APPLICATION NOTE: AN2303
TECHNOLOGY: Hg
INDUSTRY: ENV

Green Chemistry: Calibration Parameters for a 20 Percent Aqua Regia Matrix Using the QuickTrace® M-7600 CVAA Mercury Analyzer

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INTRODUCTION

Mercury (Hg) is a naturally occurring element, known to be toxic to humans. Consequently, the testing of food and environmental samples for mercury is essential to minimize exposure to this hazardous element. To test various matrices from time to time one needs to veer away from conventional methodologies.

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

The matrix of 20 percent aqua regia to my knowledge hasn't been officially approved as a matrix for CVAA. Most methods appear to be performance-based in the European community, as they include or allude to verbiage in the SW 846 solid waste manual governed by the USEPA. The SW 846 quality manual seems to indicate that methods are a guidance or otherwise approved if the quality control is adhered to and passes the criteria. With that said, most methods reliably quantitate the amount of mercury in samples; unfortunately, they also generate a large amount of waste and take extra hardware and labware to dilute samples in preparation for analysis. This part of mercury analysis is wasteful due to the extra sample tubes and solutions to make dilutions. In recent years, green chemistry has been of increasing importance to the scientific community.

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 laboratories' bottom line.

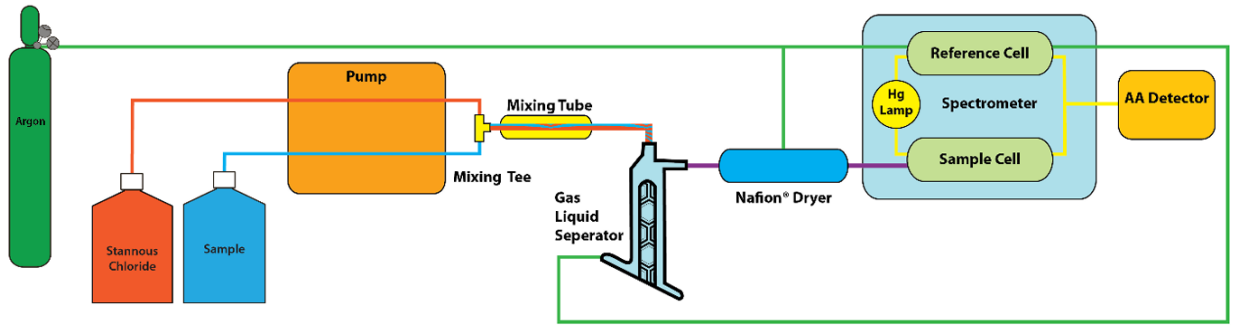
This technical matrix demonstration will show that by reducing the internal diameter (ID) of the tubing used on the QuickTrace® M-7600 mercury analyzer, accurate calibration results can be achieved while decreasing reagent cost and hazardous waste—even for a difficult matrix such as 20 percent aqua regia. It will be shown that 20 percent aqua regia can be introduced into the system without sacrificing performance.

INSTRUMENTATION

The Teledyne Leeman Labs 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 in excess of 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 analyzer in this matrix demonstration was equipped with an ASX-520 autosampler, which is discontinued. Current model ASX-560 (Figure 1) is the replacement for the older ASX-520 model which was used in the original experiment.

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 2.

Figure 2 QuickTrace® M-7600 Process Diagram



EXPERIMENTAL

Calibration solutions were prepared with the addition of 10 mL of aqua regia in a pre-cleaned 50 mL polypropylene digestion tube. This was followed by aliquots from a 20 µg/L working standard in 3% HCl. The final volume of each calibration standard was diluted to 50 mL in the tube. The standards consisted of a blank, 0.04, 0.2, 1, 2, 5, and 10 µg/L which is a good representation of most applicable calibration plots for methods in existence across the globe for determination of mercury in a vast array of matrices.

