

# Total Mercury Determination in Environmental Samples Using the QuickTrace<sup>®</sup> M-7600 CVAA and Green Chemistry Tubing

Tyler Trent, Teledyne LABS

**environmental, mercury analysis, green chemistry, Leeman Labs, QuickTrace M-7600, CVAA, USEPA Method 7470A – wastewater, USEPA Method 7471B- sediment**

## Introduction

### Mercury in Environmental Samples

Mercury is a persistent, global, and toxic heavy metal. It transforms as it is transported. Interacting with the major environmental compartments—air, soil, and water as well as flora and fauna—it cycles between its elemental, ionic, and methylated states. Each species has differences in mobility, bioavailability, and toxicity. Monitoring the mercury content of environmental samples shines a light on contamination that can lead to negative public health and ecologic outcomes. Because of its potential to bioaccumulate and biomagnify with toxic consequences, mercury levels in air, soil, and water are highly regulated.

### Why Create a Green Chemistry Tubing Option?

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. Producing less hazardous waste and consuming fewer reagents benefits the environment and improves a laboratory's bottom line.

Teledyne LABS set out to use the principles of Green Chemistry to reduce the environmental impacts of our best-selling system, the Teledyne LABS QuickTrace<sup>®</sup> M-7600 CVAA Mercury Analyzer. This would not only reduce operational cost for customers but benefit the environment by reducing the waste generated by daily use. With instruments all over the world, creating an alternate Green Chemistry pump tubing configuration for the QuickTrace<sup>®</sup> M-7600 would support current and future customers' climate conscious initiatives while creating a more sustainable future for this product line.

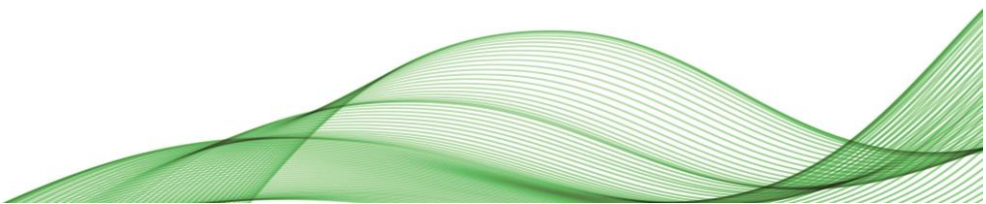
The main questions for this project were:

1. Can Teledyne LABS support the green goals of customers by reducing the environmental impact of the QuickTrace<sup>®</sup> M-7600?
2. Does this change produce results comparable to current instrument performance specification?
3. Is this modification simple for the customer to implement?

The answer to all those questions was yes! The aim was to make the transition seamless for the customer, while creating a tubing harness with a smaller internal diameter (ID) to reduce uptake that still met current instrument performance criteria.



**Figure 1** QuickTrace<sup>®</sup> M-7600 CVAA Mercury Analyzer and CETAC ASX-560 Autosampler



## Summary

By reducing the internal diameter of the tubing used on the QuickTrace® M-7600 mercury analyzer, accurate results can be achieved while decreasing reagent cost and hazardous waste generation. Two types of environmental samples were analyzed to demonstrate the capability of the QuickTrace® M-7600 CVAA mercury analyzer to determine total mercury concentrations while employing the Green Chemistry tubing harness. The following tests will be summarized:

- Analysis of certified reference material (CRM) ERM- CA713 'Wastewater Effluent' by USEPA method 7470A
- Analysis of standard reference material (SRM) NIST 2704 'Buffalo River Sediment' by USEPA method 7471B

## Instrumentation

Analysis was performed using the Teledyne LABS QuickTrace® M-7600 Cold Vapor Atomic Absorption spectroscopy (CVAA) Mercury Analyzer and the CETAC ASX-560 Autosampler shown in Figure 1. The QuickTrace® M-7600 is an independent stand-alone analyzer that uses Cold Vapor Atomic Absorbance (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 internal diameter (ID) peristaltic pump tubing. This dynamic quantitative range allows mercury concentrations to be determined in a broad range of sample substrates without dilution or pre-concentration.

