

Green Chemistry: Decreased Reagent Consumption and Waste Using Reduced ID Tubing on the QuickTrace® M-7600 CVAA Mercury Analyzer

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Page | 1

Introduction

Mercury (Hg) is a naturally occurring element, known to be toxic to humans. Consequently, the testing of food and environmental samples for Hg is essential to minimize exposure to this hazardous element. The methods approved by government agencies such as EPA 7471B¹ and FDA EAM 4.5² reliably quantitate the amount of mercury in samples, however, they also generate a large amount of waste. In particular, stannous chloride, one of the reagents required for this analysis, is hazardous as well as expensive.

In recent years, green chemistry has been of increasing importance to the scientific community and the EPA and ACS have partnered to create a "Green Chemistry Challenge" to encourage scientific solutions and promote the use of green chemistry principles. The first and most important of these principles is waste prevention³, which includes the reduction of the reagents required for analysis.

This application note will demonstrate that by reducing the internal diameter (ID) of the tubing used on the QuickTrace® M-7600 mercury analyzer, accurate results can be achieved while decreasing reagent cost and hazardous waste. To validate the reduced ID tubing and prove its effectiveness, the following tests were performed:

- Instrument Detection Limit (IDL) study using normal quality control (QC) testing
- Analysis of certified reference materials (CRM) by FDA EAM 4.5
- Analysis of certified reference materials (CRM) by EPA 7471B

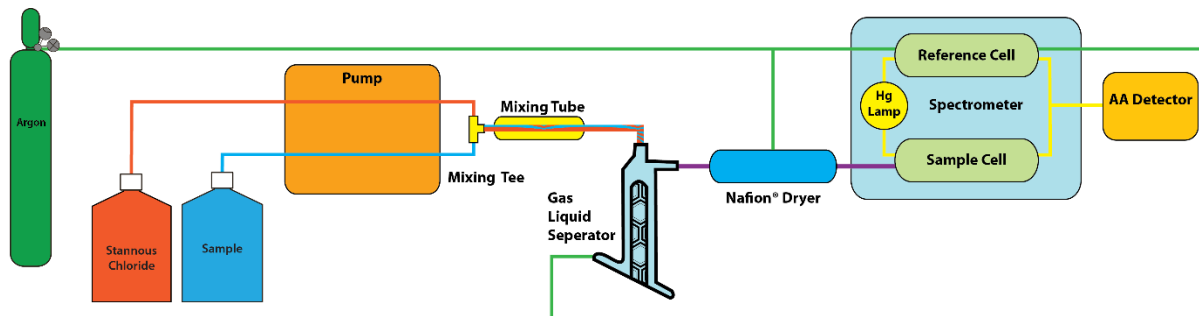
Instrumentation

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 <0.5 ng/L to >500 µg/L. 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 peristaltic pump that ensures consistent sample uptake to 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 (GLS), where the sample is purged with argon as elemental mercury is liberated. The mercury then passes through the Perma Pure® drying cartridge and into the sample cell where it is measured at 253.7 nm. Refer to [Figure 1](#).

The analyzer was also equipped with an optional ASX-560 autosampler that allowed automated analysis of the samples.

Figure 1 QuickTrace® M-7600 Process Diagram



Experimental

The M-7600's QuickTrace® software instrument controls include, but are not limited to, argon flow, lamp, pump control, smart rinse threshold, and over range protection. Parameter optimization allows for the quantitation of mercury in the ultra-trace ng/L range. This application note will demonstrate the use of reduced ID system tubing to deliver accurate results. The stannous chloride was added using flared orange/yellow 0.51 mm tubing (TLL PN 15-4309-102). The sample and waste lines were both white/white 1.02 mm tubing (TLL PN 15-4308-102). To verify the detection limit of the instrument with the reduced ID tubing, 25 blanks and five 5 ng/L samples were analyzed. To demonstrate the effectiveness of the reduced ID tubing in the presence of a high matrix, seafood samples and CRMs were digested according to either FDA EAM 4.5 or EPA 7471B. Inorganic mercury in standards and digested samples was reduced to elemental mercury by excess online addition of 10% stannous chloride in 7% HCl. EPA 7471B specifies the use of stannous sulfate, however, stannous chloride is a permissible substitution per the method.

