Hydra AA **Application Note: # 1038**

The Determination of Mercury in Waters by Cold Vapor Atomic Absorption Spectroscopy

Introduction

Hydra AA Mercury Analyzer

Mercury is a toxic element found throughout the environment. Its mobile nature allows it to diffuse through the air, soils, and ultimately water systems. Fish have the ability to bio-accumulate mercury (in its methylated form) to 100,000 times the concentration of the waters they inhabit. As a result, fish consumption advisories are posted for over 2,000 bodies of water within the United States. Many laboratories are charged with the important task of monitoring mercury in effluent, waste, and ambient waters. This method provides details for the operation of the Hydra AA according to existing EPA methodology (7470 and 245.1).

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. 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 hydrochloride.

Calibration standards of 0.0, 0.2, 0.5, 1.0, 2.0, and 6.0 ppb mercury are prepared in 2% HCl. Prior to analysis, samples and standards are taken through the same digestion procedure. This is accomplished by placing 4 mls of sample or calibration standard into 15 ml polypropylene test tubes. Reagents 1 - 4 listed in Table 1 are then added to each test tube and mixed. The tubes are then placed into a water bath at 95^{o}C for 2 hours after which they are removed and allowed to cool to room temperature. At this stage all solutions should appear purple in color or the sample digestion requires more permanganate. If all the solutions are purple, then reagents 5 and 6 in Table 1 are added and the solutions are allowed to sit for 15 minutes before bubbling each with argon 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 an interferent if not removed.

Heater setting	95°C
Sample size	4 ml
Sample matrix	0.2% HCl:0.2% HNO_3
Reagents	
1	0.2 ml H_2SO_4 (conc.)
2	0.1 ml HNO_3 (conc.)
3	1.2 ml $KMnO_4$ (5%)
4	0.32 ml $K_2S_2O_8$ (5%)
5	1.333 ml NaCl:$(NH_2OH)_2 \cdot H_2SO_4$
6	1.000 ml distilled water

Table 1: Sample and Standard Pretreatment

Analysis

The Hydra AA is designed to react samples and standards with stannous chloride to produce free gaseous mercury which is transported via carrier gas to a 30 cm absorption cell for determination. The instrument settings used for this work appear in Table 2 and are optimized for the 0.1-10 ppb concentration range. Sample volumes required for analysis are about 6.5 ml per replicate reading at these instrument settings. To work at higher concentrations the operator simply decreases the peristaltic pump rate used for sample delivery or increase the gas flow.

Pump rate	7 ml/min
Gas flow	0.15 L/min
Gas type	Argon
Rinse	45 sec
Uptake	20 sec
Replicates	3
Integration	25 sec

Table 2: Hydra Instrument Conditions

During analysis the Hydra AA (Figure 1) 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 occurs (Hg^0). 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% NaCl) can be employed in place of the stannous chloride; however, the signal response will be less than with the stannous chloride.