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.

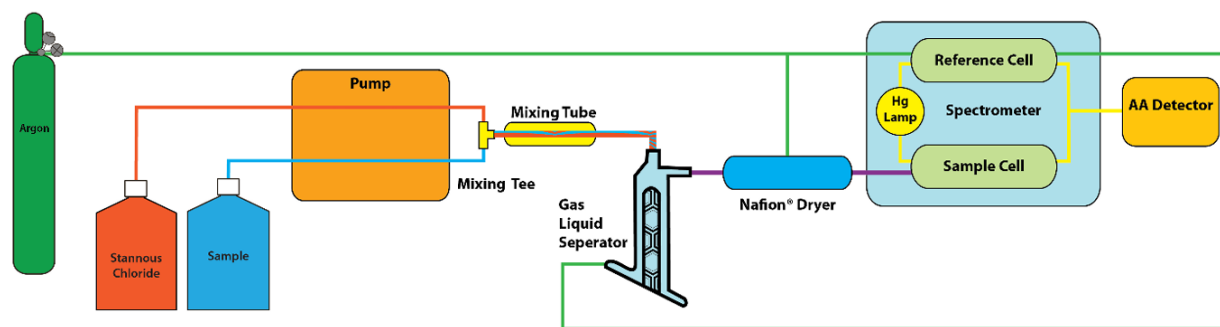


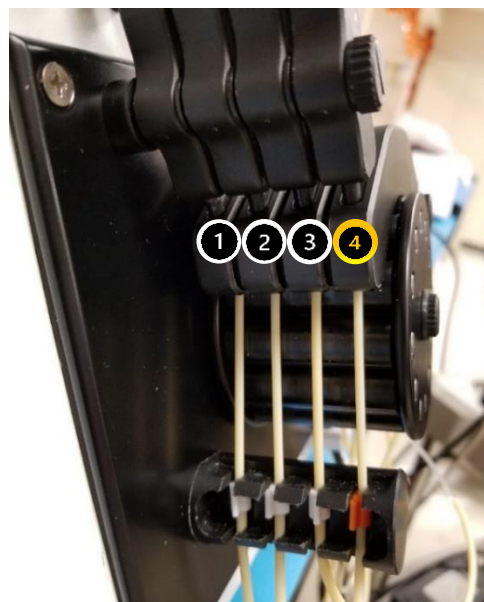
Figure 2 QuickTrace® M-7600 Process Diagram

## Experimental

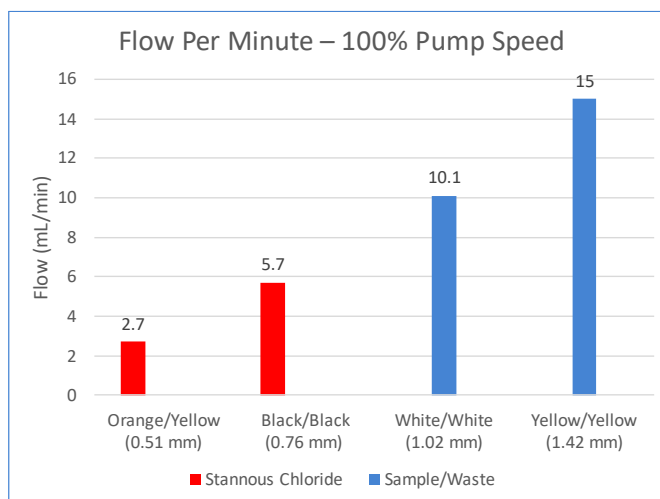
The reduced ID green chemistry tubing harness was installed on the peristaltic pump. The sample uptake and waste lines were white/white 1.02 mm tubing (PN 15-4308-102), installed in channels 1-3. The stannous chloride reagent line was flared orange/yellow 0.51 mm tubing (PN 15-4309-102), installed in channel 4. The QuickTrace® software provided 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. Table VI in the Appendix highlights the capability of reduced ID and standard ID tubing.

