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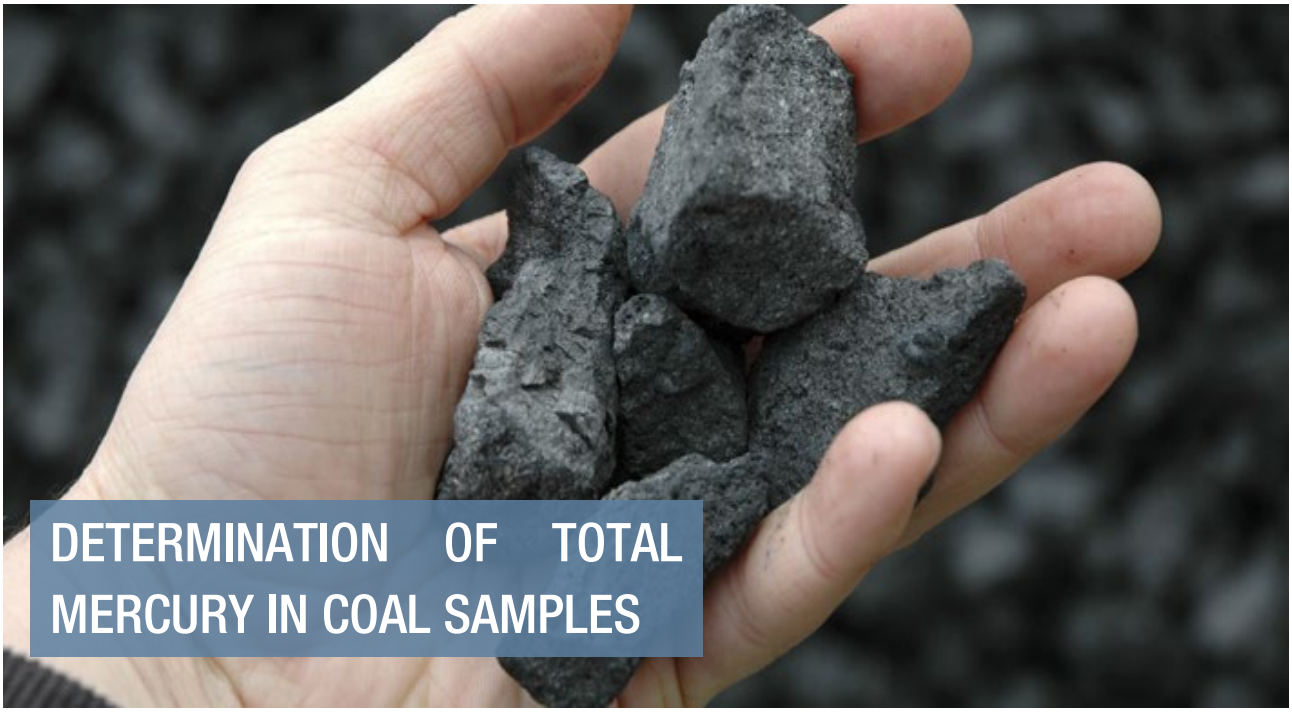


DETERMINATION OF TOTAL MERCURY IN COAL SAMPLES

Determination of Total Mercury in Coal Utilizing Direct Combustion for Mercury Analysis for coal and fly ash samples

| 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 methylmercury – 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.

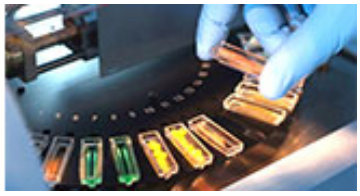
These initiatives have driven many facilities to investigate ways in which to test their mercury emissions.

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)



| EXPERIMENTAL

INSTRUMENT

The DMA-80 *evo* from Milestone, as referenced in EPA Method 7473, was used in this study.

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

The DMA-80 *evo* features a circular, stainless steel, interchangeable 40-position autosampler for virtually limitless throughput and can accommodate both nickel (500 mg) and quartz boats (1500 µL) 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.

PRINCIPLE OF OPERATION

Direct mercury analysis incorporates the following operating 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 sulfuric 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 double beam, fixed wavelength atomic absorption spectrophotometer. Absorbance is measured at 253.7 nm as a function of mercury content.

