

Green Chemistry: Determination of Mercury in Sediment (NIST SRM-2704) Following US EPA Method 7471B and Using the QuickTrace® M-7600 CVAA Mercury Analyzer

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INTRODUCTION

Mercury is a toxic chemical that can be released to the atmosphere, soil and water from a variety of anthropogenic sources.¹ Monitoring this toxin in sediment is required by many governments to ensure human and environmental health. On-going monitoring helps control mercury movement through ecosystems, as well as establish sources of contamination.

Green chemistry is a fast-growing discipline in the field of sustainability. One of the most important green chemistry principles is waste prevention, which includes the reduction of reagents required for analysis and the reduction of waste generation.^{2,3} Producing less hazardous waste and consuming fewer reagents benefits the environment and improves a laboratories' bottom line.

Many current methods approved to quantify mercury in environmental samples utilize wet chemistry preparations that require the use of hazardous chemicals. Stannous chloride, one of the reagents required for this analysis, is hazardous as well as expensive. By reducing the volume of stannous chloride required for analysis, laboratories can cut their hazardous waste generation and reduce overall operating expenses.

Following our study of the use of reduced internal diameter (ID) tubing when performing US EPA 7471B in application note [AN1905](#), this application note will again demonstrate the use of reduced ID tubing to deliver accurate results, while decreasing reagent/hazardous waste generation.⁴ This study will also develop a performance-based method and optimize the Teledyne Leeman Labs' QuickTrace® M-7600 mercury analyzer parameters for US EPA 7471B. The total elemental mercury (Hg⁰) in National Institute of Standards and Technology (NIST) standard reference material (SRM) 2704 "Buffalo River Sediment" will be determined.

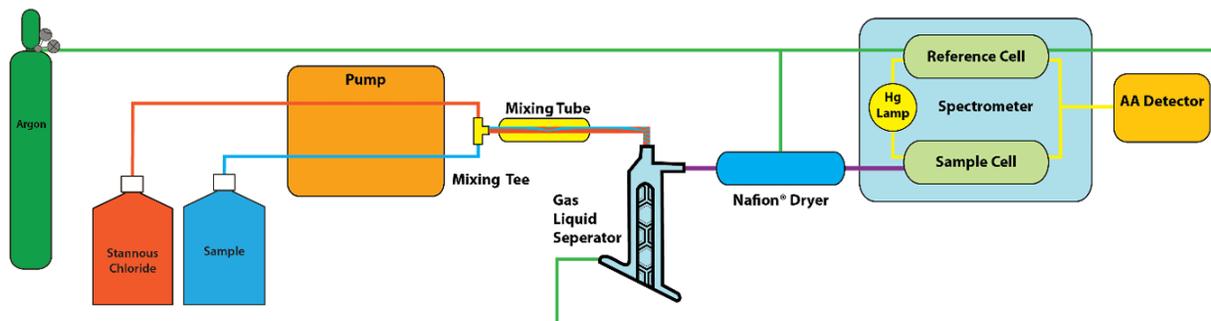
INSTRUMENTATION

Analysis was performed using the Teledyne Leeman Labs' QuickTrace® M-7600 cold vapor atomic absorption (CVAA) spectroscopy mercury analyzer and the Teledyne CETAC ASX-560 autosampler shown in [Figure 1](#). The QuickTrace® M-7600 is an independent stand-alone analyzer that uses CVAA spectrometry to obtain reliable quantitative data from simple to complex sample matrices. The working range for the QuickTrace® M-7600 mercury analyzer is from <0.7 ng/L to >700 µg/L when using the reduced ID peristaltic pump tubing. This dynamic quantitative range allows mercury concentrations to be determined in a broad range of sample substrates without dilution or preconcentration.