Figure 4 compares the flow per minute (FPM) of standard and reduced ID tubing sizes. The flow data is an average of more than a month of daily testing. For the green chemistry tubing, the stannous chloride reagent flow is 2.7 mL/min which is about 47% of the standard flow. The sample flow is 10.1 mL per minute which is 67% of the standard tubing flow. The flows were reduced while maintaining a similar ratio between the set tubing sets. With the combined reduction in stannous chloride and sample flows, the amount of waste generated was reduced by ~40%. 1 hour of analysis using the reduced ID tubing, with the pump speed set to 100%, saved ~180 mL of stannous chloride and ~470 mL of waste was eliminated.

Operating parameters for both methods are shown in Table 1. While the sample preparation and digestion procedures vary greatly between the two methods demonstrated, the instrument setup, the tubing harness, and the operating parameters were very similar. The only difference in setup was the carrier gas flow was optimized to be slightly higher for the USEPA 7471B method compared to the USEPA 7470A method.



**Figure 3** Peristaltic Pump with Green Chemistry Tubing Harness Installed



**Figure 4** Reduction of Method Reagents and Waste Using Reduced ID Tubing

**Table I Method Specific Instrument Parameters Using Reduced ID Tubing**

Operating Parameter	US EPA 7470A (AN2201)	US EPA 7471B (AN2202)
ASX Rinse Pump Speed (%)	50	50
Sample Uptake (sec)	35	35
Rinse Time (sec)	60	60
Gas Flow (mL/min)	150	200
Pump Speed (%)	70	70
Replicate Read Time (Sec)	0.75	0.75
Replicates	4	4

## USEPA Method 7470A - Wastewater

### Sample Preparation

ERM®-CA713 was collected from the effluent of a wastewater treatment works located in Flanders, Belgium. The outside of the ampoule was rinsed with deionized water to remove any contaminants, shaken for 2 minutes to ensure homogeneity, and then opened using a diamond tip cutter. According to EPA 7470A, samples and standards use a working sample size of 100 mL. To further reduce the volume of reagents required for analysis, the working sample size was 1/10 the volumes listed in the method. Sample and reagents were processed using 10 mL aliquots and total reagents added were 3.65 mL per digestion tube.

In EPA 7470A, samples and standards are taken through the same preparation and digestion procedure:

1. 10 mL aliquots of the CRM samples and calibration standards were added to 50 mL polypropylene copolymer digestion tubes, in which they remained throughout analysis.
2. Acidified with 0.5 mL of concentrated sulfuric acid and 0.25 mL of concentrated nitric acid.
3. Oxidized with 1.5 mL of 5% potassium permanganate solution and 0.8 mL of 5% potassium persulfate.
4. Digested according to EPA 7470A.
5. Post-digestion, neutralized of excess oxidants using 0.6 mL of 12% (w/v) sodium chloride/hydroxylamine hydrochloride solution.
6. Reduction of inorganic mercury ( $\text{Hg}^{2+}$ ) to elemental mercury ( $\text{Hg}^0$ ) 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 were analyzed along with the appropriate quality control (QC) checks used to validate the instrument. 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 using 4.1 mL of sample. The integration mode was set to peak height utilizing four replicates at 0.75 seconds per replicate. A six-point calibration curve was created, which included five non-zero standards and one blank. An initial calibration verification (ICV) and initial calibration blank (ICB) were analyzed to validate calibration accuracy and method performance. A continuing calibration verification (CCV) and continuing calibration blank (CCB) were analyzed to evaluate instrument drift and carryover. ERM-CA713 is certified at 1.84 µg/L total mercury, with an uncertainty at 95% of  $\pm 0.11$  µg/L.

