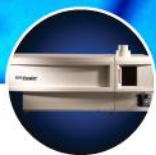


Hydra-C



Application Note: 1076

The Determination of Mercury in Samples by U.S. EPA SOW 846 Method 7473 using the Hydra-C Mercury Analyzer

Introduction

The accurate determination of mercury in various samples is important for the proper and safe disposition of these materials. The **Hydra-C** Direct Mercury Analyzer provides fast, simple and convenient analyses of these materials without sample pretreatment or production of hazardous chemical waste. A typical sample analysis takes only about 5 minutes and requires virtually no sample preparation. The **Hydra-C** employs U.S. EPA Method 7473 which has been approved for both laboratory and field analysis.

Instrumentation

The **Hydra-C** (shown in Figure 1) is fully automated for unattended operation, comes complete with a 70 position autosampler and has on-the-fly loading capability for virtually unlimited sampler capacity. **Hydra-C** operates from a single 110/220V, 50/60 Hz power supply and oxygen supplied at 15-20 psig. All instrument operating parameters (e.g. furnace temperatures, gas flows, autosampler control and process stages) are computer controlled for ease-of-use.



Figure 1. Hydra-C Mercury Analyzer

Principle of Operation

Hydra-C operates on the principle of thermal decomposition to liberate elemental mercury from solid or liquid samples. Figure 2 shows a schematic diagram of **Hydra-C's** principle of operation. First, a weighed sample is deposited into a sample boat and introduced into the decomposition furnace. After the furnace is closed, an oxidant (typically oxygen or compressed air) begins to flow over the sample and the furnace temperature is ramped in two stages; first to dry the sample, then to decompose it.

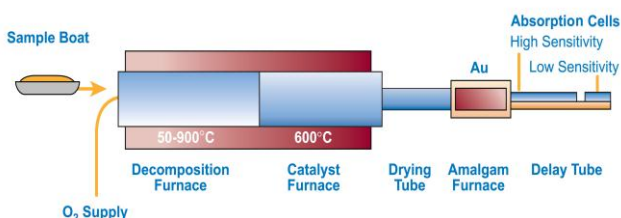


Figure 2. The Hydra-C principle of operation

The analytical process typically involves combusting (thermal decomposition) the sample at high temperatures with oxygen; although, for some applications gentle heating of the sample in air is adequate to release the mercury. During the combustion step the evolved gases are carried through a heated catalyst to produce free mercury while removing halogens, nitrogen oxides, and sulfur oxides. The remaining combustion products including elemental mercury (Hg⁰) are swept first through a dryer and then through a gold amalgamation trap where all elemental mercury is captured. Following the decomposition step, the amalgamation trap is heated and the free mercury is carried into an atomic absorption spectrometer. The mercury level is reported using a wide dynamic range detection system that operates from 0.005 ng (its detection limit) to its upper limit of 1000 ng. For applications requiring significantly higher detection capability an optional high range detection system is available which can be used to analyze samples containing up to 20,000 ng of Hg per sample deposition.

Experimental

Table 1 shows the instrument parameters employed for the calibration. Some of the sample matrices analyzed required slightly different drying conditions for optimum results. Nickel boats were used for all the samples in this analysis.

Table 1: System Parameters

| Parameter | Water | Biological | Coal | Soil |
|----------------------|-----------------------|--------------------|--------------------|--------------------|
| Dry | 300°C for 30-140 sec. | 300°C for 70 sec. | 300°C for 30 sec. | 300°C for 30 sec. |
| Decomposition | 800°C for 150 sec. | 800°C for 150 sec. | 800°C for 250 sec. | 800°C for 150 sec. |
| Catalyst | 600°C | | | |
| Catalyst Wait Period | 60 sec. | | | |
| Gold Trap | 600°C for 30 sec. | | | |
| Measurement | 100 sec. | | | |
| Oxygen Flow | 350 ml/min | | | |

Calibration

Calibration was completed using aqueous standards prepared in 1% HNO₃. Working standards included a blank, 0.1, 1.0 and 10.0 ppm solution. The calibration curves are displayed in Figures 3 and 4 as micro absorbance vs. total mercury injected.

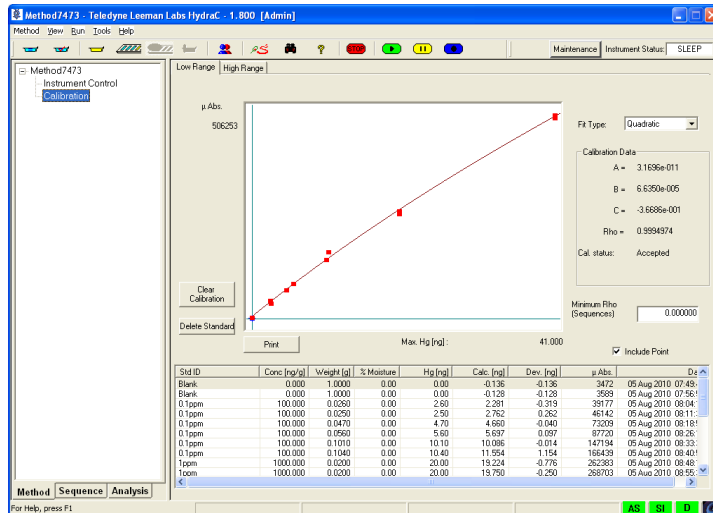


Figure 3. Hydra-C Low Concentration Range (0-40 ng)