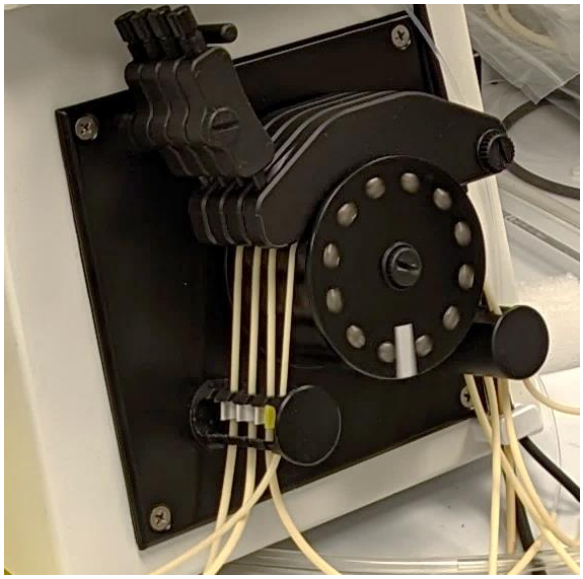
The QuickTrace® M-7600 peristaltic pump was outfitted with the smaller ID pump tubes designed to deliver less reagent and sample while keeping the working ranges and MDL's within the historical values for the system. The smaller ID pump tubing consumes 33% less sample and 53% less stannous chloride than that of the original or standard pump tubing harness.

Table I Tubing Configuration for Reduced Flows	
Channel 1 & 2 (Parallel Drain Connections)	15-4308-102; PUMP TUBING, SAMPLE / DRAIN TUBING, White/White, (PACK OF 12), 1.02 mm (ID)
Channel 3 (Sample)	15-4308-102; PUMP TUBING, SAMPLE / DRAIN TUBING, White/White, (PACK OF 12), 1.02 mm (ID)
Channel 4 (Reducing Reagent)	15-4309-102; PUMP TUBING, STANNOUS CHLORIDE REAGENT TUBING, Orange/Yellow, (PACK OF 12), 0.51 mm (ID), Flared
Pump Lever Tension	Set as described in the manual: Adjust flow so it's a bit jerky in the transfer line. Then one 360 ° clockwise revolution "Set It & Forget It"

The QuickTrace software makes the transition to the new peristaltic pump tubing harness seamless.

Figure 3 QuickTrace® M-7600 CVAA System With ASX-520 Autosampler

Figure 4 QuickTrace® M-7600 CVAA Peristaltic Pump W/Smaller ID tubing



Peak Height Calibration Procedure

1. Navigate to Method Editor | Standards and select Avg Peak Height for Quantitation Mode then enter your desired standards.
2. Navigate to Method Editor | Conditions and perform a reading “Peak Profile” of the highest standard concentration. In this example a 10 µg/L (ppb) standard was used. (See Figure 5 and Table II.)
3. Adjust the system timing and other parameters to achieve the lowest peak height % RSD.
4. In most cases a standard above 0.1 to 0.2 µg/L should be less than 1% and often less than 0.5% (See Figure 6 and Figure 8).

The system parameters were set up to use the natural pre-peak lag time as the decay time for the previous peak. With that a single baseline correction point was chosen at 4s in duration to end at ~ 4s prior to the peak inflection point (See Figure 9 and Figure 10). This approach allowed for ultra-trace results at 0.04 µg/L while maintaining a calibration range up to 10 µg/L (See Figure 7).

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Figure 5 QuickTrace® M-7600 CVAA (10 µg/L Peak Profile, Height)