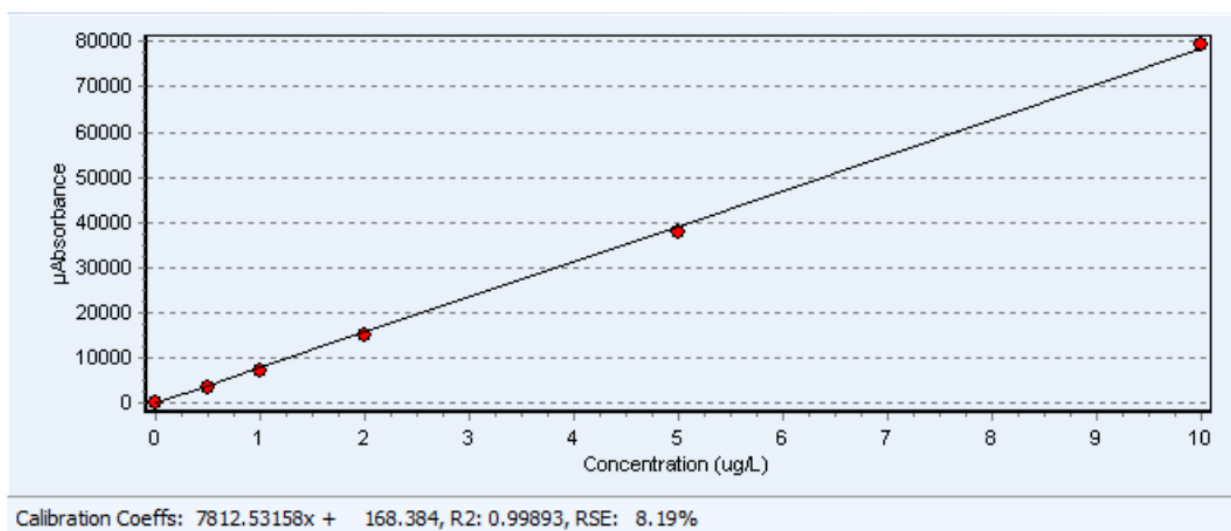
### Calibration

Calibration standards were prepared using aliquots of a 100 µg/L mercury solution prepared from serial dilutions of a purchased 1000 µg/mL stock standard. Standards were created with a final volume of 100 mL. Calibration standards were prepared by aliquot volume additions of 0.5 mL, 1.0 mL, 2.0 mL, 5.0 mL and 10.0 mL of 100 µg/L working standard added to 100 mL volumetric flasks containing 3% hydrochloric acid solution, as listed in Table II. 10 mL of the calibration standards were added to 50 mL digestion tubes.

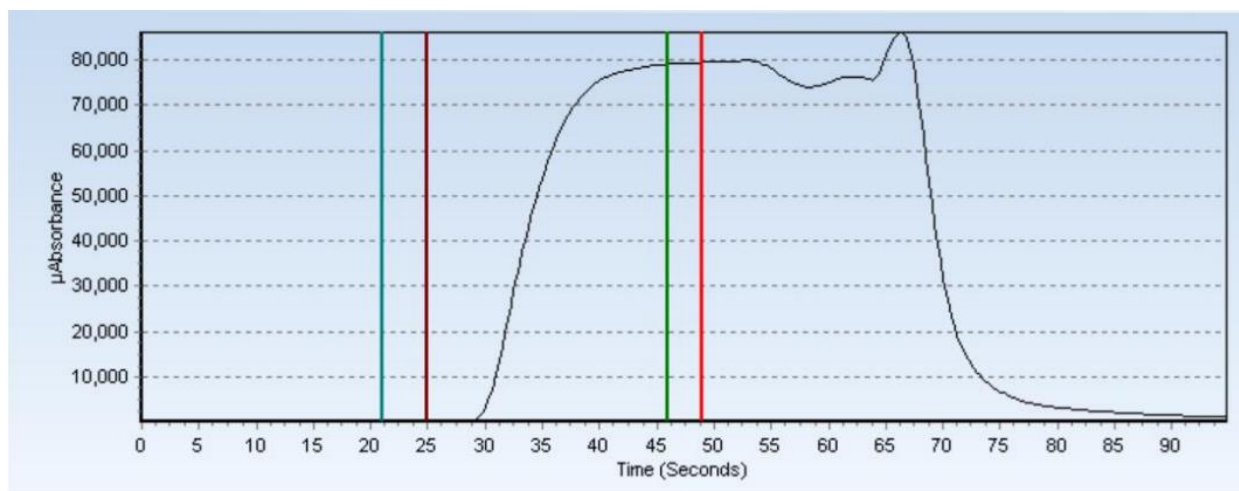
**Table II Calibration Standard Preparation USEPA 7470A**

