Tech Note

The 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.

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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 ICP- MS 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 a cost-effective, proven alternative to these labor-intensive, wet chemistry techniques. 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.milestonesci.com/mercury) was used in this study

Figure 1. Milestone's DMA-80 Direct Mercury Analyzer

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

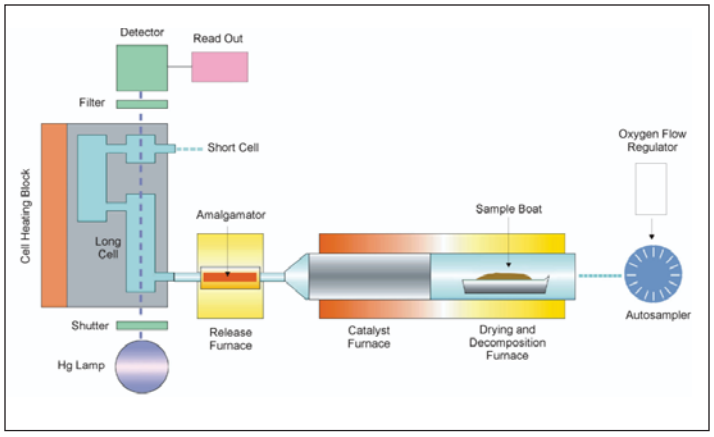

Figure 2. An Internal Schematic of Milestone's DMA-80 Direct Mercury Analyzer.

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 wave-length atomic ab- sorption 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 SARM 20 Coal, 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 (SRM's).

Calibration

Calibration standards were prepared using a NIST traceable stock solution of 1000 ppm Hg preserved in 5 % HNO_3. Working standards of 100 ppb and 1 ppm were prepared and preserved in 3.7% 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 – 500 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 1. Analysis Operating Parameters

Parameter	Setting
Drying Temp/Time	90 seconds to 200 °C
Decomposition Ramp	120 seconds to 750 °C
Decomposition Hold	90 seconds at 750 °C
Catalyst Temp	600 °C
Purge Time	60 seconds
Amalgamation Time	12 seconds at 900 °C
Recording Time	60 seconds
Oxygen Flow	120 mL/min

Results

The results of the standard reference materials (SRM's) are shown in Table 2. All results were within 10% of the certified value. Table 3 shows all data for the unknown coal analysis.

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 shows that the reproducibility of the technique is comparable to wet chemistry techniques, keeping in mind that coal samples are notorious for

Table 2. Summary of results of QA/QC analysis (SARM 20 Coal)

Sample	Concentration (ppm)	Certified (ppm)
SARM 20	0.249	0.25
SARM 20	0.260	0.25
SARM 20	0.250	0.25
SARM 20	0.228	0.25
SARM 20	0.258	0.25

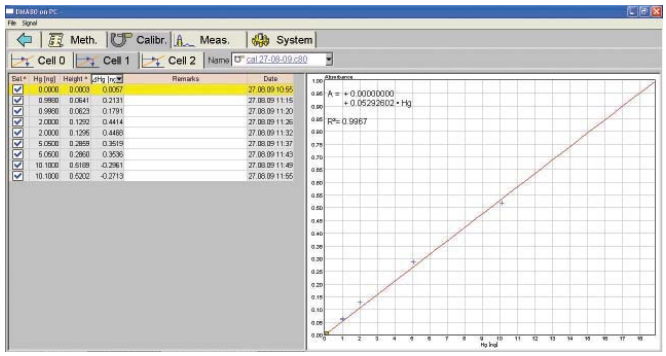

Figure 3. 0 ng – 20 ng Calibration Graph for ultra-level analysis (ppt; ppb)

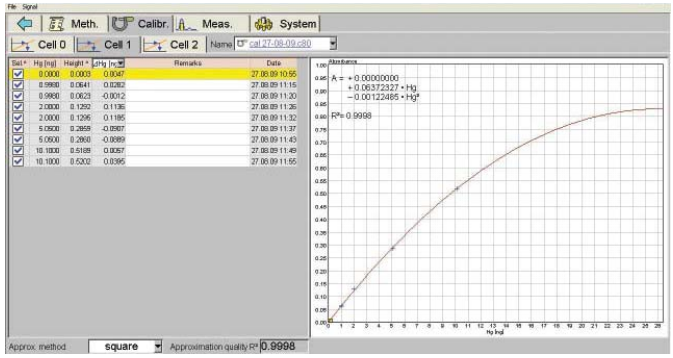

Figure 4. 20 ng – 1000 ng Calibration Graph for low to mid-level analysis (ppb; ppm)

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.

About Milestone

Our full suite of Microwave Sample Prep productivity tools is backed by over 50 patents and 26 years of industry expertise. Milestone is committed to providing safe, reliable and flexible platforms to enhance your productivity. Over 18,000 customers worldwide look to Milestone to improve their metals digestions, organic extractions, mercury analyzers or synthetic chemistry processes.

Table 3. Summary of results of QA/QC analysis (Coal Fly Ash)

Sample	Concentration (ppm)	Certified (ppm)
NIST 1633b	0.142	0.14 ± 0.02
NIST 1633b	0.142	0.14 ± 0.02
NIST 1633b	0.139	0.14 ± 0.02
NIST 1633b	0.135	0.14 ± 0.02
NIST 1633b	0.140	0.14 ± 0.02

Table 4. Data from unknown coal analysis. All results are noted in parts-per-million (ppm)

A	B	C	D	E
0.160	0.153	0.040	0.11	0.094
0.135	0.144	0.043	0.102	0.109
0.155	0.144	0.039	0.096	0.090
0.143	0.153	0.036	0.092	0.094

Table 5. Summary of results of unknown coal analysis Sample

Sample	Concentration (PPM)
A	0.15 ± 0.02
B	0.148 ± 0.02
C	0.039 ± 0.02
D	0.10 ± 0.02
E	0.10 ± 0.02

Learn more or request an onsite demonstration:
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