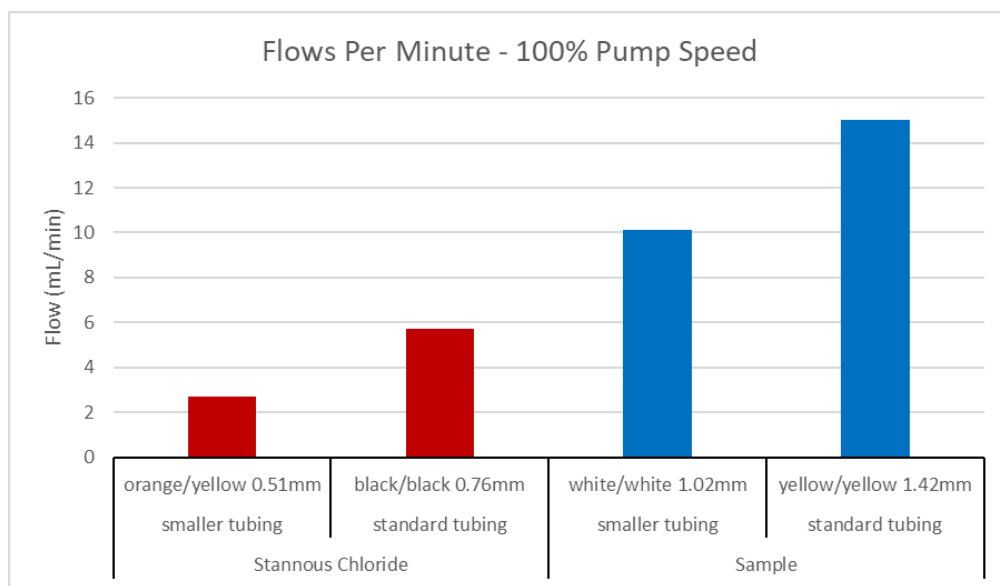
Operating Parameters

Instrument parameters for the IDL study were based on established protocol. The parameters for FDA EAM 4.5 were derived from the method. For EPA 7471B, the default QuickTrace® template "M7600 Normal Range - ASX 560" was used with optimized sample uptake and rinse times. Method parameters are shown in [Table I](#).

Table I Method Specific Instrument Parameters			
Operating Parameters	IDL Study	FDA EAM 4.5	EPA 7471B
Sample Uptake (sec)	60	30	35
Rinse Time (sec)	100	65	80
Gas Flow (mL/min)	40	125	100
Pump Speed (%)	100	80	50
Replicate Read Time (sec)	2.5	1	1.5
Replicates	4	3	4