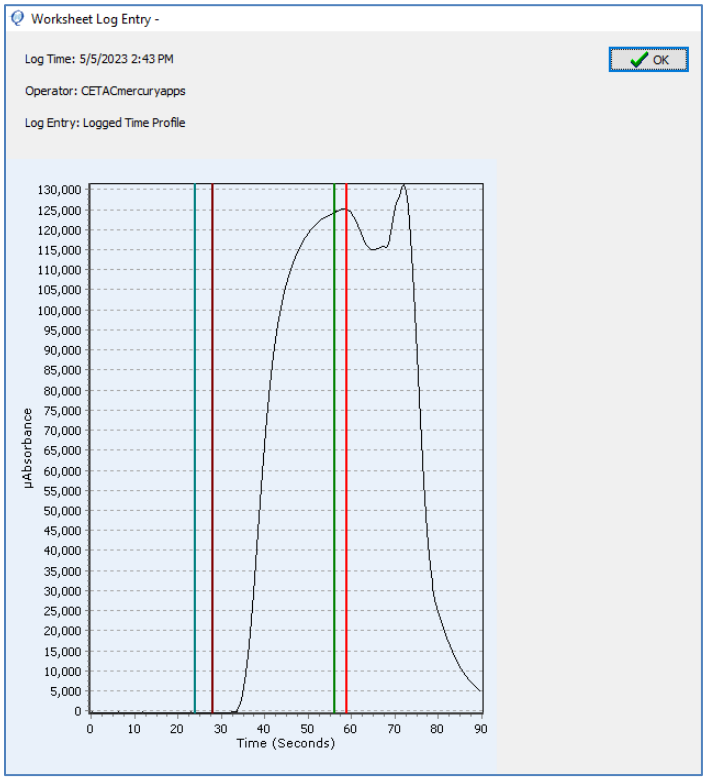

Table II Optimized Peak Height Parameters—20% Aqua Regia (Peak Height) Conditions	
Autosampler	
Sample Probe depth (mm) *Raise Higher for Particulate Matter	145-150
ASX Rinse Pump Speed (%) **Recycled**	50
Sample uptake time (s)	35
Rinse time (s)	55
Analyzer	
Gas Flow (mL/min)	100
Pump speed (%)	70
Read delay time (s)	56
Replicate read time (s)	0.75
Replicates	4
Baseline Drift Correction: Start read (s)	24
Baseline Drift Correction: End read (s)	28

