanganate and 1.7 mL of 12% hydroxylamine. The quality controls were brought up to a final volume of 40 mL with ultra-pure mercury-free deionized water. The quality control spike was spiked post-digest with 10 mL of a 200 µg/L working standard with the same matrix to give a concentration of 50 µg/L. This ensured that the calibration standards, samples, and quality controls were all matrix-matched.

RESULTS

Total mercury in soil in the ppb range was easily recovered and quantitated by optimizing instrumental settings in the QuickTrace™ software. Samples were analyzed with a linear calibration, quality controls, and spike recovery to validate the instrument. Seven replicates of the digested sample were analyzed and total mercury concentration was calculated from the peak area. The results of 32.3 mg/kg ± 2.5 are shown in figures 5 and 6. Measured concentration values were compared with the known concentration values of the standard reference material 2710, Montana Soil, which was certified at 32.6 mg/kg ± 1.8 mg/kg. The uncertainty value for the seven replicates was calculated from total mercury concentrations from the QuickTrace™ Mercury Analyzer M-8000 and was based on a 95% confidence level.

Total mercury analysis in soil samples is an important part of environmental, geological, and biological monitoring. The QuickTrace™ M-8000 requires minimal reagents, cost, and maintenance and allows the analyst to optimize instrument parameters for analysis in a broad working linear range while giving reliable, consistent quantitative data.

NIST Mercury In Soil, SRM 2710, 32.6 mg/kg ± 1.8		
Digest	mg/kg	
1	31.49	
2	30.96	
3	33.87	
4	33.88	
5	32.88	
6	31.16	
7	31.69	
Mean =	32.28	
Uncertainty =	2.455	
n = 7 Replicates	STD = 1.2528	RSD% = 3.882

Figure 5. Dilution Corrected Results

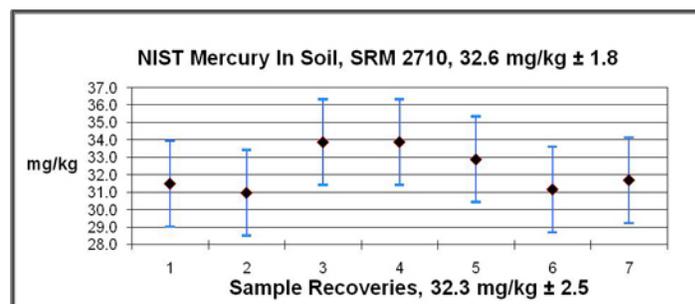


Figure 6. Dilution Corrected Results with Uncertainties

REFERENCES

EPA method 245.5, Mercury in Sediment (Manual Cold Vapor Technique).