

Mercury Determination in Soil, SRM 2710, EPA Method 245.5, using the CETAC QuickTrace™ M-6100 CVAFS

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INTRODUCTION

Total mercury measurement in soil plays a critical part in agriculture health, human health, and overall environmental status. Soil analysis gives quantitative data for crops, wildlife habitat, water quality, and air quality. Mercury concentration in soil is dependent on many variables including location, industry, human impact, and volatility conditions. The goal of this application is to validate the QuickTrace™ Mercury Analyzer M-6100 Cold Vapor Atomic Absorbance analyzer in the upper ppb range. This is carried out by quantifying the concentration of mercury in the standard reference material 2710, Montana Soil. The method used is EPA method 245.5, Mercury in Sediment (Cold Vapor Technique).

INSTRUMENTATION

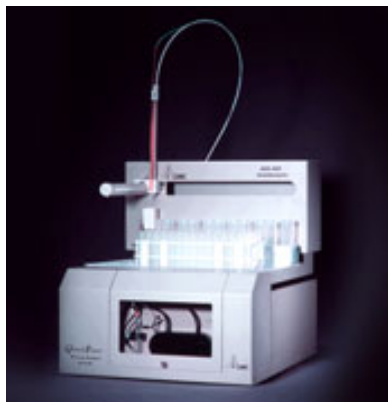


Figure 1. QuickTrace™ M-6100 Mercury Analyzer

The QuickTrace™ M-6100 is an independent stand-alone analyzer that uses cold vapor atomic absorption spectrometry for obtaining reliable quantitative data. The auto sampler allows for hands-free sample batch analysis. The QuickTrace™ M-6100 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 flows into the non-foaming gas-liquid separator where argon is purged through the sample as elemental mercury is liberated and enters into the system. The sample then passes into a filtered CCD 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 gas flow, lamp intensity, pump control and smart rinse

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EXPERIMENTAL

The QuickTrace™ Mercury Analyzer M-6100 is a stand-alone instrument and requires minimal analyst participation. The instrument detection limit is < 5 ppt to > 500 ppb. Minimal instrument drift provides long-term stability for large sample batch analysis. The QuickTrace™ Mercury Analyzer M-6100 is operated using the QuickTrace™ software that allows for method development and parameter optimization. The goal of this application note is to quantify mercury in the ppb range using EPA method 245.5, Mercury in Sediment. Highly elevated trace element soil samples are digested from standard reference material 2710, Montana Soil, purchased from the National Institute of Standards and Technology, certified December 2007 through December 2011.

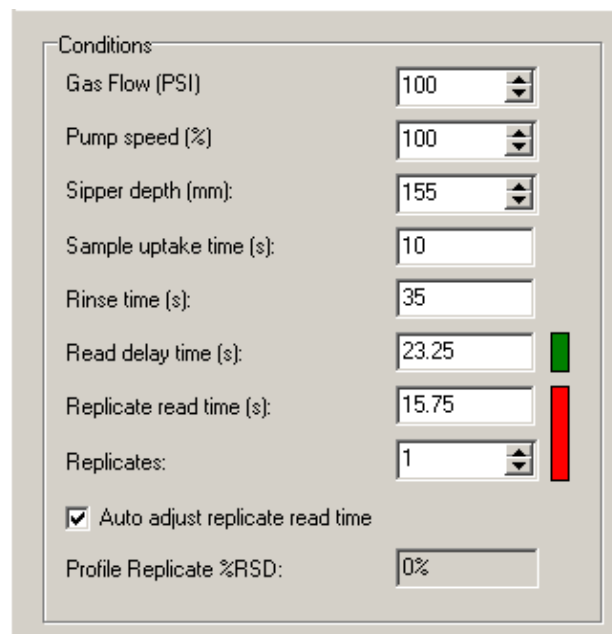


Figure 2. Method Parameters

The standard reference material was collected along Silver Bow Creek near Butte, Montana. Instrument method parameters are set for the ppb range. Gas pressure was set to 100 psi for this method. Argon flow is ~ 350 mL/min

through the system. The standard reference material is stored in 50g sampling bottles. Prior to analysis the bottle was shaken for approximately five minutes to ensure sample homogeneity. The samples are digested and analyzed in 50 mL borosilicate digestion tubes. The tubes are pre-cleaned with a detergent wash, 30% nitric acid wash, and three ultra-pure deionized water rinses. Samples are 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 is then reduced by the addition of hydroxylamine. Liberated inorganic mercury is reduced to elemental mercury by excess online addition of stannous chloride at a rate of 1.6 mL/min at 100% pump speed. Seven replicates of the standard reference material are analyzed along with appropriate quality control checks to validate the instrument. Total sample time is 45 minutes with each sample analysis lasting 45 seconds. A calibration is analyzed and included five 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 $\mu\text{g/L}$ working standard were used to prepare a calibration curve that ranged from 5 to 100 $\mu\text{g/L}$. Standard reference material 2710, Montana Soil, is certified at 32.6 mg/kg, with an uncertainty of ± 1.8 mg/kg. Method parameters for this application are optimized for high $\mu\text{g/L}$ concentrations.