Standard Concentration	Stock 1000 mg/L	Working 10 mg/L	Working 1 mg/L	Working 100 µg/L	Calibration 10 µg/L	Calibration 5 µg/L	Calibration 2 µg/L	Calibration 1 µg/L	Calibration 0.5 µg/L
3% HCl		99 mL	90 mL	90 mL	90 mL	95 mL	98 mL	99 mL	99.5 mL
Standard Added Volume		1 mL	10 mL	10 mL	10 mL	5 mL	2 mL	1 mL	0.5 mL
Standard Added Concentration		Stock	10 mg/L	1 mg/L	100 µg/L	100 µg/L	100 µg/L	100 µg/L	100 µg/L
Total Volume		100 mL	100 mL	100 mL	100 mL	100 mL	100 mL	100 mL	100 mL

The standards were matrix matched by adding sulfuric acid, nitric acid, 5% potassium permanganate, 5% potassium persulfate, and post-digestion 12% (w/v) sodium chloride-hydroxylamine hydrochloride. Before analysis, all standards were taken through the digestion procedure specified in EPA 7470A. Each peak was integrated for a total of 3 seconds. The final calibration curve is shown in Figure 5 and a 10 µg/L peak profile is shown in Figure 6.



**Figure 5** Six-Point Calibration Curve (0-10 µg/L)



**Figure 6** 10 µg/L Peak Profile

### Results (USEPA Method 7470A)

Total mercury in wastewater samples at  $\mu\text{g/L}$  levels was easily recovered using the reduced ID tubing and optimized QuickTrace<sup>®</sup> software method parameters. Seven replicates of the digested CRM were analyzed and the total mercury concentration in  $\mu\text{g/L}$  was recorded. ERM<sup>®</sup>-CA713 is certified at  $1.84 \mu\text{g/L}$  total mercury, with an uncertainty at 95% of  $\pm 0.11 \mu\text{g/L}$ . A separate 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. The mean concentration, standard deviation and uncertainty at 95% are shown in Figure 7. QC check results are shown in Figure 8.

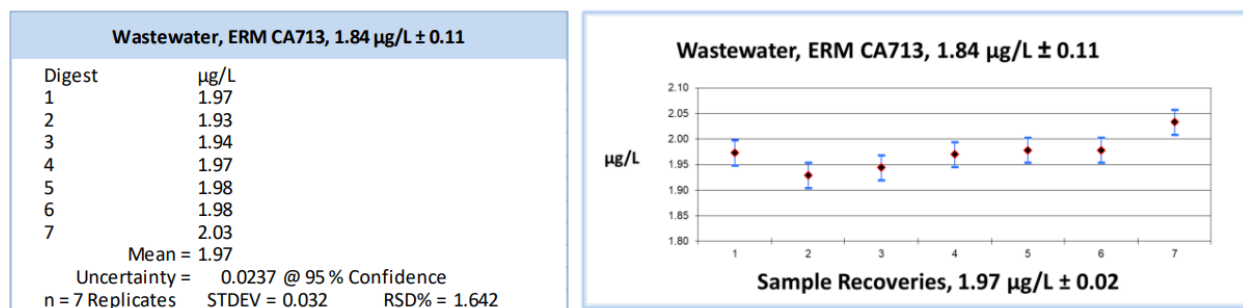


Figure 7 Results (left) and Results with Uncertainties (right)