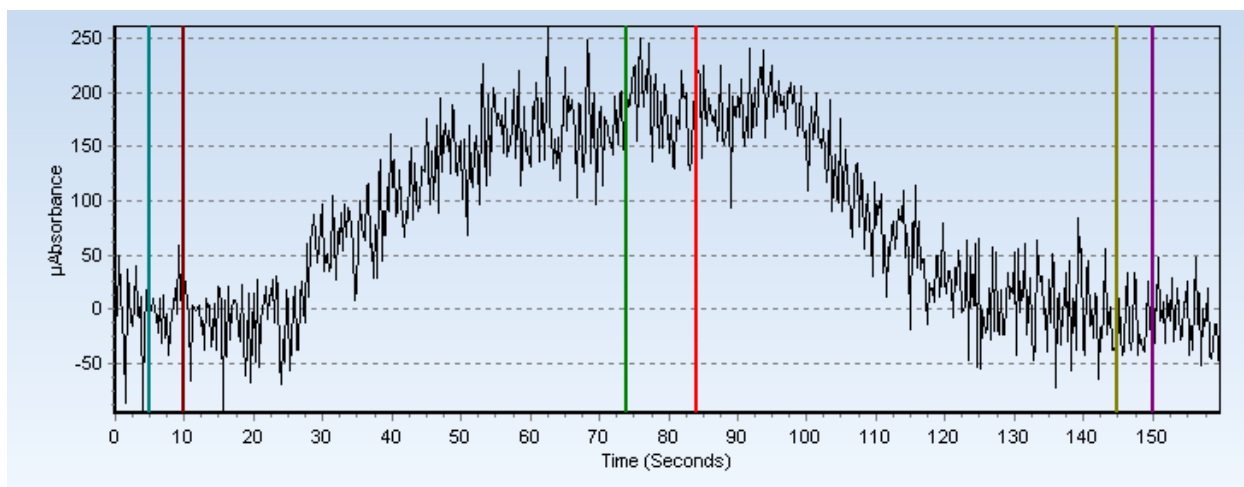
To determine the required flow rate for the reduced ID tubing, the pressure placed on the tubing was adjusted according to the *QuickTrace® M-7600 Operators Manual*. **Figure 2** compares the flow per minute (FPM) of standard and reduced ID tubing sizes. The reduced ID tubing flow data is an average of more than a month of daily testing. The standard tubing flow data was obtained from the *QuickTrace® M-7600 Operators Manual*. 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.**

Figure 2 Reduction of Method Reagents and Waste Using Reduced ID Tubing



It should be noted that the reduction in sample consumption produces a ~30% decrease in μ Absorbance for standards and samples. This change in signal resulted in the IDL increasing from 0.34 ng/L to 0.77 ng/L as tested on the system used for this study. Because the GLS on the QuickTrace® M-7600 is very efficient, the 5 ppt standard still produced a distinct peak as shown in **Figure 3**.

Figure 3 5 ng/L Standard in 3% HCl with Reduced ID Tubing



Calibration

The instrument was calibrated using standards appropriate to each method.

Table II Method Specific Calibration Standards		
Method	Calibration Standards	Unit
FDA EAM 4.5	0, 50, 100, 250, 500 and 1000 in 10% HNO ₃ , 7% HCl, 1% NaCl	ng/L
EPA 7471B	0, 0.2, 1, 2, 5 and 10 digested with samples	µg/L

Calibrations must have a correlation coefficient of 0.998 or better to be considered valid. FDA EAM 4.5 and EPA 7471B were validated using a second-source standard that was prepared at a concentration equal to half of the highest standard in the curve, and had an acceptance criterion of $\pm 10\%$. For both methods, a continuing calibration verification (CCV) standard and a continuing calibration blank (CCB) were analyzed every 10 samples and at the end of the sequence. The CCV was required to be within 10% of its known value while the CCB must be less than half of the lowest standard of the curve. Calibration curves are shown in Figure 4 and Figure 5. A peak from the FDA EAM 4.5, 1000 ng/L calibration standard is shown in Figure 6. The calibration curves for both methods demonstrate the excellent linearity (≥ 0.9999) of the system equipped with the reduced ID tubing, and indicate no significant impact to peak shape.