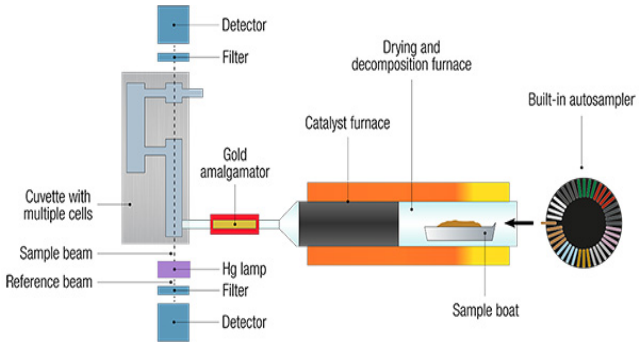
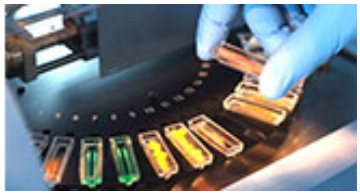


Figure 2 An Internal Schematic of Milestone's DMA-80 evo.

EXPERIMENTAL DISCUSSION

For this study, a power-generating company provided eight unknown coal samples. Prior to analysis, all samples were ground to a 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 0.37% HCl and stored in amber glass vials. By injecting increasing sample volumes of standard into the quartz sample boats calibration graphs of 0 – 1500 ng of mercury were created using aqueous standards.

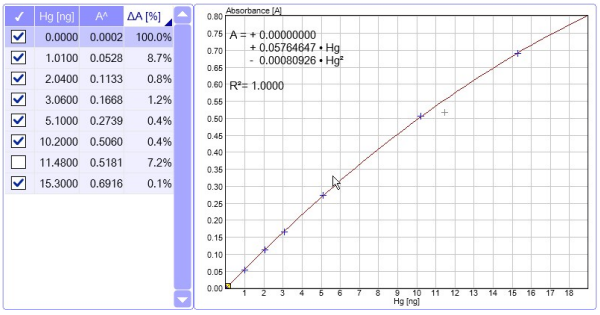


Figure 3 0 ng – 20 ng Calibration Graph for ultra-low level

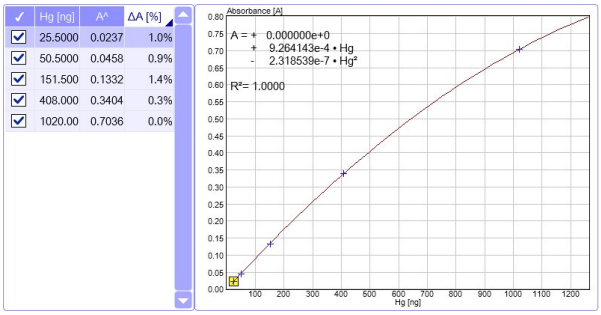


Figure 4 20 ng – 1000 ng Calibration Graph for low to mid-level analysis (ppb, ppm)

| OPERATING CONDITIONS

The DMA-80 *evo*'s operating conditions for all analyses are shown in Table 1.

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	565 °C
Purge Time	60 seconds
Amalgamation Time	12 seconds at 900 °C
Recording Time	30 seconds
Oxygen Flow	120 mL/min

Table 1 Analysis Operating Parameters

RESULTS

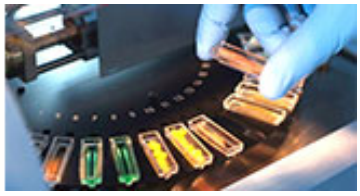
The results of the SRM's are shown in Table 2. All results were within 10% of the certified value. Table 3 shows all data for the unknown coal analyses.

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

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

Sample	Concentration(ppm)	Certified (ppm)
NIST 1633b	0.142	0.14±0.02
NIST 1633b	0.142	0.14±0.02
NIST1633b	0.139	0.14±0.02
NIST 1633b	0.135	0.14±0.02
NIST 1633b	0.140	0.14±0.02

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



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 4 Data from unknown coal analysis. All results are noted in ppm

Sample	Mean concentration (ppm)	SD
A	0.148	0.009
B	0.148	0.005
C	0.039	0.003
D	0.100	0.008
E	0.097	0.008

Table 5 Summary of results of 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 not being homogeneous in their chemical composition. The DMA-80 *evo* does not require any sample preparation which results in lower detection level 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
http://www.epa.gov/waste/hazard/testmethods/sw846/pdfs/7473.pdf

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

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

Methylmercury
http://en.wikipedia.org/wiki/Methylmercury

Mercury in Fish
http://www.epa.gov/waterscience/fish/advice/mercupd.pdf

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

Mercury Analysis
http://www.milestonesci.com

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At Milestone we help chemists by providing the most innovative technology for metals analysis, direct mercury analysis and the application of microwave technology to extraction, ashing and synthesis. Since 1988 Milestone has helped chemists in their work to enhance food, pharmaceutical and consumer product safety, and to improve our world by controlling pollutants in the environment.