Quality Control ( $\mu\text{g/g}$ )	% Recovery	RPD%
ICV	96.1	
CCV/LCS	96.2	
MS	94.6	
MSD	95.9	1.04

Figure 8 Quality Control (QC) Results

This study 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 7470A of  $\sim 38$  unknown and QC checks results reported per hour. The sample rate is 1 sample every  $\sim 1.58$  minutes. 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 ID tubing harness. As a result, the costly stannous chloride reagent lasted twice as long using this green chemistry reduced ID tubing configuration.

### USEPA Method 7471B- Sediment

#### Sample Preparation

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  $\sim 136.5$  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  $\sim 0.2$  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:  $\sim 0.2$ g 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.
3. 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.
  4. 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.
  5. 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.
  6. Reduction of the inorganic mercury ( $\text{Hg}^{2+}$ ) to elemental mercury ( $\text{Hg}^0$ ) 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

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 III and calibration standard preparations are summarized in Table IV.

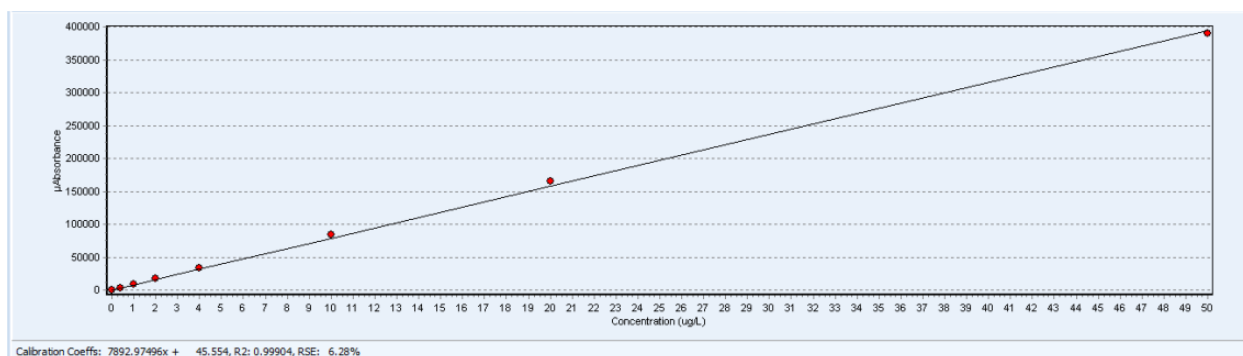
A 10 mL aliquot of each calibration standard was added to 50 mL digestion tubes. With a dilution factor of 50:10, the final calibration standard concentrations were 0.4 µg/L, 1.0 µg/L, 2.0 µg/L, 4.0 µg/L, 10.0 µg/L, 20.0 µg/L and 50 µg/L. The standards were matrix matched by the addition of reagent water, 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 9 and Figure 10.

