Determination of Total Mercury in Coal

Utilizing Direct Combustion for Mercury Analysis for coal and fly ash samples

Summary
Coal-fired power plants have been shown to be the largest contributor of anthropogenic mercury. This prompted the U.S. EPA, in March 2005, to issue a rule to cap and reduce mercury emissions from coal-fired utilities making the U.S. the first country in the world to regulate mercury emissions from such facilities.

Many laboratories have testing procedures in place to analyze for mercury in coal and other coal combustion by-products. These procedures have typically included the use of Cold Vapor Atomic Absorption (CVAA) or ICP-MS. Both of these techniques, although effective, require costly and time-consuming sample digestion prior to analysis. Direct mercury analysis, an alternative to these methods, has been used successfully to determine total mercury in coal and related matrices. This technique requires no sample preparation and delivers results in as little as six (6) minutes per sample.

Introduction
A 2005 EPA study showed that coal-fired power plants emit approximately 50 tons of mercury every year. This mercury is ultimately redistributed and accumulates in lakes and rivers where it is converted, by anaerobic organisms, to methyl mercury – its most toxic form.

This prompted the EPA, in March 2005, to initiate the Clean Air Interstate Rule (CAIR) and the Clean Air Mercury Rule (CAMR) with the goal of reducing mercury emissions from coal-fired utilities by almost 70% by 2018. These initiatives have driven many facilities to investigate ways in which to test their mercury emissions.

Several methods exist for the determination of mercury in coal.
Traditional analytical methods such as Cold Vapor Atomic Absorption (CVAA) and ICPMS both require sample preparation prior to analysis. This results in both techniques being costly, labor-intensive and subsequently, having a long turnaround time.

Direct mercury analysis, as described in EPA Method 7473 and ASTM Method 6722-01, is an intensive, wet chemistry technique. Direct analysis affords the laboratory many benefits including:

- Reduced Sample Turnaround (6 Minutes)
- No Sample Preparation
- Reduced Hazardous Waste Generation
- Reduction of Analytical Errors
- General Cost Savings (70% versus CVAA)

**Instrumentation**

The DMA-80, as referenced in EPA Method 7473, from Milestone Inc. (www.milestoneinc.com/direct-mercury-analyzer) was used in this study.

The DMA-80 features a circular, stainless steel, interchangeable 40 position autosampler for virtually limitless throughput and can accommodate both nickel (500 mg) and quartz boats (1500 uL) depending on the requirements of the application. It operates from a single-phase 110/220V, 50/60 Hz power supply and requires regular grade oxygen as a carrier gas. As the process does not require the conversion of mercury to mercuric ions, both solid and liquid matrices can be analyzed without the need for acid digestion or other sample preparation. The fact that zero sample preparation is required also eliminates all hazardous waste generation. All results, instrument parameters including furnace temperatures, are controlled and saved with easy export capabilities to Excel or LIMS.

**Principles of Operation**

Direct mercury analysis incorporates the following sequence: Thermal Decomposition, Catalytic Conversion, Amalgamation, and Atomic Absorption Spectrophotometry. Controlled heating stages are implemented to first dry and then thermally decompose a sample introduced into a quartz tube. A continuous flow of oxygen carries the decomposition products through a hot catalyst bed where halogens, nitrogen, and sulfur oxides are trapped. All mercury species are reduced to Hg(0) and are then carried along with reaction gases to a gold amalgamator where the mercury is selectively trapped. All non-mercury vapors and decomposition products are flushed from the system by the continuous flow of gas. The amalgamator is subsequently heated and releases all trapped mercury to the single beam, fixed wavelength atomic absorption spectrophotometer. Absorbance is measured at 253.7 nm as a function of mercury content.
Experimental Discussion
For this study, a power-generating company provided eight unknown coal samples. Prior to analysis, all samples were ground to 60-mesh particle size. Sample weights ranged from 0.09 g – 0.26 g, and were placed inside the nickel sample boats (500 mg) for analysis on the DMA-80.

In addition, NIST 1633b Coal Fly Ash and NIST 2691, in weights ranging from 0.059 g – 0.075 g, were analyzed periodically throughout the sequence to evaluate the instrument’s performance on standard reference materials.