Figure 1 QuickTrace® M-7600 CVAA Mercury Analyzer and CETAC ASX-560 Autosampler



Figure 2 QuickTrace® M-7600 Process Diagram



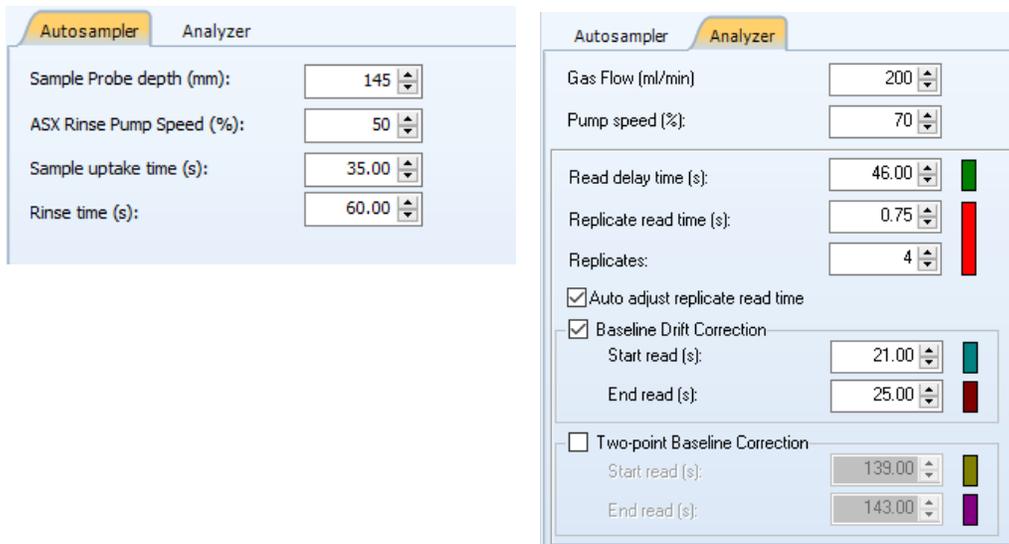
The QuickTrace® M-7600 has a four-channel, twelve-roller peristaltic pump that ensures consistent sample uptake to the analyzer and allows for online reduction of the sample in a closed system. The reduced sample then flows into the non-foaming gas-liquid separator (GLS), where the sample is purged with argon as elemental mercury (Hg^0) is released. The mercury then passes through the Nafion® drying cartridge and into the sample cell where it is measured at 253.7 nm. The QuickTrace® software includes, but is not limited to, the following controls: gas flow rate, lamp control, pump speed, autosampler control, smart rinse threshold and over-range protection. Parameter optimization allows for sensitivity adjustments and easy method development.

EXPERIMENTAL

Reduced ID tubing was installed on the analyzer's peristaltic pump. The sample and waste lines were white/white 1.02 mm tubing (TLL PN 15-4308-102). The stannous chloride reductant line was flared orange/yellow 0.51 mm tubing (TLL PN 15-4309-102). The QuickTrace® software provides method specific control of the system and autosampler. Adjusting the gas flow, analyzer pump speed and sample uptake times allows parameter optimization for the quantitation of mercury in a dynamic range. Method parameters are shown in [Table I](#) and [Figure 3](#).

Table I US EPA Method 7471B Using Reduced ID Tubing Method Specific Instrument Parameters		
Autosampler	Rinse Pump Speed (%)	50
	Sample Uptake (sec)	35
	Rinse Time (sec)	60
Analyzer	Gas Flow (mL/min)	200
	Pump Speed (%)	70
	Replicate Read Time (sec)	0.75
	Replicates	4

Figure 3 US EPA 7471B Autosampler and Analyzer Conditions Shown in the M-7600 QuickTrace® Software



The screenshot displays two panels of settings for the M-7600 QuickTrace software. The left panel is titled 'Autosampler' and the right panel is titled 'Analyzer'.

Autosampler Settings:

- Sample Probe depth (mm): 145
- ASX Rinse Pump Speed (%): 50
- Sample uptake time (s): 35.00
- Rinse time (s): 60.00

Analyzer Settings:

- Gas Flow (ml/min): 200
- Pump speed (%): 70
- Read delay time (s): 46.00
- Replicate read time (s): 0.75
- Replicates: 4
- Auto adjust replicate read time
- Baseline Drift Correction
 - Start read (s): 21.00
 - End read (s): 25.00
- Two-point Baseline Correction
 - Start read (s): 139.00
 - End read (s): 143.00

Sediment samples were digested from NIST SRM-2704. The SRM is freeze-dried river sediment from the Buffalo River in Buffalo, New York. To homogenize the sample, the jar was shaken for 1 minute prior to sampling. According to EPA 7471B, a sample size of 0.5 - 0.6 g is diluted with 100 mL of reagent water to have a final volume of ~136.5 mL. To further reduce the volume of reagents required for analysis, and to increase accuracy, the samples were prepared in 50 mL volumetric flasks. This required a 36.8% reduction to all weights and volumes listed in EPA 7471B. The sample weight was reduced to ~0.2 g and the final volume was 50 mL. Sample and standards were processed using 10 mL aliquots and 3.65 mL of total reagents was added to each digestion tube.