Figure 6 10 µg/L Calibration Point

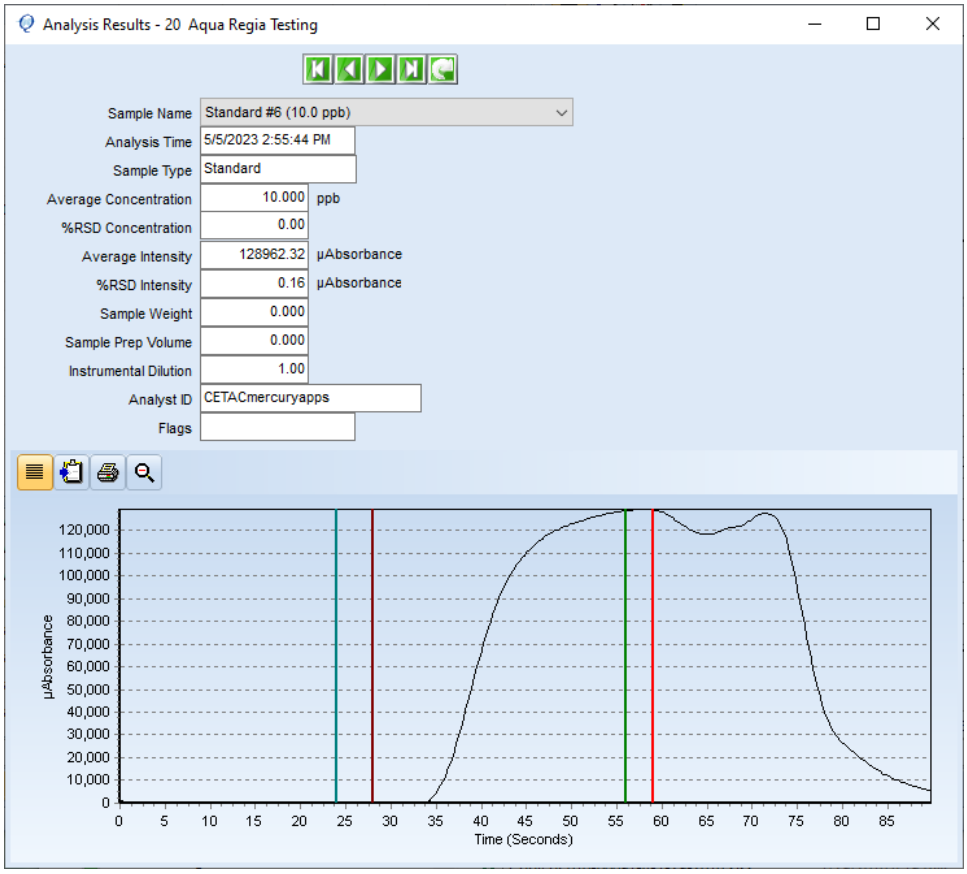

Figure 7 Peak Height Calibration Plot

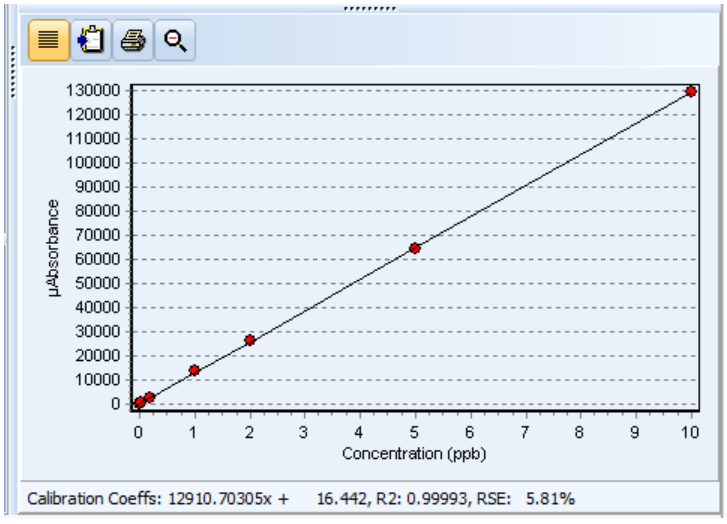

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Figure 8 Peak Height Calibration with Random Placed Read Backs

Tube	Sample Label	Conc (ppb)	µAbs	%RSD	Flag	%Residual
S:1	Calibration Blank	0.000	16.4	117.84		
S:2	Standard #1 (0.04 ppb)	0.040	561.8	1.69		5.60
S:3	Standard #2 (0.2 ppb)	0.200	2809.4	1.83		8.17
S:4	Standard #3 (1.0 ppb)	1.000	13664.5	0.30		5.71
S:5	Standard #4 (2.0 ppb)	2.000	26387.9	0.34		2.13
S:6	Standard #5 (5.0 ppb)	5.000	64516.1	0.27		-0.08
S:7	Standard #6 (10.0 ppb)	10.000	128962.3	0.16		-0.12
1:1	Blank	-0.008	-86.5	17.72		
1:2	5 ug/L	5.038	65056.5	0.20		
1:3	0.04 ug/L	0.040	533.5	3.67		
1:4	10 ug/L	9.866	127390.3	0.20		
1:5	2 ug/L	2.095	27059.4	0.26		
1:6	0.2 ug/L	0.210	2724.6	0.66		
1:7	1 ug/L	1.058	13675.1	0.48		
1:8	10 ug/L (3% HCL)	10.235	132155.3	0.33		

Figure 9 0.04 µg/L Read Back Directly Following a 5.0 µg/L

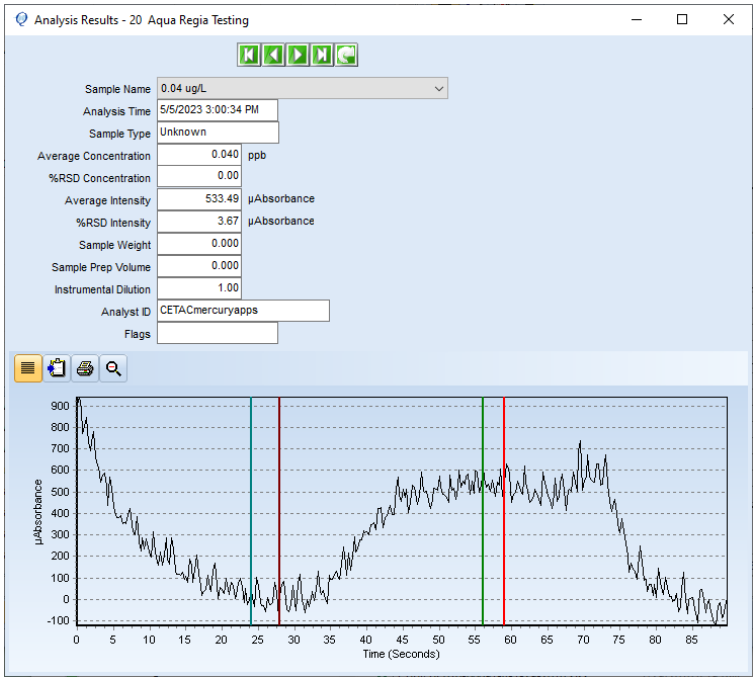
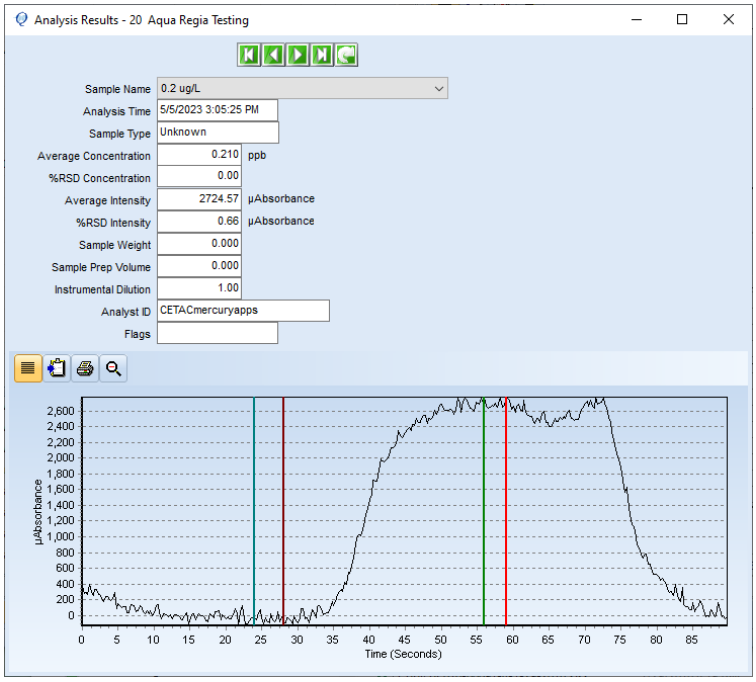


