

Mercury Determination in Water, SRM 1641c, EPA Method 245.1, using the CETAC QuickTrace™ M-6100 CVAAS

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INTRODUCTION

Total mercury determination in water allows quantitation for many different applications. The goal of this specific application is to validate the QuickTrace™ M-6100 Mercury Analyzer Absorption Spectrometer by analyzing SRM 1641c, Mercury in Water. The standard reference material was digested according to EPA Method 245.1, Determination of Mercury in Water by Cold Vapor Atomic Absorption Spectrometry, revision 3. Mercury contamination is prevalent in many different water sources. Quantifying mercury contamination in these sources is important for preservation and overall health of the environment. Detection is dependent on instrument stability and sensitivity.

INSTRUMENTATION

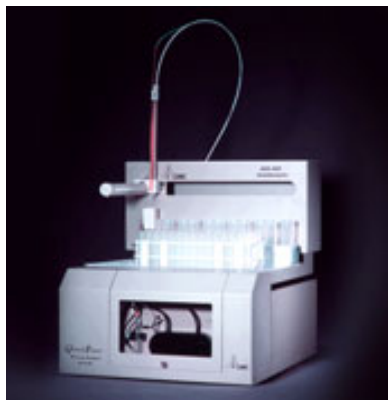
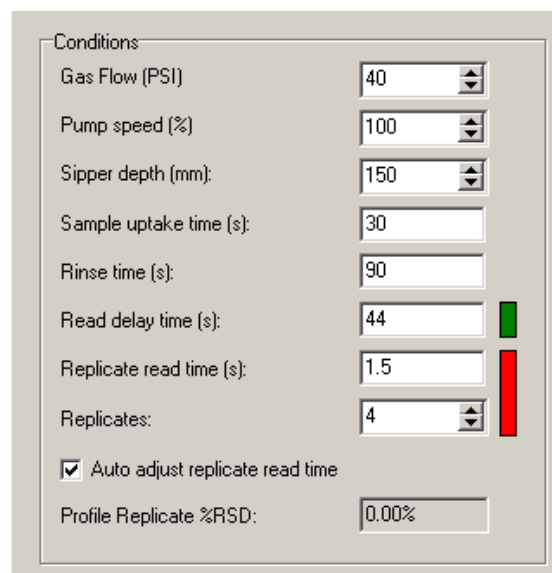


Figure 1. QuickTrace™ M-6100 Mercury Analyzer

The QuickTrace™ M-6100 Mercury Analyzer Absorbance Spectrometer is a standalone mercury analysis system. The instrument working range is from < 5 ppt to > 500 ppb and is dependent on instrument settings. The large working range of the system allows for analysis at the trace level up to very high concentrations. The QuickTrace™ M-6100 is accompanied with an autosampler that allows hands-free sample batch analysis. The four-channeled peristaltic pump ensures consistent sample/reagent uptake in a closed system. The sample, inorganic mercury, is reduced by the online addition of stannous chloride. The reduced sample then flows into the patented gas-liquid separator (GLS) where the elemental mercury is liberated from the liquid stream as mercury vapor, flows through the Nafion® dryer where excess moisture is removed and then into the analyzer. The sample is detected by the CCD detector, and quantitated in the QuickTrace™ software. Software instrument controls include but are not limited to gas flow, pump control and smart rinse threshold. Parameter optimization allows analysis with increased or decreased sensitivity.

EXPERIMENTAL

The standard reference material, SRM 1641c, Mercury in Water, is certified for 1.47 mg/L with an uncertainty of ± 0.04 mg/L, and was purchased from The National Institute of Science and Technology (NIST). The standard reference material was packaged in 10 mL ampoules. Proper dilution was prepared immediately prior to digestion to give a concentration within the working range of the QuickTrace™ M-6100. Dilution aliquots of the standard reference material were taken from a pre-cleaned polystyrene beaker to minimize contamination of the stock standard reference material ampoule. Dilutions were made into pre-cleaned 50 mL polypropylene tubes. The tubes were soaked overnight in 10% trace-metal grade nitric acid and rinsed three times with mercury-free deionized water rated at 18.2 M Ω . Samples were digested with 0.5N sulfuric acid, 50% nitric acid, 5% potassium permanganate, 5% potassium persulfate and 12% hydroxylamine hydrochloride. Inorganic mercury was reduced to elemental mercury by on-line addition of 10% stannous chloride in 7% hydrochloric acid. Instrument gas flow was set to 40 psi which yields ~ 140 mL/min carrier gas flow. Seven replicates of the standard reference material were analyzed along with the appropriate quality control checks to validate the instrument. A six point calibration was analyzed, and included five non-zero standards and one blank.



