



The Determination of Mercury in Waters by U.S. EPA Method 245.1 Cold Vapor Atomic Absorption Spectroscopy

Introduction

Mercury is a toxic element found throughout the environment. Its mobile nature allows it to diffuse through the air, soils and ultimately into water systems. Fish have the ability to bio-accumulate mercury (in its methylated form) at much higher concentrations than the waters they inhabit. People and wildlife that consume fish high in mercury are at risk. Today, there are over 2000 water bodies in the United States where advisories are posted to limit consumption of fish known to contain significant levels of mercury. The Clean Water Act (CWA) requires monitoring mercury concentrations in effluent, waste and ambient waters to ensure that our waters remain safe to both mankind and wildlife. Many laboratories employ U.S. EPA Method 245.1 to monitor mercury in effluent, waste and ambient waters. This report provides the details for the operation of the Hydra II_{AA} according to EPA method 245.1.

Instrumentation

The analysis was performed using the Hydra II_{AA} shown in Figure 1. The Hydra II_{AA} includes an extended range spectrometer, a high-capacity autosampler, variable speed peristaltic pump, serpentine gas/liquid separator, and flow-through rinse. The tri-cell optical design allows the analyst to select the optimum system sensitivity, achieving either part-per-trillion detection limits or linearity in excess of 1 part-per-million. This flexibility delivers optimum results for both clean water and contaminated soil analyses. The autosampler design addresses issues of recurring QC volume with built-in reservoirs for repetitive checks and sample capacity with up to 270 sample locations available. Its 5-channel peristaltic pump precisely delivers sample and reductant solutions under computer control while actively removing system waste solutions. The Hydra II_{AA} employs the same bubble-busting serpentine gas/liquid separator as its predecessor so that difficult to digest and frothy samples can be analyzed easily. With the Hydra II_{AA} less waste is produced since its flow-through rinse is replenished by a separate pump which is active only when the sample probe is at the rinse station. Laboratories that require high reliability and low service costs will appreciate the Hydra II_{AA}'s modular design that facilitates overnight replacement of any component.

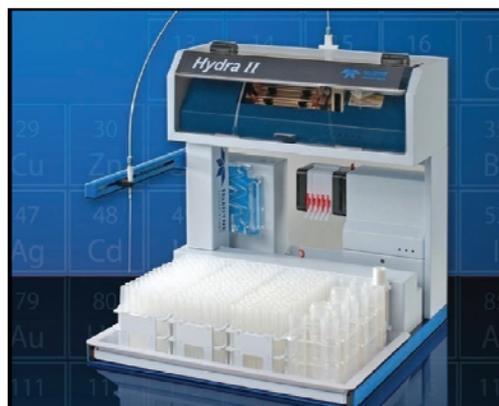


Figure 1: The Hydra II_{AA}

Experimental

Sample and Standard Pretreatment

In water samples, mercury must be oxidized to the mercuric (Hg^{+2}) state before it can be reduced with stannous chloride to free mercury (Hg^0) and then measured by cold vapor atomic absorption spectroscopy. Oxidation to the mercuric form is accomplished by reaction with potassium permanganate and potassium persulfate at low pH. Immediately before analysis the excess oxidants are neutralized with hydroxylamine sulfate/sodium chloride.

Calibration standards of 0.0, 0.2, 0.5, 1.0, 5.0, and 10.0 ppb mercury were prepared. Prior to analysis, samples and standards are taken through the same digestion procedure specified by U.S. EPA method 245.1. 100 mls of sample or spiked standard are placed in a BOD bottle. Acids and reagents are placed in the bottle and the samples are then put into a water bath at 95°C for 2 hours. They are then removed and allowed to cool to room temperature. At this stage all solutions should appear purple in color or the sample digestion requires more potassium permanganate. If all the solutions are still purple hydroxylamine sulfate/sodium chloride is added and the solutions are bubbled with argon for 15 minutes to remove free chlorine. This final bubbling step should not be skipped as free chlorine absorbs light at the wavelength used for Hg analysis and is therefore a possible interferent if not removed. At this point, solutions should be clear and colorless.

Analysis

The Hydra II_{AA} is designed to react samples and standards with stannous chloride to produce free gaseous mercury which is transported via carrier gas to a 10 inch absorption cell for determination. The instrument settings used for this work appear in Table 1 and are optimized for the 0.01-10 ppb concentration range. Sample volumes required for analysis are about 5 ml per sample at these instrument settings. To work at higher concentrations the operator can decrease the peristaltic pump rate used for sample delivery or increase the gas flow. For additional linear range the operator can substitute the 1 inch optical cell supplied with the instrument.