Figure 10 0.2 µg/L Read Back Directly Following a 2.0 µg/L



Peak Area Calibration Procedure

1. Navigate to Method Editor | Standards and select Peak Area for Quantitation Mode then enter your desired standards.
2. Navigate to Method Editor | Conditions and perform a reading “Peak Profile” of the highest standard concentration. In this example a 10 µg/L (ppb) standard was used. (See Figure 11 and Table III)
3. Adjust the system timing and other parameters to achieve a baseline to baseline peak area.

The system was set up to achieve results in ~ 60s while maintaining a discernable signal at the trace levels. This approach allowed for ultra-trace results at 0.04 µg/L while maintaining a calibration range up to 10 µg/L (See Figure 13).

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Figure 11 QuickTrace® M-7600 CVAA (10 µg/L Peak Profile, Area)

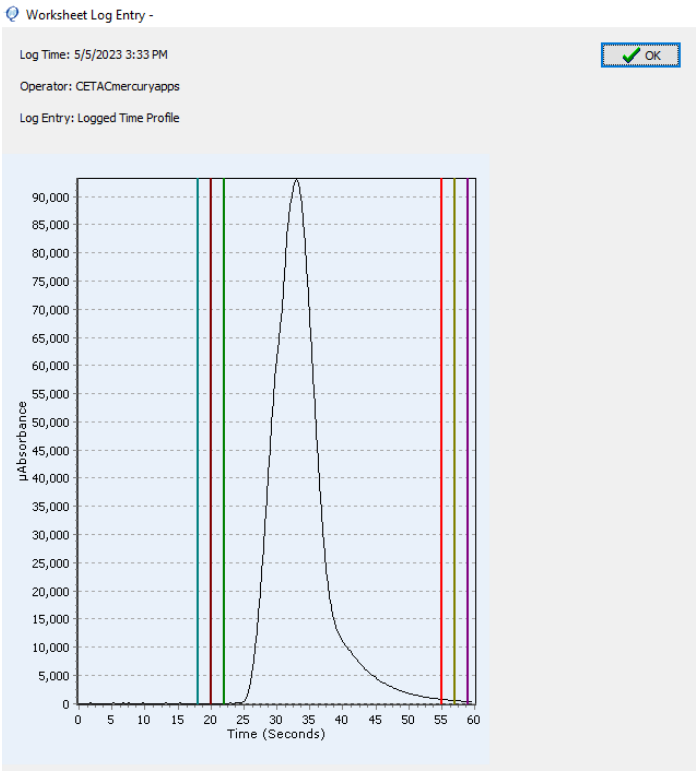


Table III Optimized Peak Area Parameters—20% Aqua Regia (Peak Area) Conditions	
Autosampler	
Sample Probe depth (mm) *Raise Higher for Particulate Matter	145-150
ASX Rinse Pump Speed (%) **Recycled**	50
Sample uptake time (s)	6
Rinse time (s)	54
Analyzer	
Gas Flow (mL/min)	150
Pump speed (%)	100
Peak start time (s)	22
Peak width (s)	33
Baseline Drift Correction: Start read (s)	18
Baseline Drift Correction: End read (s)	20
Two-point Baseline Correction: Start read (s)	57
Two-point Baseline Correction: End read (s)	59

