Green Chemistry: Determination of Mercury in Wastewater (ERM®-CA713) Following US EPA Method 7470A 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 sources. Monitoring this toxin in wastewater is required to ensure human and environmental health.

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.[1,2] 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, laboratories can cut their hazardous waste generation and reduce overall operating expenses.

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

Following our study of the use of reduced internal diameter (ID) tubing when performing 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 when performing US EPA Method 7470A.[3,4] This study will also demonstrate the development of a performance-based method and optimization of the Teledyne Leeman Labs' QuickTrace® M-7600 mercury analyzer parameters for EPA 7470A. The total elemental mercury (Hg^0) in Institute for Reference Materials and Measurements (IRMM) certified reference material (CRM) ERM®-CA713 "Wastewater Effluent" 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 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 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 preconcentration.

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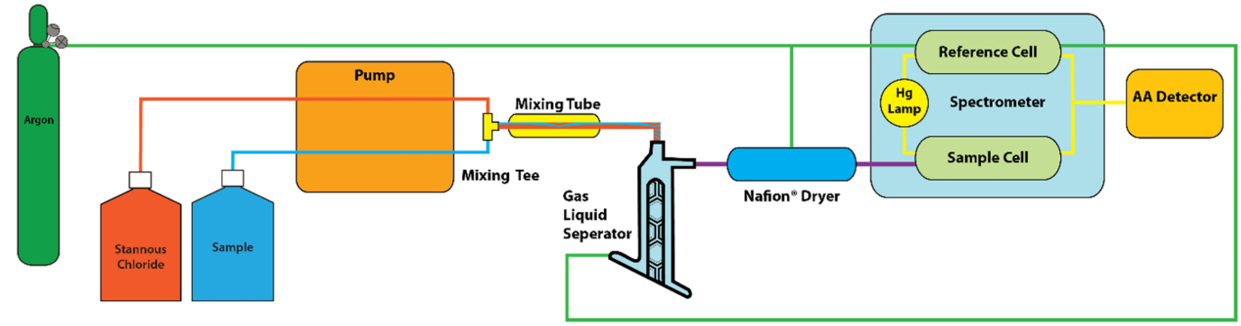
Figure 2 QuickTrace® M-7600 Process Diagram



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: sample and waste lines were white/white 1.02 mm tubing (TLL PN 15-4308-102), while the stannous chloride reductant line was flared orange/yellow 0.51 mm tubing (TLL PN 15-4309-102). The QuickTrace® software provided method specific control of the analyzer and autosampler, allowing parameter optimization for the quantitation of mercury in a chosen dynamic range. Method parameters are shown in Table I and Figure 3.

Table I US EPA Method 7470A 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)	150
	Pump Speed (%)	70
	Replicate Read Time (sec)	0.75
	Replicates	4

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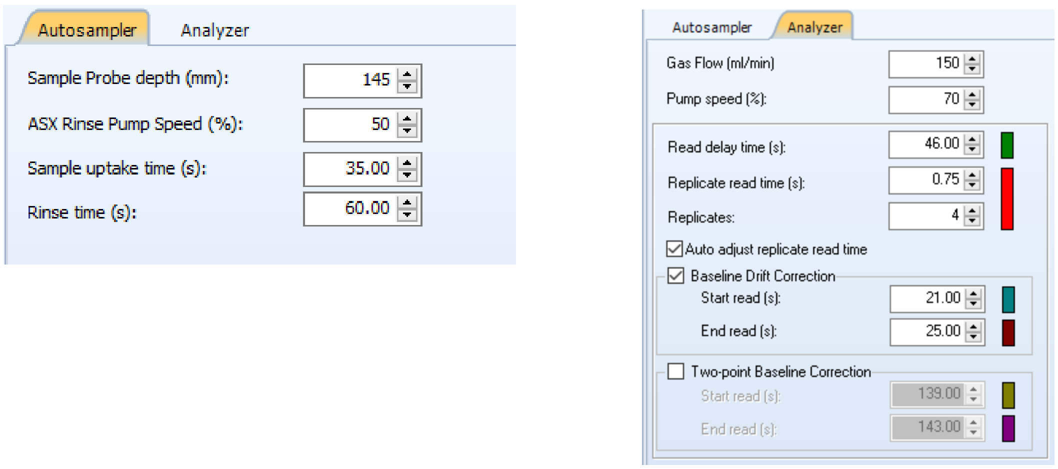
Figure 3 EPA 7470A Autosampler and Analyzer Conditions shown in the M-7600 QuickTrace® Software



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. A 10 mL aliquot 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 (Hg^{2+}) to elemental mercury (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 ±0.11 µg/L.

CALIBRATION STANDARDIZATION

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. 10 mL of the calibration standards were added to 50 mL digestion tubes.

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Table II Calibration Standard Preparation									
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 4 and a 10 µg/L peak profile is shown in Figure 5.

