

Hydra II_{AA}

Application Note # 1062



The Determination of Mercury in Soils, Sediments and Sludges by U.S. EPA Method 245.5 Cold Vapor Atomic Absorption Spectroscopy

Introduction

Mercury is a toxic element found throughout the environment. The natural abundance of mercury in most soils is usually quite low (0.08 ppm)¹; however, elevated levels of mercury may be found in areas where gold mining, chlor-alkali production or paper manufacture has taken place. Also, leakage from landfills where objects high in mercury (such as auto parts, batteries, fluorescent bulbs, medical products, thermometers, and thermostats) have been disposed can result in high mercury concentrations in soil. In some cases significant mercury concentrations in soil result from atmospheric deposition. Regardless of the source, the runoff of soil with high mercury levels threatens any nearby waters, any fish that inhabit these waters, and the wildlife & people who consume the native fish. To protect the environment and ensure public safety, many laboratories are involved in monitoring mercury in soils, sediments and sludges. This note provides the details for the operation of the Hydra II_{AA} according to EPA method 245.5, the reference method for the determination of mercury in soils, sediments and sludges by cold vapor atomic absorption spectroscopy.

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.



Figure 1: Hydra II AA

¹¹ "[Mercury-containing Products](http://www.epa.gov/epaoswer/non-hw/reduce/epr/products/mercury.htm)". United States Environmental Protection Agency (EPA). <http://www.epa.gov/epaoswer/non-hw/reduce/epr/products/mercury.htm>.

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.

Experimental

Sample and Standard Pretreatment

In soil, sediment and sludge samples the mercury is first leached from the insoluble material by reaction with aqua regia, followed by oxidation to the mercuric (Hg^{+2}) state by reaction with potassium permanganate. Immediately before analysis the excess oxidants are neutralized with hydroxylamine sulfate sodium chloride.

Calibration standards of 0.0, 10.0, 20.0, 50.0, and 100.0 ppb mercury were prepared. Prior to analysis, samples and standards are taken through the same digestion procedure specified by the method. About 0.5 gm of sample or 10.0 mL of standard is placed in each BOD bottle. 5 mL of aqua regia is added to each bottle and the bottles are then placed into a water bath at 95°C for 2 minutes. The bottles are then removed and allowed to cool to room temperature before adding 50 mL of de-ionized water and 1.0 mL of potassium permanganate (5%) solution. Bottles are again placed in the water bath at 95°C and heated for 30 minutes. At this stage all solutions should appear purple in color or the sample digestion requires more permanganate. If all the solutions are still purple, 6.0 mL of hydroxylamine sulfate/sodium chloride is added and the solutions are allowed to sit for 15 minutes bubbling 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 a possible interferent if not removed. Finally, all samples and standards are brought to 100 mL with de-ionized water.

Analysis

The Hydra II_{AA} is designed to react liquid 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 reading 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.

Pump rate	7 mL/min
Gas flow	0.2 L/min
Gas type	Argon
Rinse	55 sec
Uptake	55 sec
Replicates	2
Integration	3 sec

Table 1: Hydra II_{AA} Instrument Conditions

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 (Hg⁰) 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% NaBH₄ in 0.6% NaOH) can be employed in place of the stannous chloride; however, the signal response will be somewhat lower than with the stannous chloride.

Calibration standards are entered into the Hydra II_{AA} software at their original concentrations. In the sequence table the weight for each sample is entered along with 10.0 for volume to compensate for the dilution of samples and standards. The resultant calibration curve appears in Figure 2. The calibration exhibits excellent linearity with a correlation coefficient of 0.9999+.

NOTE- The actual concentration of the high standard is 100ppb * 10.0mL/100mL or 10ppb, well within the linear range of the Hydra II_{AA}.

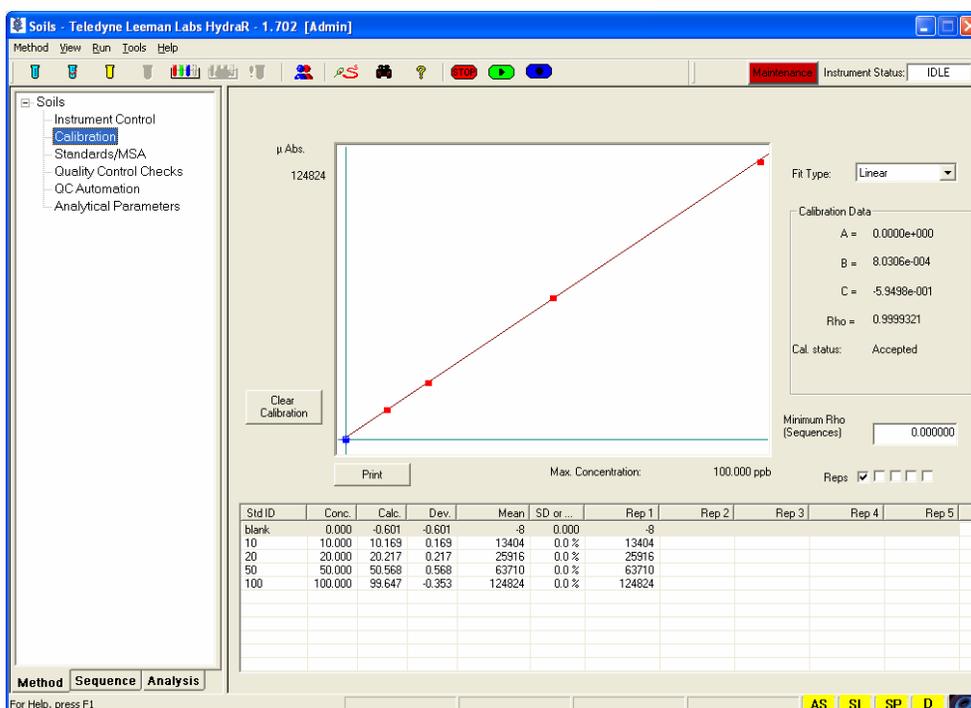


Figure 2: Calibration Curve

Four quality control soil samples were obtained from NIST² for analysis. Some sample and spikes were above the linear range of the calibration and were diluted with de-ionized (DI) water after digestion but prior to analysis. The sample results appear in Table 2.

² National Institute of Standards and Technology, 100 Bureau Drive, Stop 1070, Gaithersburg, MD 20899-1070

Standard Reference Material Number	Standard Reference Material Name	Certified Value (ppm)	Result (ppm)	% Accuracy
1646a	Estuarine Sediment	N.A	0.022	-
2704	Buffalo River Sediment	1.44 ±0.07	1.47	102.1%
2709	San Joaquin soil	1.40 ±0.08	1.41	100.7
2710 ³	Montana Soil	32.6 ±1.8	33.1	101.5
2711 ⁴	Montana Soil	6.25 ±0.19	6.17	98.7

Table 2. Standard Reference Materials

Conclusions

The Hydra II_{AA} demonstrates excellent accuracy and precision even at low concentrations. The relative standard deviation for the two replicates for each standard was <1% and the standards were all within 2.1% of their true concentrations.

The accuracy of the digested soils and sediments were well 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 detect high level samples and monitor the return to baseline before beginning the next sample.

The system can be easily converted over for direct thermal combustion AA analysis of samples without the need for digestion.

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

³ This sample required an additional 1:5 dilution to fall within the calibration range.

⁴ This sample required an additional 1:2 dilution to fall within the calibration range.