Figure 12 10 µg/L Calibration Point (Peak Area)

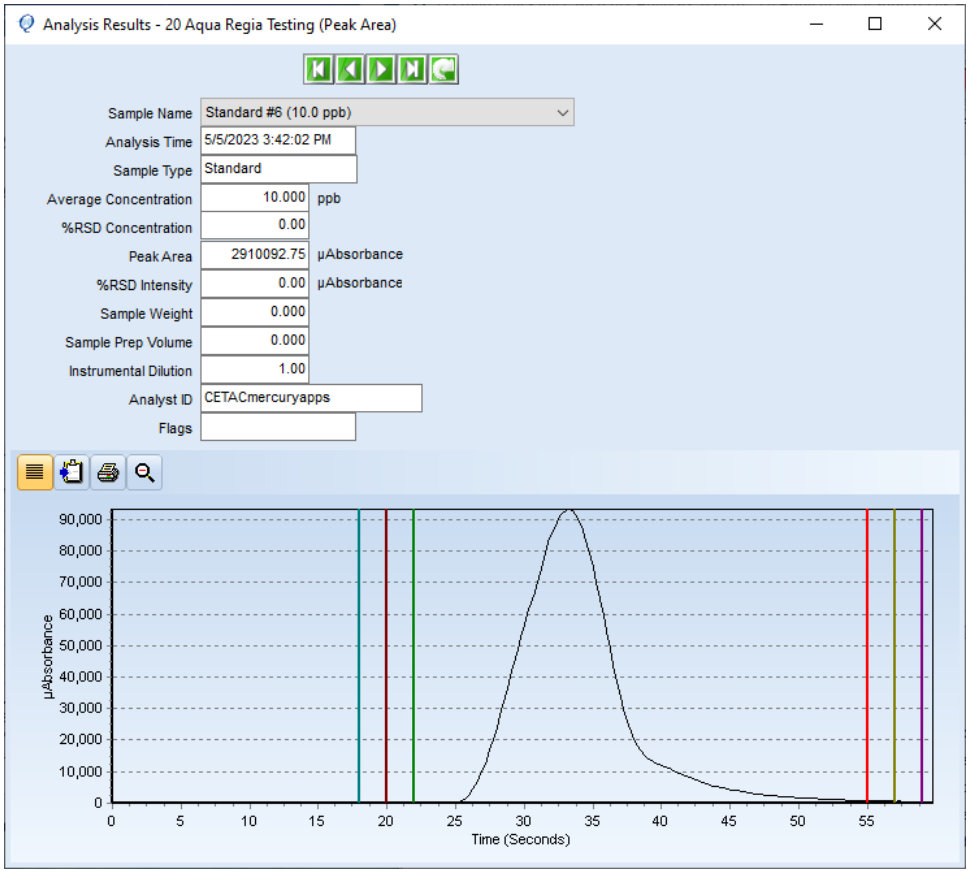


Figure 13 Peak Area Calibration Plot

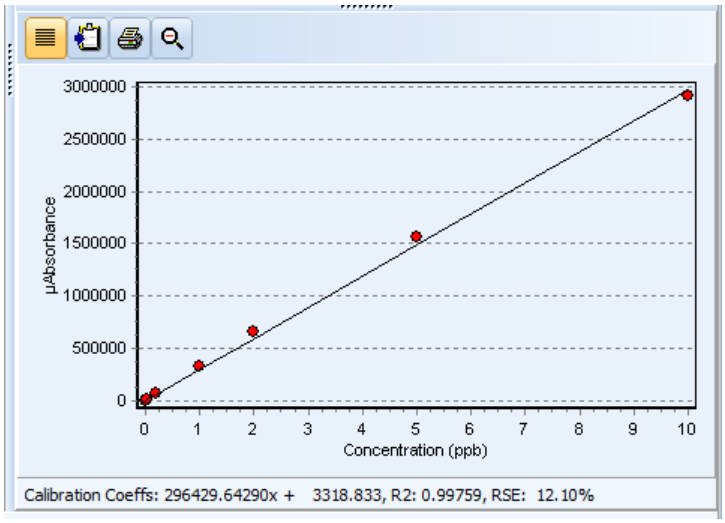


Figure 14 Peak Area Calibration with Random Placed Read Backs

Tube	Sample Label	Conc (ppb)	µAbs	%RSD	Flag	%Residual
S:1	Calibration Blank	0.000	3318.8	0.00		
S:2	Standard #1 (0.04 ppb)	0.040	16601.0	0.00		12.02
S:3	Standard #2 (0.2 ppb)	0.200	70528.3	0.00		13.37
S:4	Standard #3 (1.0 ppb)	1.000	331169.6	0.00		10.60
S:5	Standard #4 (2.0 ppb)	2.000	659707.7	0.00		10.72