Figure 4 Six-Point Calibration Curve

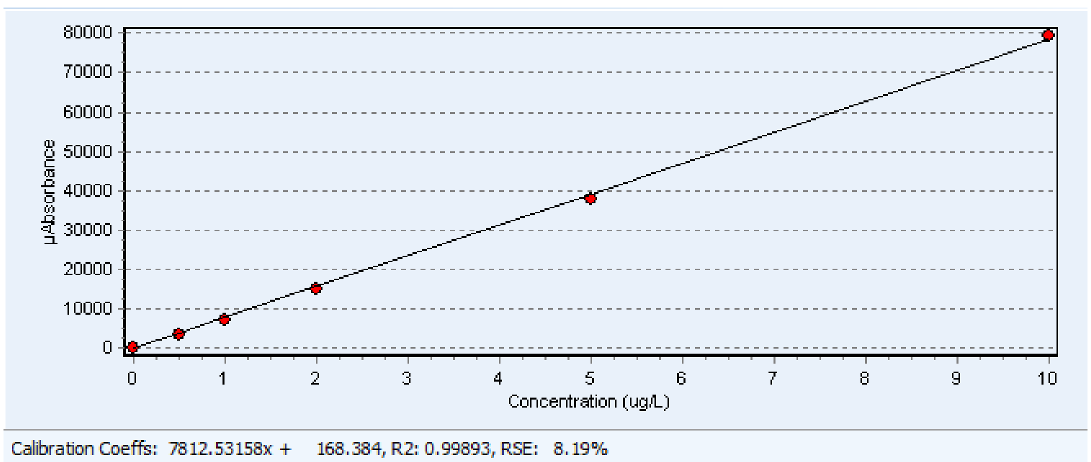
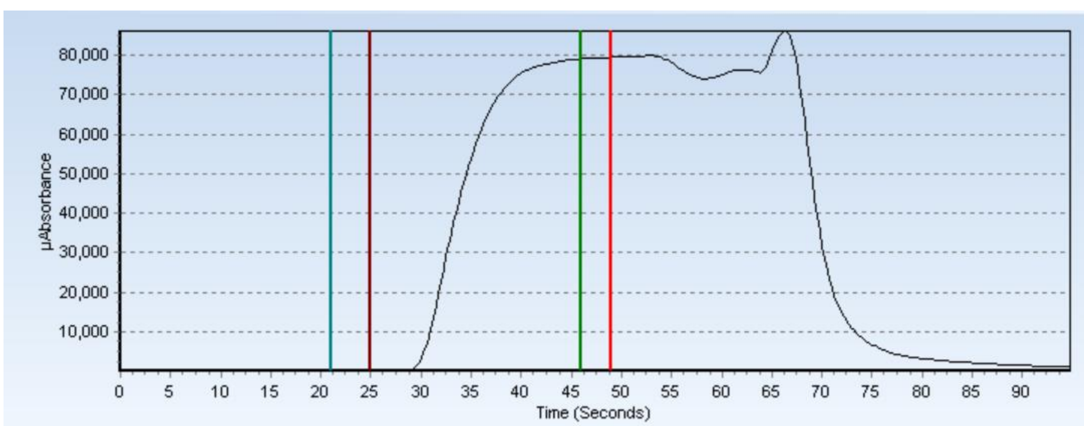


Figure 5 10 µg /L Peak Profile



RESULTS

Total mercury in wastewater samples at µg/L levels was easily recovered using the reduced ID tubing and optimized QuickTrace® software method parameters. Seven replicates of the digested CRM were analyzed and the total mercury concentration in µg/L was recorded. ERM®-CA713 is certified at 1.84 µg/L total mercury, with an uncertainty at 95% of ±0.11 µg/L. A separate 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.[5] The mean concentration, standard deviation and uncertainty at 95% are shown in Figure 6. QC check results are shown in Figure 7.

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

Wastewater, ERM CA713, 1.84 µg/L ± 0.11		
Digest	µg/L	
1	1.97	
2	1.93	
3	1.94	
4	1.97	
5	1.98	
6	1.98	
7	2.03	
Mean =	1.97	
Uncertainty =	0.0237 @ 95 % Confidence	
n = 7 Replicates	STDEV = 0.032	RSD% = 1.642

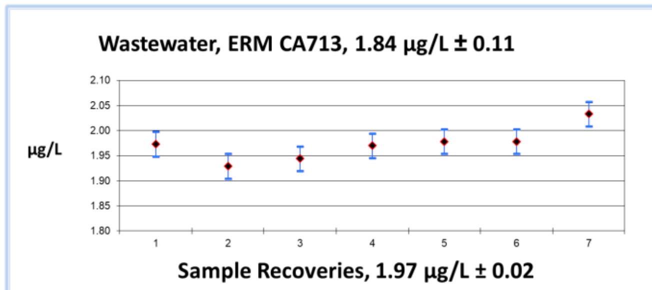


Figure 7 Quality Control (QC) Results

EPA 7470A Quality Control		
Quality Control (µg/g)	% Recovery	RPD%
ICV	96.1	
CCV/LCS	96.2	
MS	94.6	
MSD	95.9	1.04

DISCUSSION

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 ~38 unknown and QC checks results reported per hour. The sample rate is 1 sample every ~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 ~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.

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.

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