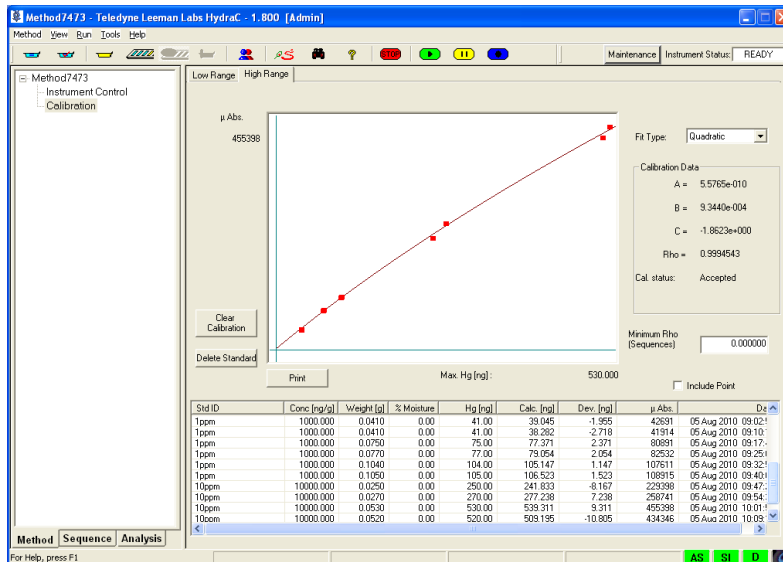


Figure 4. Hydra-C High Concentration Range (40-500ng)

Results

Before any analysis began the Instrument Detection Limit (IDL) and Method Detection Limit (MDL) were determined. The IDL was obtained by analyzing seven replicate blanks and the MDL was determined by analyzing seven replicates of NIST SRM8437 (Hard Red Spring Wheat Flour). The IDL was determined to be 0.005 ng and the MDL was determined to be 0.02 ng. The data used to calculate these are presented below in Table 2.

Table 2: IDL and MDL results

| Replicate | IDL (ng Hg) | MDL (ng Hg) |
|-----------|-------------|-------------|
| 1 | 0.010 | 0.192 |
| 2 | 0.011 | 0.179 |
| 3 | 0.010 | 0.179 |
| 4 | 0.014 | 0.189 |
| 5 | 0.013 | 0.195 |
| 6 | 0.011 | 0.180 |
| 7 | 0.012 | 0.182 |
| Std Dev | 0.0015 | 0.0067 |
| IDL | 0.0047 | 0.021 |

The method blank must be either below the MDL or $\leq 10\%$ the sample concentration for the results to be reportable. Quality control checks were analyzed every ten samples for both the low and high curves. The method requires the results for the quality control checks to be within $\pm 20\%$ of the certified value.

Four sample matrices were analyzed by this method. Each sample type was analyzed in duplicate and a spike was analyzed to determine recovery. A certified reference material of a similar matrix type was analyzed to check for accuracy. The results of the analysis are presented in Table 3. The average sample weight analyzed also is displayed in Table 3. Sample spike (MS) recovery and spike duplicate (MSD) relative percent difference are presented in Table 4. Spike recovery must be within $\pm 20\%$ and the relative percent difference between the spike and spike duplicate must be less than $\pm 20\%$.

Table 3: Certified reference material results

| Sample Matrix | Name | Average sample weight | Certified Concentration (PPM) | Measured Concentration (PPM) |
|---------------|---------------|-----------------------|-------------------------------|------------------------------|
| Water | ERA WasteWatR | 0.215g | 0.015 | 0.016 |
| Coal | SABS SARM20 | 0.133g | 0.250 | 0.233 |
| Biological | NIST 1515 | 0.135g | 0.044 | 0.043 |
| Soil | NIST 2704 | 0.121g | 1.480 | 1.451 |

Table 4: Recovery and precision study

| QC sample | Spike Added (ug/g) | MS/MSD Result (ug/g) | Sample Result (ug/g) | MS/MSD % Recovery* | MSD RPD |
|----------------------|--------------------|----------------------|----------------------|--------------------|---------|
| Prep Blank | | | 0.00001 | | |
| LCS | 0.025 | 0.026 | NA | 104.4 | 4.1 |
| | 0.025 | 0.025 | | 100.2 | |
| sample wastewater MS | 0.197 | 0.440 | 0.269 | 87.0 | 1.0 |
| | 0.175 | 0.423 | | 87.9 | |
| sample coal MS | 0.230 | 0.244 | 0.027 | 94.1 | 7.4 |
| | 0.183 | 0.187 | | 87.4 | |
| sample leaves MS | 0.033 | 0.040 | 0.010 | 89.7 | 11.4 |
| | 0.056 | 0.067 | | 100.5 | |
| sample soil MS | 0.058 | 0.110 | 0.057 | 92.4 | 15.0 |
| | 0.061 | 0.122 | | 107.4 | |

*MS %Recovery is calculated by subtracting the sample result from the spike result and dividing the difference by the spike added. To report as a percentage the calculated value is multiplied by 100.

Conclusion

All the quality control requirements of U.S. EPA Method 7473 were satisfied. Sample results obtained showed excellent precision and recovery. All CRM's showed good accuracy without any sample pretreatment requiring only about 5 minutes per sample analysis. Proper drying and decomposition conditions produce a matrix independent analysis of mercury in many sample types.