S:6	Standard #5 (5.0 ppb)	5.000	1568488.0	0.00		5.60
S:7	Standard #6 (10.0 ppb)	10.000	2910093.0	0.00		-1.94
1:1	Blank	-0.009	767.9	0.00		
1:2	5 ug/L	5.429	1612574.0	0.00		
1:3	0.04 ug/L	0.040	15239.5	0.00		
1:4	10 ug/L	9.965	2957260.0	0.00		
1:5	2 ug/L	2.201	655893.4	0.00		
1:6	0.2 ug/L	0.220	68466.4	0.00		
1:7	1 ug/L	1.133	339034.3	0.00		
1:8	10 ug/L (3% HCL)	10.024	2974678.0	0.00		

Figure 15 0.04 µg/L Read Back Directly Following a 5.0 µg/L

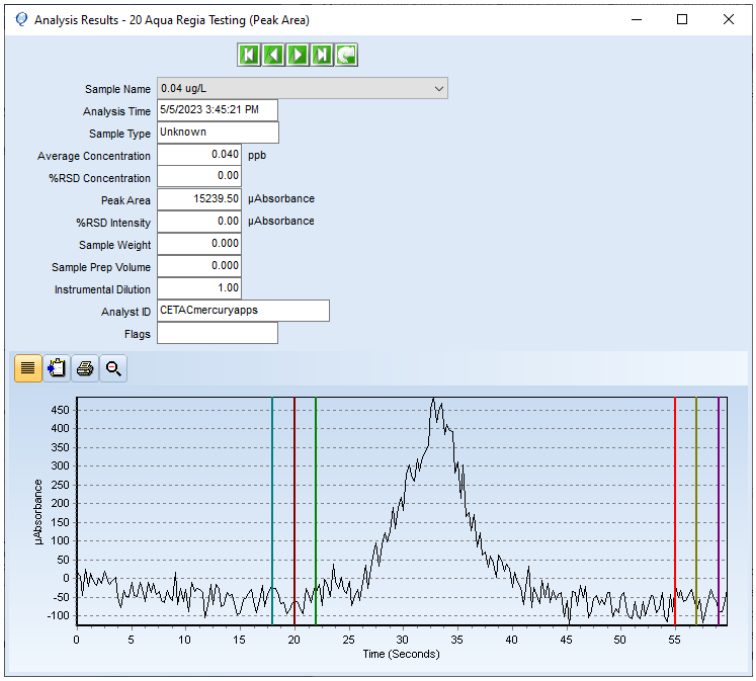
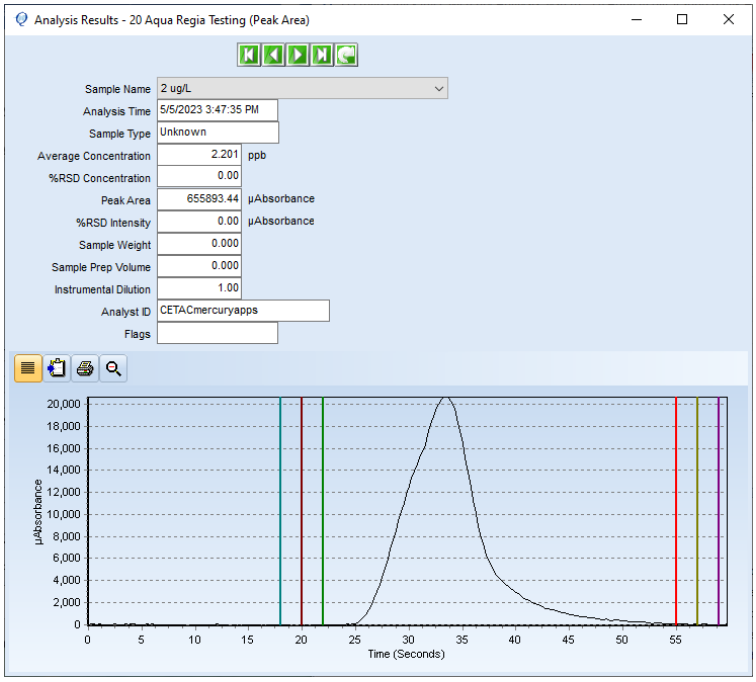