Conditions	
Gas Flow (PSI)	40
Pump speed (%)	100
Sipper depth (mm)	150
Sample uptake time (s)	30
Rinse time (s)	90
Read delay time (s)	44
Replicate read time (s)	1.5
Replicates	4
<input checked="" type="checkbox"/> Auto adjust replicate read time	
Profile Replicate %RSD:	0.00%

Figure 2. Method Parameters

CALIBRATION STANDARDIZATION

Calibration standards were prepared with appropriate aliquots of a 100 µg/L working mercury standard. This standard was prepared from correct serial dilutions of a 1000 mg/L certified mercury standard. Aliquots of 0.3 mL, 0.9 mL, 1.5 mL, 3.0 mL, and 7.5 mL were added to ~ 10 mL of 3% HCl and brought to a final volume of 30 mL with 3% HCl for concentrations of 1, 3, 5, 10 and 25 µg/L respectively. Calibration standards were prepared in pre-cleaned 50 mL polypropylene tubes that were soaked overnight with 10% trace metal grade nitric acid. The tubes were then rinsed three times with ultra-pure mercury-free deionized water rated at 18.2 MΩ. Each standard was matrix-matched with 1.5 mL of 0.5N sulfuric acid, 0.75 mL of 50% nitric acid, 4.5 mL of 5% potassium permanganate, 2.4 mL of 5% potassium persulfate and 1.8 mL of 12% hydroxylamine. One calibration blank and five non-zero standards were analyzed starting with the lowest concentration standard. Peak height was integrated for a total of 6 seconds and the correlation coefficient was calculated.

PROCEDURE

Correct dilutions were prepared from the standard reference material 1641c, Mercury in Water, to give a good working concentration for mid-range analysis. The SRM was shaken for ~ 5 minutes to ensure homogeneity. Excess volume of the standard reference material was directly poured into a pre-cleaned 50 mL polystyrene beaker to minimize contamination. Dilutions were made with 0.075 mL aliquots of the standard reference material, and added to 30 mL of 3% hydrochloric acid to give a dilution factor of 400 and a concentration in solution of ~ 3.7 µg/L. The standard reference material was digested with 1.5 mL of 0.5N sulfuric acid, 0.75 mL of 50% nitric acid, 4.5 mL of 5% potassium permanganate, 2.4 mL of 5% potassium persulfate and 1.8 mL of 12% hydroxylamine. Inorganic mercury was reduced to elemental mercury by the excess online addition of 10% stannous chloride in 7% hydrochloric acid, at a volume of 1.6 mL/min. Peak height for each sample was integrated for a total of 6 seconds. The %RSD was calculated based on standard deviation and mean concentration for each sample. 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 by adding a 1.5 mL aliquot of a 100 µg/L secondary mercury standard to ~ 10 mL of 3% HCl and brought to a final volume of 30 mL with 3% HCl. The ICV standard was matrix-matched with 1.5 mL of 0.5N sulfuric acid, 0.75 mL of 50% nitric acid, 4.5 mL of 5% potassium permanganate, 2.4 mL of 5% potassium persulfate and 1.8 mL of 12% hydroxylamine. The concentration was 5 µg/L. Quality control spike, matrix spike, and matrix spike duplicate were prepared in the same manor by adding 1.5 mL of the 100 µg/L mercury working standard for a concentration of 5 µg/L.

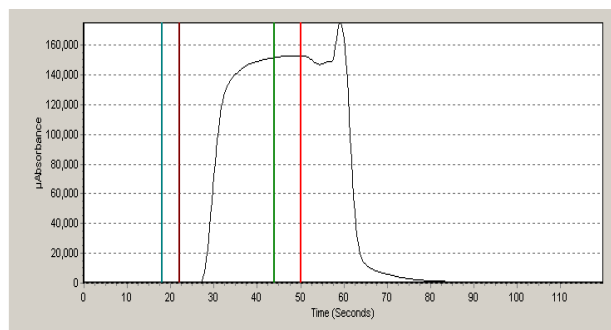


Figure 3. High Standard Peak Profile

RESULTS

Total mercury in SRM 1641c, Mercury in Water, was easily recovered and quantitated using the QuickTrace™ Mercury Analyzer Absorption Spectrometer. The results of 1.49 mg/L ± 0.042 are shown in figures 4 and 5. Optimizing pump speed, sample uptake, and argon flow allowed for mid-range total mercury determination. Calibration, quality controls, and spike recovery were all analyzed to validate the QuickTrace™ M6100. SRM 1641c, Mercury in Water, is certified at 1.47 mg/L with an uncertainty of ± 0.04 mg/L, and is based on a 95% confidence level.

NIST Mercury In Water 1641c, 1.47 mg/L ± 0.04	
Digest	mg/L
1	1.46
2	1.46
3	1.48
4	1.48
5	1.51
6	1.50
7	1.51
Mean = 1.49	
Uncertainty = 0.042	
n = 7 Replicates STD = 0.0215 RSD% = 1.447	

Figure 4. Dilution Corrected Results

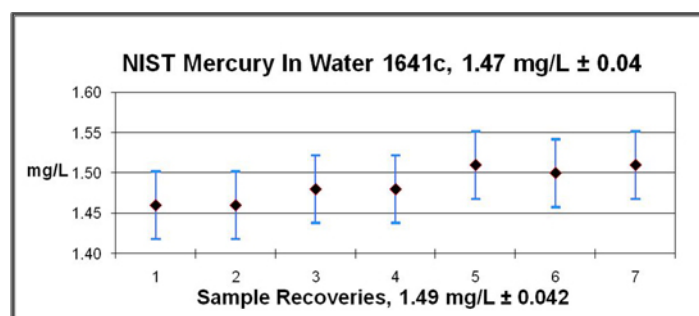


Figure 5. Dilution Corrected Results with Uncertainties

REFERENCES

US EPA Method 245.1, Determination of Mercury in Water by Cold Vapor Atomic Absorption Spectrometry, Revision 3.