Figure 4 FDA EAM 4.5 Calibration Curve

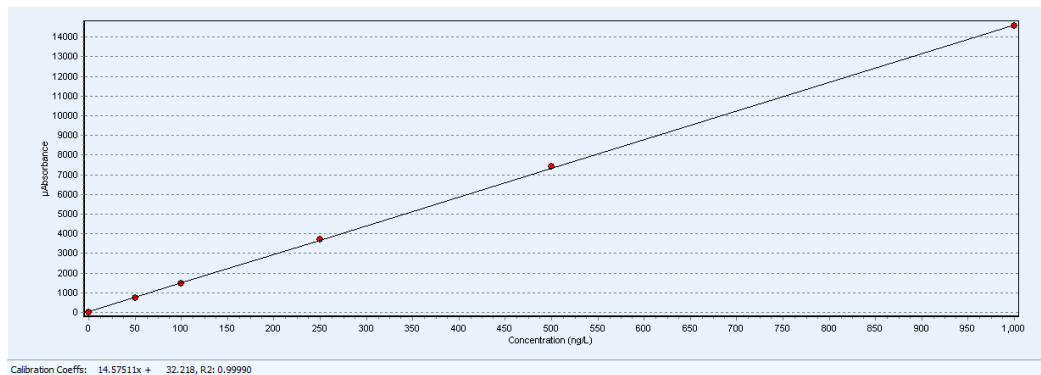


Figure 5 EPA 7471B Calibration Curve

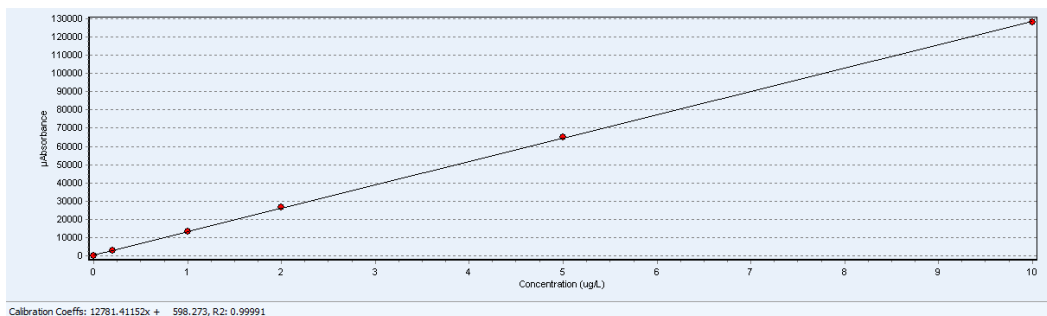
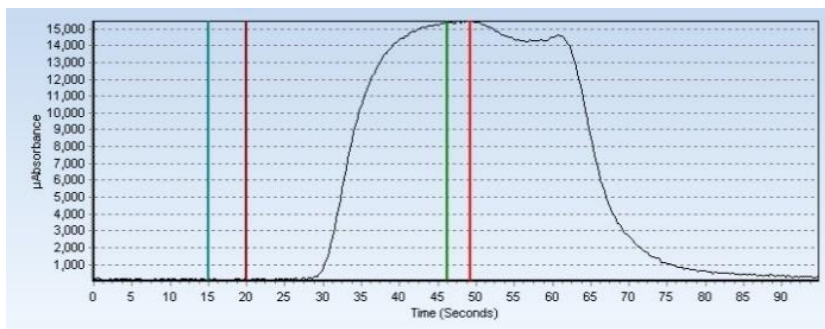


Figure 6 Representative Peak FDA EAM 4.5


Procedure

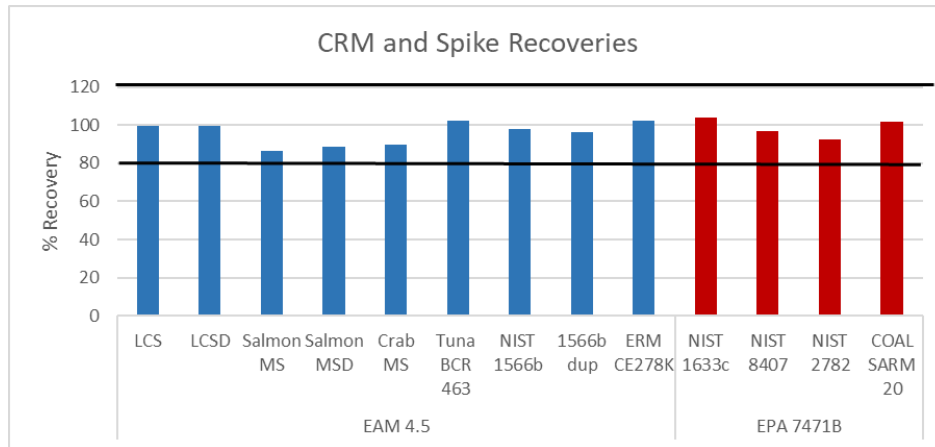
All CRMs were digested according to method protocols. The CRMs digested for FDA EAM 4.5 consisted of NIST 1566b Oyster Tissue, ERM-CE278K Mussel Tissue and BCR-463 Tuna Fish. Store purchased canned salmon and crab samples were also digested with a matrix spike. The CRMs digested for EPA 7471B consisted of NIST 1633c Trace Elements in Coal Fly Ash, NIST 8407 Mercury in Tennessee River Sediment, NIST 2782 Industrial Sludge and SARM 20 Coal.