**Table III Working Standard Preparation USEPA 7471B**

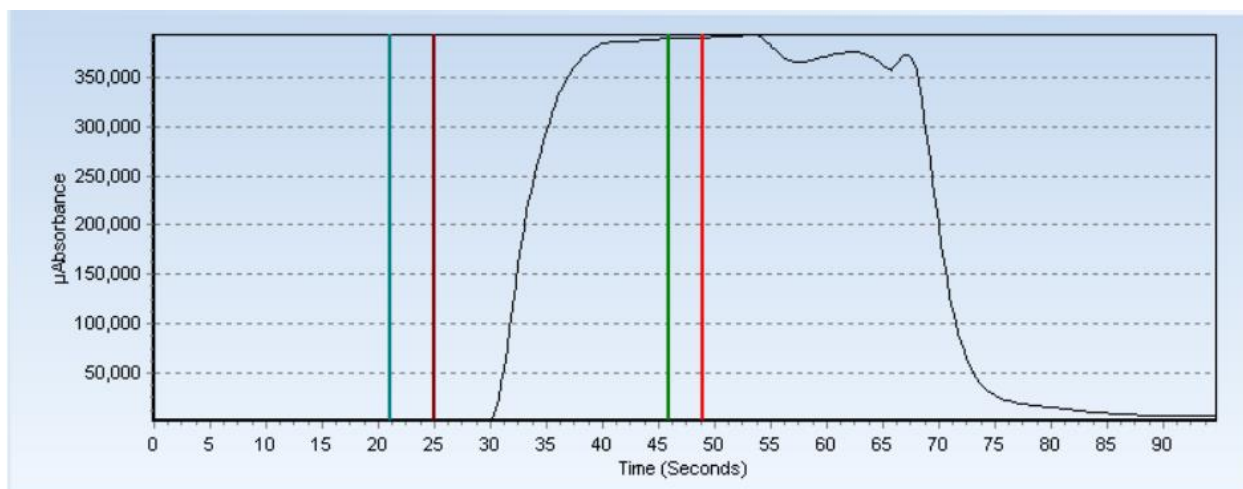
Standard Concentration	Stock 1000 mg/L	Working 10 mg/L	Working 1 mg/L	Working 100 µg/L
3% HCl		99 mL	90 mL	90 mL
Standard Added Volume		1 mL	10 mL	10 mL
Standard Added Concentration		Stock, 1000 mg/L	10 mg/L	1 mg/L
Total Volume		100 mL	100 mL	100 mL

**Table IV Calibration Standard Preparation USEPA 7471B**

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		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	51mL	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 9** Eight-point Calibration Curve (0-50 µg/L)



**Figure 10** 50 µg/L Standard Peak Profile

**Results (USEPA Method 7470A)**

Total mercury in sediment was accurately recovered at µg/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 µg/L was recorded. In solution, the samples contained ~5.8 µg/L of mercury. The results were converted from µg/L to µg/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 11. QC results are shown



in Figure 12. NIST SRM 2704 total mercury is certified at 1.44 µg/g with an uncertainty of ±0.07 µg/g. 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 µg/L for the parameters associated with this application. For a 0.2 g digested sample and a 50 mL final sample size, this calculates to 0.004 µg/g.

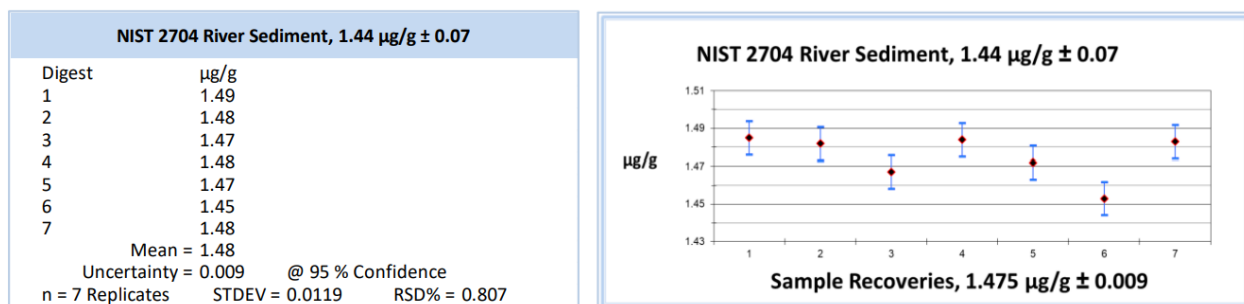


Figure 11 Results (left) and Results with Uncertainties (right)

EPA 7471B Quality Control		
Quality Control (µg/g)	% Recovery	RPD%
ICV (20)	103.6	
CCV/LCS (20)	105.0	
MS	102.2	
MSD	99.3	2.10

Figure 12 Quality Control (QC) Results

This study 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 ~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.