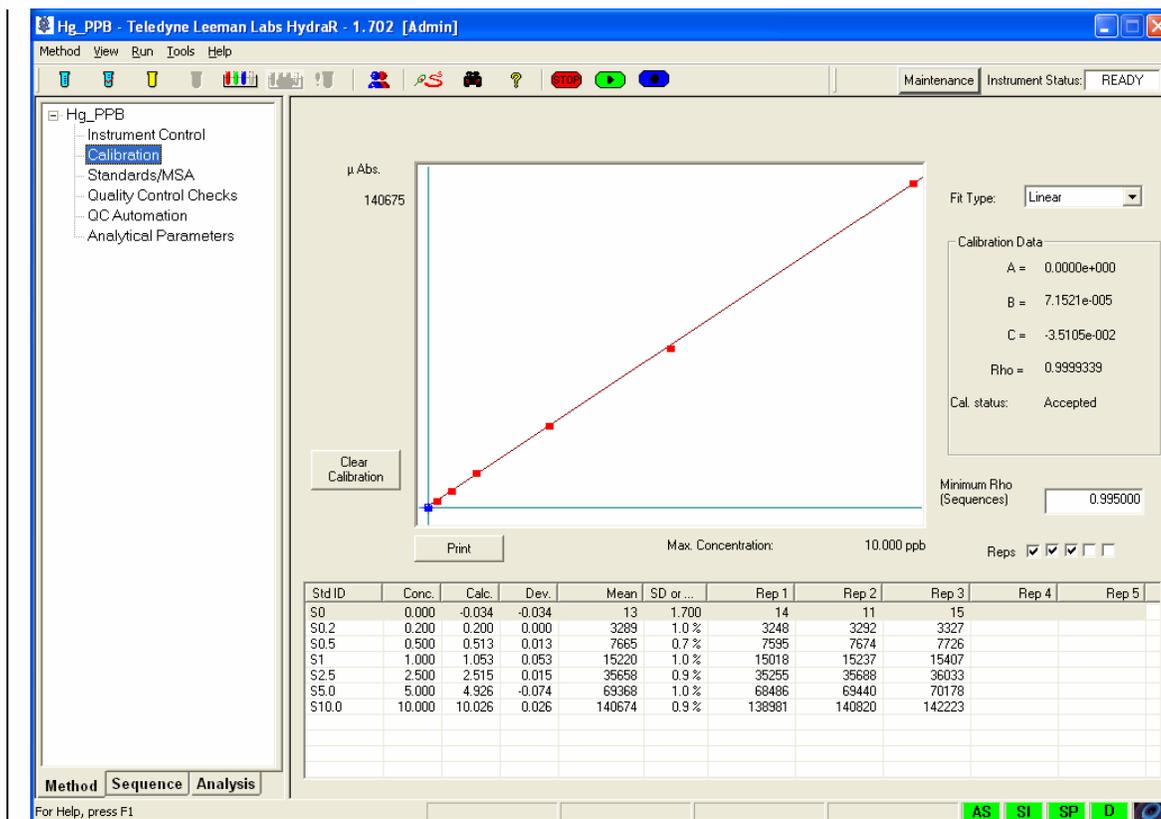
Table 1: Hydra II_{AA} Instrument Conditions

Pump rate	7 ml/min
Gas flow	0.2 L/min
Gas type	Argon
Rinse	55 sec
Uptake	55 sec
Replicates	3
Integration	3 sec

During analysis the Hydra II_{AA} combines a solution of 10% (w/w) stannous chloride in 10% HCl together with samples or standards in a mixing tee where reduction to mercury vapor (Hg^0) occurs. The mixed solution enters a gas/liquid separator where argon passes through the solution carrying the mercury vapor to the absorption cell for measurement. Alternatively, sodium borohydride solution (1% NaBH_4 in 0.6% NaOH) can be employed in place of the stannous chloride; however, the signal response will be less than with the stannous chloride.

Calibration standards are entered into the Hydra II_{AA} software at their original concentrations as dilution of samples and standards by reagents is identical. The resultant calibration curve appears in Figure 1. Note the accuracy at the low concentrations necessary to pass the method 245.1 CRA quality control requirement ($0.2 \pm 20\%$). The calibration exhibits excellent linearity with a correlation coefficient of 0.9999.

Figure 1. Calibration curve



Two quality control samples were obtained from Environmental Resource Associates, one wastewater (Lot P164-514) and one potable water (Lot S145-666) for analysis. The digestions include a Laboratory Reagent Blank (LRB), a Laboratory Fortified Blank (LFB) and sample duplicate and Laboratory Fortified Sample Matrix for each sample. Some samples and spikes were above the linear range of the calibration and were diluted 1:3 with DI water after digestion. The sample results appear in Table 2.

Table 2. Certified reference material results (ppb)

Sample name	Certified Value	QC PALs TM	Result	% Accuracy
P164-514	15.0	13.1-17.8	13.96	93.1 %
S145-666	7.57	6.16-10.3	7.44	98.3 %

QC PALs is the QC Performance Acceptance Limits

The sample quality controls are presented in Table 3 with the relative percent difference for the duplicates and % recovery for the spikes.

Table 3. Sample quality control results (samples spiked at 10ppb)

Sample	Result (ppb)	Relative Percent Difference	Recovery
514	13.96		
514 Dup	14.42	3.2%	
514 Spike	24.08		101.2%
666	7.44		
666 Dup	7.83	5.1%	
666 Spike	16.98		95.4%

Conclusions

The Hydra II_{AA} demonstrates excellent accuracy and precision. Recovery of the 0.2 ppb standard was 100% indicating good accuracy at low concentrations. The relative standard deviation for the three replicates of each standard was 1% or less.

The recovery of the digested water samples and all method and sample QC was within specifications.

The system linearity was good and higher level samples can be run without dilution if needed by adjusting the analysis parameters or substituting the smaller optical cell to increase the linear range. The system's automated over-range protection can be used to prevent high level Hg contamination and monitor the return to baseline before continuing with the next sample.

The system can be easily converted to direct thermal combustion AA analysis to eliminate the need for sample digestion.

Because of its accuracy, precision, linear range and flexibility the Hydra II_{AA} is an ideal tool for the determination of drinking and waste waters by cold vapor atomic absorption spectroscopy.