CRM Samples (except for the coal) were homogenized by agitating the containers for 1 minute prior to sampling. Samples for EPA 7471B were weighed into tared vessels to $0.2 \text{ g} \pm 0.02 \text{ g}$ and digested using a graphite digestion block. Because the method recommended sample size was reduced by 50%, the quantity of digestion reagent was also reduced proportionally. Samples were filled to a final volume of 50 mL after digestion. FDA EAM 4.5 CRMs were weighed into tared PTFE microwave vessels to $0.1 - 0.5 \text{ g} \pm 10\%$ depending on expected concentrations. The canned salmon and crab were homogenized and weighed to $0.5 \text{ g} \pm 0.05$. The samples were digested using a microwave accelerated reaction system (MARS®) 6 system (CEM Corporation, Matthews, North Carolina) with the reagents and microwave conditions specified by the method. As the CRM samples were not dried prior to digestion, a dry weight study was performed and CRM sample results were adjusted accordingly.

Results

Results for the laboratory control sample (LCS), matrix spikes (MS) and CRMs are shown in Figure 7. The LCS and MS/MSD were spiked with 0.25 mL of a $100 \text{ } \mu\text{g/L}$ Hg standard before the addition of digestion reagents. The true value of the spike after final dilution of samples was 500 ng/L . FDA EAM 4.5 requires a recovery of $\pm 20\%$ for spikes and CRMs, which the QC results exceeded. There is no equivalent requirement for EPA 7471B, however, **all CRMs for both methods had a recovery of $\pm 10\%$** . The passing recoveries for MS/MSDs and CRMs demonstrate that the reduced ID tubing did not compromise analytical integrity when running difficult sample matrices.

Figure 7 Recovery Results



Detection Limits

To demonstrate system precision when using the reduced ID tubing, seven aliquots of two CRMs were digested and analyzed using both methods. For EPA 7471B, 0.2 ± 0.02 g of sample was measured into digestion vessels. For FDA EAM 4.5, 0.1 ± 0.01 g of sample was measured into PTFE microwave vessels. After digestion, the samples were diluted 10x with a digested reagent blank to give an approximate instrument response in the range of 500 ng/L, at the conditions used for validation. The results were corrected for moisture content, and mean concentration/standard deviation were calculated.

Uncertainty values correspond to a level of confidence of 95% and were calculated for the seven replicates of the CRM analyzed. Results are shown in Table III and Table IV and Figure 8 and Figure 9. The uncertainty for both CRMs is less than the uncertainty in the certified value. Additionally, the RSDs are less than 2%, indicating excellent precision when using the reduced ID tubing.

Table III Trace Elements in Coal Fly Ash, 1633c, 1.005 mg/Kg ± 0.022	
Digest	Mg/Kg
1	1.020
2	1.011
3	1.018
4	1.005
5	1.014
6	0.996
7	1.008
Mean=1.010	
Uncertainty=0.006 95% Confidence	
N=7 Replicates Standard Deviation=0.008 %RSD=0.791	