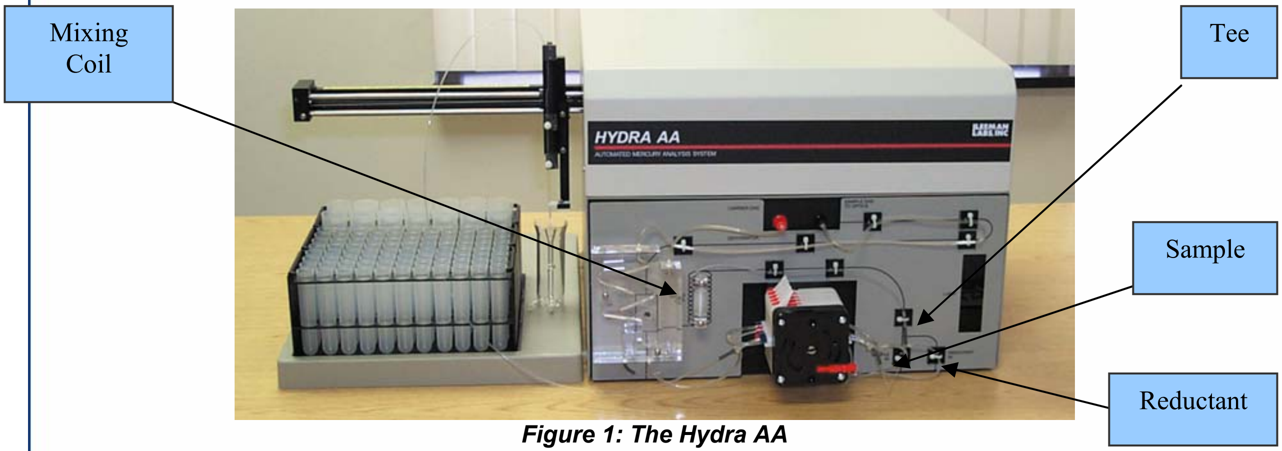
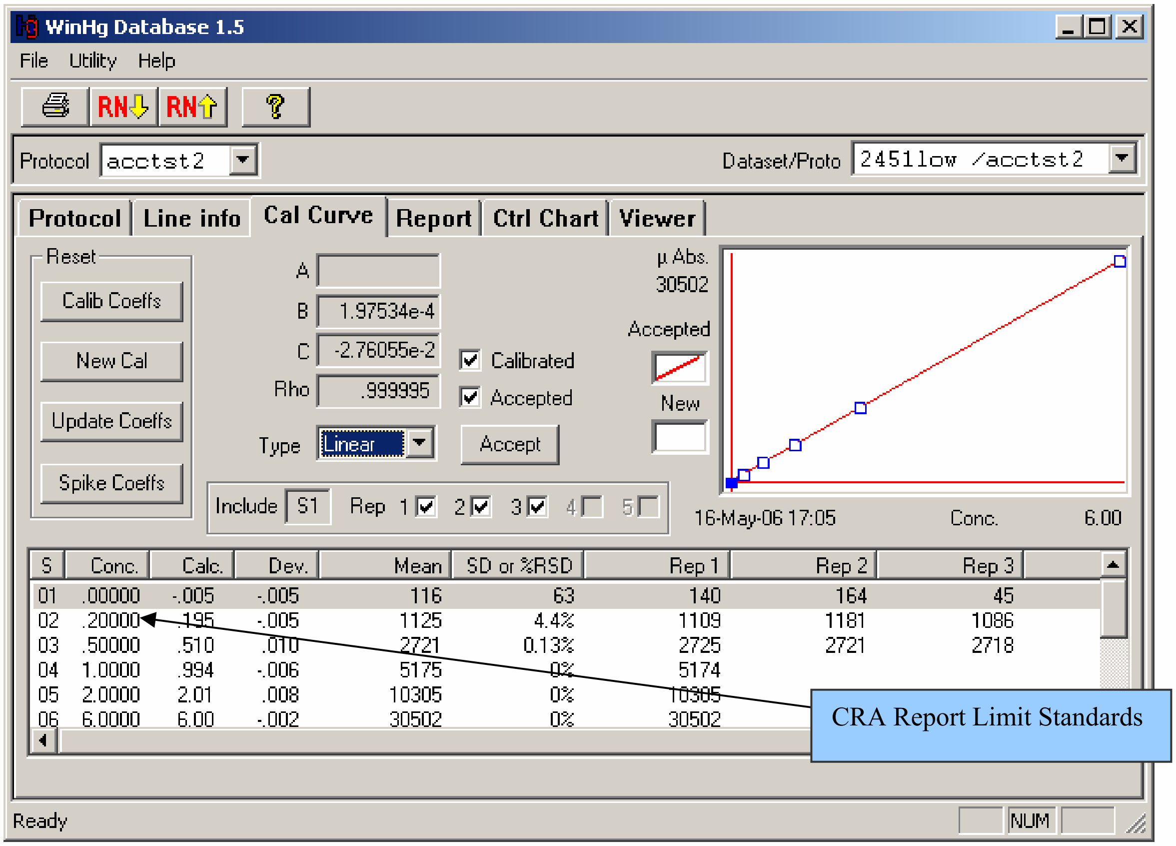


Figure 1: The Hydra AA

Calibration standards are entered into the Hydra AA software at their original concentrations as dilution of samples and standards by reagents is identical. The resultant calibration curve appears in Figure 2. Note the accuracy at the low concentrations necessary to pass the method 245.1 CRA quality control requirement (0.2 ± 20%). The calibration exhibits excellent linearity with a correlation coefficient of 0.999995.



Protocol acctst2

Dataset/Proto 2451low /acctst2

A

B 1.97534e-4

C -2.76055e-2

Rho .999995

Type Linear

☑ Calibrated

☑ Accepted

Include S1 Rep 1 ☑ 2 ☑ 3 ☑ 4 ☐ 5 ☐

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S	Conc.	Calc.	Dev.	Mean	SD or %RSD	Rep 1	Rep 2	Rep 3
01	.00000	-.005	-.005	116	63	140	164	45
02	.20000	.195	-.005	1125	4.4%	1109	1181	1086
03	.50000	.510	.010	2721	0.13%	2725	2721	2718
04	1.0000	.994	-.006	5175	0%	5174		
05	2.0000	2.01	.008	10305	0%	10305		
06	6.0000	6.00	-.002	30502	0%	30502		

CRA Report Limit Standards

Ready

Figure 2: Hydra Calibration

A reference material was analyzed to determine method accuracy. The sample contains mercury at elevated concentration and must be diluted about 1000-fold prior to use. Sample dilution was performed prior to digestion. Results appear in Table 3.

Sample	**Diluted Conc.**	**Corrected Conc.**	**True Conc.**	**Recovery**
1641d	1.47 µg/L	1.47 mg/L	1.59 mg/L	92.5%

Table 3. Certified Reference Material

Conclusions

The Hydra AA demonstrates excellent accuracy, even at low concentrations, as can be seen in the CRA report limit standard shown in Figure 2. Some states require laboratories analyzing drinking waters with Method 245.1 to return the CRA standard (0.2 ppb) within ± 20%. From the calibration curve, three replicates for this standard returned a value of 0.195 ppb (98%) at a precision of 4.4% RSD.

The analysis of NIST 1641d water shows good recovery for digested water samples (92.5%).

The system linearity is exceptionally good. Note that none of the standards shown in Figure 2 exhibit a concentration deviation greater than 10 ppt using a standard linear fit algorithm (unweighted).

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