In EPA 7471B, sample and standards are taken through the same preparation and digestion procedure using 50 mL polypropylene copolymer digestion tubes:

- Preparation began with the following:
 - For samples: ~0.2g of sample was added to a digestion tube.
 - For standards: a 10 mL aliquot of each concentration was added to a digestion tube.
- Both samples and standards were then diluted with 1.84 mL reagent water and acidified with 1.84 mL aqua regia. All samples were digested at 95 °C for 2 minutes and allowed to cool.
- Next, the digestion tubes were further diluted with 18.4 mL reagent water and then oxidized with 5.52 mL of 5% potassium permanganate solution.
- All samples and standards were then digested a second time at 95 °C for 30 minutes and allowed to cool. After digestion, excess oxidants were neutralized with 2.2 mL of 12% (w/v) sodium chloride-hydroxylamine hydrochloride solution.
- After neutralization of excess oxidants:
 - Sediment samples were vacuum filtered, rinsed and quantitatively transferred to a 50 mL volumetric flask and brought to a final volume of 50 mL with reagent water. Samples were then transferred into new 50 mL tubes.
 - ~20.2 mL of reagent water was added to the standard tubes to make a final volume of 50 mL.
- Reduction of the inorganic mercury (Hg^{2+}) to elemental mercury (Hg^0) was carried out by excess online addition of 10% (w/v) stannous chloride in 7% (v/v) hydrochloric acid, at a rate of 1.9 mL/min at 70% pump speed.

Seven replicates of digested sediment samples were analyzed along with the appropriate quality control (QC) checks to validate the instrument and calibration. Sample uptake was 35 seconds at 70% pump speed with 60 seconds of rinse at 50% pump speed, amounting to a total sample analysis time of 95 seconds and using approximately 4.1 mL of sample. The integration mode was set to peak height, utilizing four replicates at 0.75 seconds each. The calibration algorithm was set to force through the blank point. An eight-point calibration curve was analyzed, which included one blank and seven non-zero standards. Total analysis time was approximately 36 minutes for 23 samples.

An initial calibration verification (ICV) and initial calibration blank (ICB) were analyzed to validate calibration accuracy and method performance. A continuing calibration verification/laboratory control sample (CCV/LCS) and continuing calibration blank (CCB) were analyzed to evaluate calibration drift and carryover. Mercury is detected at wavelength 253.7nm. NIST SRM 2704 total mercury is certified at 1.44 µg/g with an uncertainty of ±0.07 µg/g.