Figure 8 NIST 1633c Results with Uncertainties

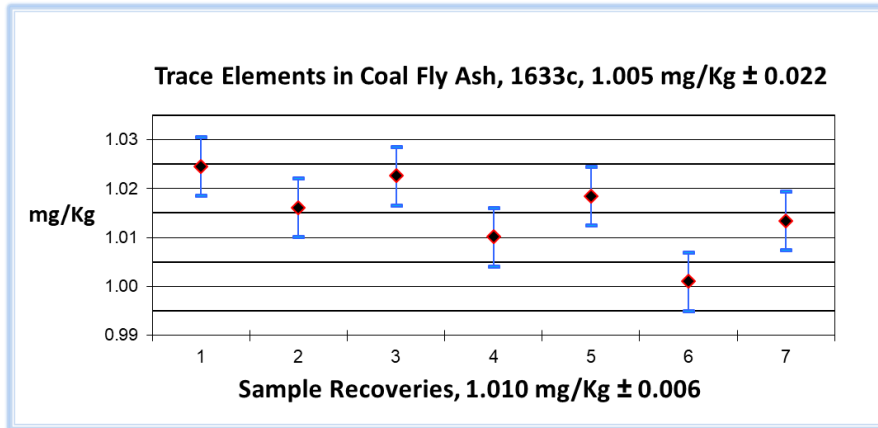
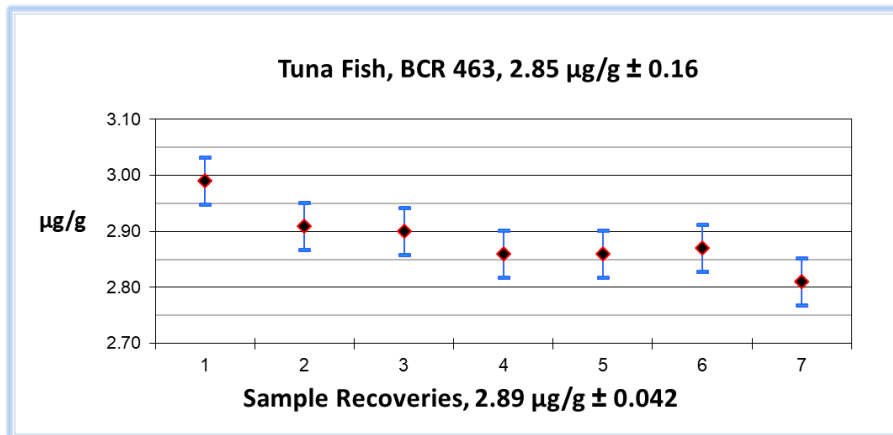


Table IV Tuna Fish, BCR 463, 2.85 µg/g ± 0.16	
Digest	µg/Kg
1	2.99
2	2.91
3	2.90
4	2.86
5	2.86
6	2.87
7	2.81
Mean=2.89	
Uncertainty=0.042 @95% Confidence	
N=7 Replicates Standard Deviation=0.056 %RSD=1.949	

Figure 9 BCR 463 Results with Uncertainties



Conclusion

By decreasing the internal diameter of the system tubing, stannous chloride reagent consumption was reduced by 53%. Moreover, the total waste produced decreased by ~40%. This application note confirms that reduction of the tubing ID does not compromise the linearity, accuracy or reproducibility of the methods. These findings, combined with the QuickTrace® M-7600 mercury analyzer's highly-efficient GLS, enables laboratories to reduce reagent costs and waste output, as well as work toward the goals of green chemistry.

References

1. U.S. Environmental Protection Agency, 1994, Method 7471B (revision 2) --Mercury in solid or semisolid waste (manual cold-vapor technique), in Inorganic analytes, chap. 3 of Test methods for evaluating solid wastes, physical/chemical methods: U.S. Environmental Protection Agency SW-846, 11 p. [Online] <https://www.epa.gov/sites/production/files/2015-12/documents/7471b.pdf> (accessed December 3, 2019).
2. Cold Vapor Atomic Absorption Spectrometric Determination of Total Mercury in Seafood Using Microwave Assisted Digestion; Official Method of Analysis of AOAC INTERNATIONAL [U.S. Food and Drug Administration, Internet]; Section 4.5, Version 1.0, 2008. [Online] <https://www.fda.gov/food/laboratory-methods-food/elemental-analysis-manual-eam-food-and-related-products> (accessed December 3, 2019).
3. "Green Chemistry." EPA, [Online] <https://www.epa.gov/greenchemistry> (accessed December 3, 2019).