CALIBRATION STANDARDIZATION

Calibration standards were prepared using appropriate aliquots of 200 $\mu\text{g/L}$ 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 1 mL, 2 mL, 5 mL, 10 mL and 20 mL of 200 $\mu\text{g/L}$ 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 5, 10, 25, 50, and 100 $\mu\text{g/L}$ respectively. The calibration was analyzed beginning with a calibration blank and then from lowest to highest concentrations. Peak area was integrated and the R^2 is calculated and recorded.

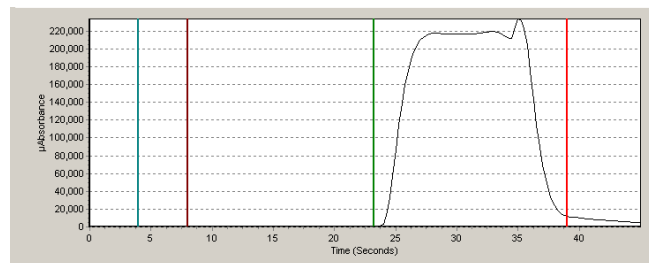


Figure 3. 100 $\mu\text{g/L}$ Peak Profile

PROCEDURE

Standard reference material 2710, Montana Soil, was digested and analyzed to quantitate the total mercury using the QuickTrace™ Mercury Analyzer M-6100. 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, $\sim 0.05\text{g}$ of sample was taken and measured into a tarred 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 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 ~ 41 $\mu\text{g/L}$. 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 1.6 mL/min at 100% pump speed. Due to the high concentration and small volume sampled, peak area was used to measure and quantitate each sample. This allows for short sample time due to the small volume of sample that is needed.

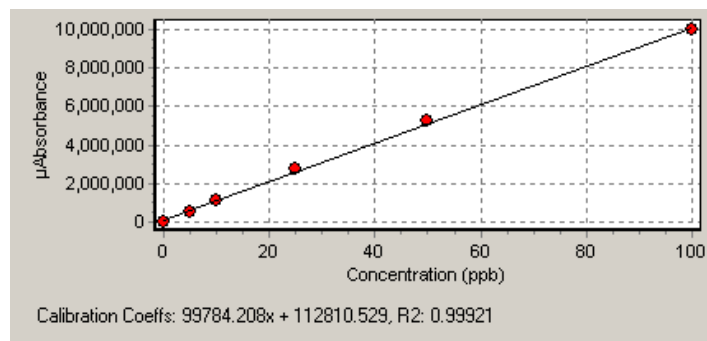


Figure 4. Calibration

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 2 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 for a concentration of 10 µg/L. 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 34.1 mg/kg ± 1.8 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-6100 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-6100 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	33.58	
2	34.69	
3	34.35	
4	33.39	
5	35.66	
6	34.26	
7	32.91	
Mean =	34.12	
Uncertainty =	1.800	
n = 7 Replicates	STD = 0.9181	RSD% = 2.691

Figure 5. Dilution Corrected Results

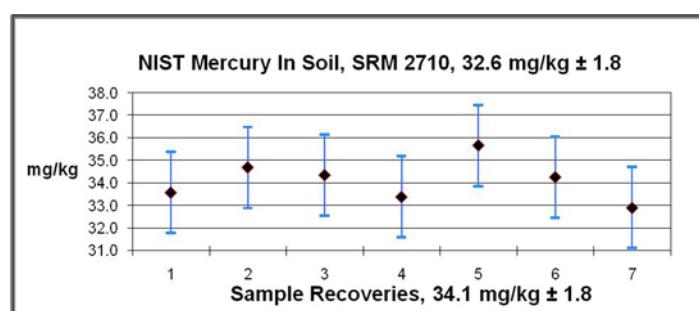


Figure 6. Dilution Corrected Results with Uncertainties

REFERENCES

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