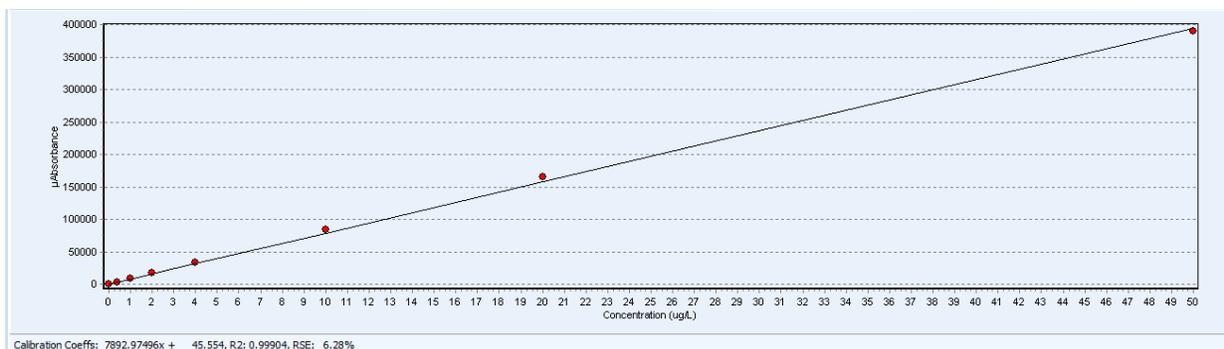
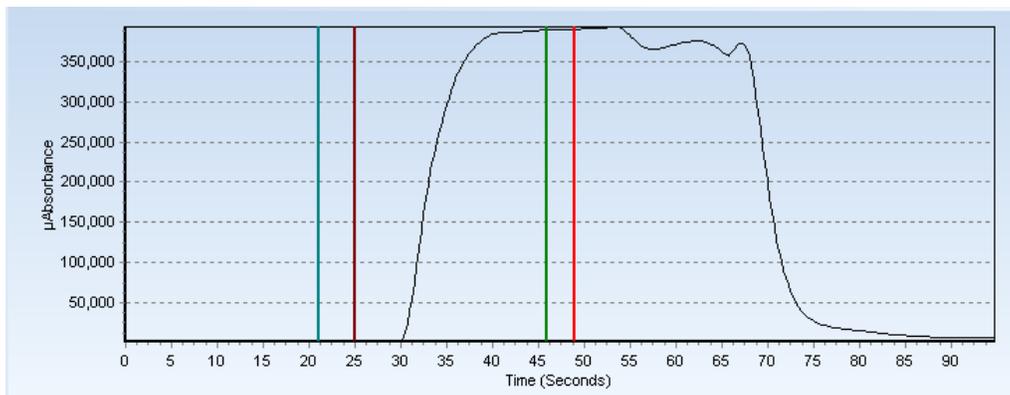
CALIBRATION STANDARDIZATION

The calibration curve consisted of one blank and seven non-zero standards. Calibration standards were prepared with aliquots of a 1000 µg/L mercury solution that was prepared from serial dilutions of a purchased 1000 mg/L mercury stock standard. Standards were created with a final volume of 100 mL. Calibration standards were prepared by aliquot volume additions of 0.2 mL, 0.5 mL, 1.0 mL, 2.0 mL, 5.0 mL, 10.0 mL and 25.0 mL of 1000 µg/L working standard added to 100 mL volumetric flasks containing 3% hydrochloric acid solution and brought to volume. Working standard serial dilutions are summarized in [Table II](#) and calibration standard preparations are summarized in [Table III](#).

A 10 mL aliquot of each calibration standard was added to 50 mL digestion tubes. With a dilution factor of 50:10, the final calibration standard concentrations were 0.4 µg/L, 1.0 µg/L, 2.0 µg/L, 4.0 µg/L, 10.0 µg/L, 20.0 µg/L and 50 µg/L. The standards were matrix matched by the addition of reagent water, aqua regia, 5% potassium permanganate solution and 12% (w/v) sodium chloride-hydroxylamine hydrochloride solution. The calibration standards were taken through the same digestion procedure as the prepared samples as specified in EPA 7471B. Each peak was integrated for a total of 3 seconds. A dynamic range spanning three orders of magnitude is possible using this method. The final calibration curve and a 50 µg/L peak profile are shown in [Figure 4](#) and [Figure 5](#).

Table II Working Standard Preparation				
Standard Concentration	Stock 1000 mg/L	Working 10 mg/L	Working 1000 µg/L	Working 100 µg/L
3% HCl		99 mL	90 mL	90 mL
Standard Added Volume		1 mL	10 mL	10 mL
Standard Added Concentration		Stock, 1000 mg/L	10 mg/L	1000 µg/L
Total Volume		100 mL	100 mL	100 mL

Table III Calibration Standard Preparation								
Standard Concentration	Working 1000 µg/L	Calibration 250 µg/L	Calibration 100 µg/L	Calibration 50 µg/L	Calibration 20 µg/L	Calibration 10 µg/L	Calibration 5 µg/L	Calibration 2 µg/L
3% HCl Added		75 mL	90 mL	95 mL	98 mL	99 mL	99.5 mL	99.8 mL
Standard Added Volume		25 mL	10 mL	5 mL	2 mL	1 mL	0.5 mL	0.2 mL
Standard Added Concentration		1000 µg/L	1000 µg/L	1000 µg/L	1000 µg/L	1000 µg/L	1000 µg/L	1000 µg/L
Total Volume		100 mL	100 mL	100 mL	100 mL	100 mL	100 mL	100 mL
Volume added to Digestion Tube		10 mL	10 mL	10 mL	10 mL	10 mL	10 mL	10 mL
Dilution		50:10	50:10	50:10	50:10	50:10	50:10	50:10
Concentration in Digestion Tube		50 µg/L	20 µg/L	10 µg/L	4 µg/L	2 µg/L	1 µg/L	0.4 µg/L