## Conclusions

Using the Green Chemistry pump tubing configuration means less is more! By reducing the internal diameters and therefore the flow:

- Stannous chloride consumption is reduced by 53%.
- Sample and rinse uptake are reduced by 33%.
- Waste generation is reduced by 40%.

These reductions also lead to other benefits. There is a possibility to scale down the sample preparation procedure since the sample uptake volume is reduced. Scaling down sample volumes from 100 mL to 10 mL (1:10) can save on sample prep and digestion reagent costs. The costly stannous chloride reagent lasted twice as long when using the reduced ID tubing. This adds up to significant laboratory saving on reagent costs.

Let's run the numbers and see how much money a 53% reduction of stannous chloride consumption could save. Assuming the following are constants, Table V demonstrates the potential savings of a high throughput laboratory:

- Price of 100 g of stannous chloride dihydrate crystals: \$134
- Reagent solution: 10% w/v stannous chloride
- Pump speed: 100%
- 8-hour workdays
- 260 workdays / year

<b>Table V Stannous Chloride Cost Savings</b>		
	<b>Reduced ID</b>	<b>Standard ID</b>
<b>1L of 10% reagent cost</b>	\$134	\$134
<b>Reagent uptake per day</b>	1.29 L	2.74 L
<b>Reagent cost per day</b>	\$172.86	\$367.16
<b>Reagent cost per year</b>	\$44,943.60	\$95,461.60
<b>Savings per year</b>	<b>\$50,518.00</b>	

Optimized methods can also reduce the amount of time per sample analysis. Less time per sample means more samples per hour! Using the parameters shown in Table I, each sample required 95 seconds for analysis for EPA 7470A and EPA 7471B. This amounts to a sampling rate of 38 samples per hour.

This application note confirms that reduction of the tubing ID does not compromise the linearity of the system or accuracy the method when performing analysis on wastewater or sediment samples for total mercury content. The implementation of this small configuration change amounts to significant laboratory savings and reduced environmental impact. 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, while still producing the reliable data the QuickTrace® M-7600 is known for.

Appendix

Table VI Comparing Capability of Reduced ID and Standard ID Tubing		
	Reduced ID	Standard ID
Sample Flow @ 100% Pump Rate	10 mL/min (67%)	15 mL/min
Stannous Chloride Flow @ 100% Pump Rate	2.7 mL/min (47%)	5.7 mL/min
Total Waste Generated @ 100% Pump Rate	12.7 mL/min (~40%)	20.7 mL/min
Sample Uptake (Min. 5s @ 100% Pump Rate)	Variable, ≥ 0.83 mL	Variable, ≥ 1.25 mL
Instrument Detection Limit (IDL)	< 1.0 ng/L	< 0.5 ng/L
Typical Usable Range	0.7 ng/L – 700 µg/L	0.5 ng/L – 500 µg/L
Short Term Precision N=5 @ 5 ng/L	< 3 % RSD	< 3 % RSD
Short Term Precision N=5 @ 20 ng/L	< 2 % RSD	< 1 % RSD
Short Term Precision N=5 @ 0.2 µg/L	< 2.5 % RSD	< 2 % RSD
0.2 µg/L Throughput	< 60s	< 60s
0.5 ng/L Throughput	N/A	< 90s
Response @ 40 mL/min Gas Flow & 100% Pump Rate	40 µAbs / ng/L	60 µAbs / ng/L
Response @ 100 mL/min Gas Flow & 100% Pump Rate	13,500 µAbs / µg/L	17,000 µAbs / µg/L