Figure 16 2.0 µg/L Read Back Directly Following a 10.0 µg/L



Results

To delineate the data from the peak height and/or peak area in 20% aqua regia the standards and read back results were gathered and comparisons of the concentrations and responses were prepared. (See Figure 17 and Figure 18.)

Figure 17 Peak Height Figures of Merit

20 % Aqua Regia Peak Height Data

Standard Solutions	Read Back Conc.	Conc. % Of Theoretical	Calibration Response	Read Back Response	Read Back % Of Calibration
5 ug/L	5.038	100.8	64516.1	65056.5	100.84
0.04 ug/L	0.040	100.0	561.8	533.5	94.96
10 ug/L	9.866	98.7	128962.3	127390.3	98.78
2 ug/L	2.095	104.8	26387.9	27059.4	102.54
0.2 ug/L	0.210	105.0	2809.4	2724.6	96.98
1 ug/L	1.058	105.8	13664.5	13675.1	100.08
10 ug/L (3% HCl)	10.235	102.4	NA	NA	NA

Figure 18 Peak Area Figures of Merit

20 % Aqua Regia Peak Area Data

Standard Solutions	Read Back Conc.	Conc. % Of Theoretical	Calibration Response	Read Back Response	Read Back % Of Calibration
5 ug/L	5.429	108.6	1568488.0	1612574.0	102.81
0.04 ug/L	0.040	100.0	16601.0	15239.5	91.80
10 ug/L	9.965	99.7	2910093.0	2957260.0	101.62
2 ug/L	2.201	110.1	659707.7	655893.4	99.42
0.2 ug/L	0.220	110.0	70528.3	68466.4	97.08
1 ug/L	1.133	113.3	331169.6	339034.3	102.37
10 ug/L (3% HCl)	10.024	100.2	NA	NA	NA

Discussion

The results from either the peak area or peak height method were very acceptable. Both methods were very speedy at 90 seconds for peak height and 60 seconds for peak area. Using the lag prior to the peak inflection point in peak height saved approximately 20 seconds of total analysis time for the peak height method. The figures of merit for both methods are shown below. (See Table IV.)

Table IV Method Figures of Merit —20% Aqua Regia

	Height	Area
Total Time / Sample (s)	90	60
Sample Time / Sample (s)	35	6
Rinse Time / Sample (s)	55	54
Sample Consumed (mL)	4.1	1
Stannous Chloride Consumed / Sample (mL)	2.8	2.7
Rinse Consumed / Sample (mL)	6.4	9.0
Total Waste / Sample (mL)	13.3	12.7

Conclusions

Either Peak Area or Peak Height parameters would generate success with a high degree of confidence. The total waste and stannous used on a per sample basis was about the same. The biggest difference is the sample pulled for Peak Area was 1 mL or about 24 percent of what was consumed in the Peak Height method. This would mean a vastly reduced digestion volume, further enhancing the green chemistry effect from the smaller ID peristaltic pump tubing harness.

The next gratifying benefit is the sample time. Peak Area was about 33% faster. The rate would mean that in a 4-hour time, Peak Area would produce 240 results comprised of standards, quality control, duplicates, and duplicate spikes, where the Peak Height totals would be just 160 results.

By reducing the internal diameter (ID) of the tubing used on the QuickTrace® M-7600 mercury analyzer, accurate calibration results can be achieved while decreasing reagent cost and hazardous waste—even for a difficult matrix such as 20 percent aqua regia while using multiple quantitation modes. It was shown that 20 percent aqua regia can be introduced into the system without sacrificing performance.