Figure 4 Calibration Curve

Figure 5 50 µg/L Standard Peak Profile


RESULTS

Total mercury in sediment was accurately recovered at $\mu\text{g/g}$ levels using the reduced ID tubing and optimized QuickTrace® software instrument parameters. A moisture analysis of the SRM was performed, and results were subtracted from the sample weights to provide dry weights. Seven replicates of the digested SRM were analyzed and total mercury concentration in $\mu\text{g/L}$ was recorded. In solution, the samples contained $\sim 5.8 \mu\text{g/L}$ of mercury. The results were converted from $\mu\text{g/L}$ to $\mu\text{g/g}$ using the dry sample weights and the final dilution volume of 50 mL. The mean concentration, standard deviation and uncertainty at 95% are shown in Figure 6. QC results are shown in Figure 7. NIST SRM 2704 total mercury is certified at $1.44 \mu\text{g/g}$ with an uncertainty of $\pm 0.07 \mu\text{g/g}$.

Figure 6 Results (Left) and Results with Uncertainties (Right)

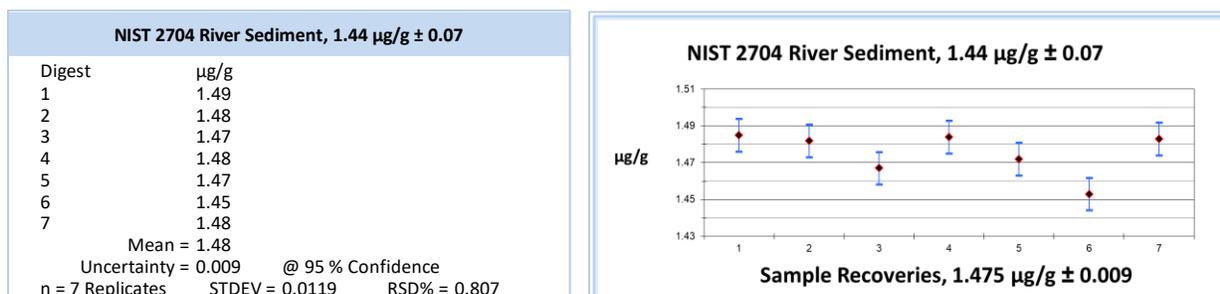


Figure 7 Quality Control (QC) Results

EPA 7471B Quality Control		
Quality Control ($\mu\text{g/g}$)	% Recovery	RPD%
ICV (20)	103.6	
CCV/LCS (20)	105.0	
MS	102.2	
MSD	99.3	2.10

A separate method detection limit (MDL) study was performed in accordance with CFR 40 Part 136 Appendix B, resulting in an MDL of $0.017 \mu\text{g/L}$ for the parameters associated with this application.⁵ For a 0.2 g digested sample and a 50 mL final sample size, this calculates to $0.004 \mu\text{g/g}$.

DISCUSSION

This application note confirms that reduced ID tubing does not compromise the linearity of the system or the accuracy of the method. Using the parameters shown in Table I, each sample required 95 seconds, amounting to a total rate of analysis for EPA 7471B of 38 samples per hour. By decreasing the internal diameter of the peristaltic pump tubing, stannous chloride reagent consumption was reduced by 53% and total waste was reduced by $\sim 40\%$ when compared to use of a standard tubing harness. As a result, the costly stannous chloride reagent lasted twice as long using this green chemistry reduced ID tubing configuration.

The use of reduced ID tubing offers a simple, environmentally responsible solution that enables laboratories to reduce reagent costs and waste output, as well as further the goals of green chemistry. The implementation of this small configuration change amounts to significant laboratory savings and reduced environmental impact.

REFERENCES

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