Calibration
Calibration standards were prepared using a NIST traceable stock solution of 1000 ppm Hg preserved in 5% HNO₃. Working standards of 100 ppb and 1 ppm were prepared and preserved in 37% HCl and stored in amber glass vials.

By injecting increasing sample volumes of standard into the quartz sample boats, calibration graphs of 0 – 20 ng (Figure 3) and 20 – 1500 ng (Figure 4) of mercury were created using the 100 ppb and 1 ppm standards respectively.

Operating Conditions
The DMA-80’s operating conditions for all analyses are shown in Table 1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Setting</th>
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<tbody>
<tr>
<td>Drying Temp/Time</td>
<td>90 seconds to 200°C</td>
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<tr>
<td>Decomposition Ramp</td>
<td>120 seconds to 750°C</td>
</tr>
<tr>
<td>Decomposition Hold</td>
<td>90 seconds at 750°C</td>
</tr>
<tr>
<td>Catalyst Temp</td>
<td>565°C</td>
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<tr>
<td>Purge Time</td>
<td>60 seconds</td>
</tr>
<tr>
<td>Amalgamation Time</td>
<td>12 seconds at 900°C</td>
</tr>
<tr>
<td>Recording Time</td>
<td>30 seconds</td>
</tr>
<tr>
<td>Oxygen Flow</td>
<td>120 mL/min</td>
</tr>
</tbody>
</table>

Table 1. Analysis Operating Parameters

Results
The results of the standard reference materials (SRM’s) are shown in Table 2. Different samples have been analyzed comparing DMA-80, CVAA and ICP results.

Table 2. Coal Samples on DMA-80 vs. Contract Laboratory.
Table 3 and 4 show that all results were within 10% of the certified value.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration DMA-80 (mg/Kg)</th>
<th>Certified (mg/Kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NIST 1633b</td>
<td>0.142</td>
<td>0.14 ± 0.02</td>
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</tbody>
</table>

Table 3. Summary of results of QA/QC analysis (NIST 1633b, Constituent Elements in Coal Fly Ash Certified Material) RSD 2.06% Mean: 0.139 mg/Kg SD: 0.028

Table 4. NIST 2691 Coal Fly Ash Certified Material RSD 1.95% Mean: 0.0588 mg/Kg SD: 0.0011

Conclusion
The results of the SRM’s shown in Table 2 indicate that direct mercury analysis is an effective technique for the determination of mercury in coal and similar products. Table 3 and 4 show that the reproducibility and accuracy of the technique is comparable to wet chemistry techniques, keeping in mind that coal samples are notorious for not being homogeneous in their chemical composition. The DMA-80 does not require any sample preparation, which results in lower detection capabilities when compared to traditional techniques.

Further Reading
To learn more about mercury and other related topics, feel free to visit these websites.

**EPA Method 7473**

**ASTM Method D6722-01**
http://www.astm.org/Standards/D6722.htm

**EPA Mercury**
http://www.epa.gov/mercury/

**Methyl Mercury**
http://en.wikipedia.org/wiki/Methylmercury

**Mercury in Fish**

**Mercury in Coal**
http://energy.er.usgs.gov/health_environment/mercury/

**Mercury Analysis**
http://www.milestonesci.com/direct-mercury-analyzer

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**About Milestone**
Established in 1998, Milestone is headquartered in Italy and has offices in Germany, Switzerland, the United States, China, Japan and Korea. We operate worldwide through a network of over 100 exclusive distributors, all providing our customers premium application and service support. Milestone’s mission is to help chemists by offering them the most advanced instrumentation for sample preparation and direct mercury analysis in the world. Our industry-leading technology, in combination with fast, responsive service and applications support, allows Milestone to support our goal of providing you the highest return on investment possible.

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**MILESTONE INC** - 25 Controls Drive - Shelton, CT 06484 - USA
Tel: (203) 925-4240 - Toll free (866) 995-5100 - Fax: (203) 925-4241
www.milestonesci.com
mwave@milestonesci.com