

Atomic Absorption



The Determination of Total Mercury in Coal and Coal Fly Ash Using Thermal Combustion and Amalgamation Coupled with Atomic Absorption

Summary

Coal-fired power plants are by far the largest source of mercury pollution in the US. Through the coal-combustion process, they emit approximately 50 tons of mercury particulates into the atmosphere every year (EPA, 2005 data). When the mercury falls back to earth it is deposited on the land and gets into the water ecosystem, where it is converted into the highly toxic organo mercury compound, methyl mercury (CH_3Hg^+) by anaerobic organisms. This toxicant enters the aquatic system food chain, and eventually ends up in the shellfish and seafood we consume. For that reason the EPA initiated the Clean Air Interstate Rule (CAIR) and the Clean Air Mercury Rule (CAMR) in March 2005, to significantly reduce the amount of mercury emission from coal-fired power stations from 48 tons to 15 tons by the year 2018.

Mercury is an undesirable constituent in lignite and bituminous-type coals used in coal-fired power stations. These low-grade coals are typically high in pyrite (iron sulfide) content, in which the mercury is chemically bound. The EPA mercury rule will therefore translate into a significant requirement for measuring the mercury content of all coal used in power plants. In addition, coal combustion products (CCP), such as coal fly ash will also have to be monitored for mercury, because of its widespread use for the manufacture of concrete products.

This note will focus on a rapid test method for determining mercury directly in coal and coal fly ash using the principles of thermal decomposition, amalgamation and detection by atomic absorption described in EPA Method 7473 and ASTM Method 6722-01. Because there is no sample dissolution required, this novel approach can determine the total mercury content of a coal related sample in less than five minutes, which is significantly faster than the traditional wet chemical reduction method.

Introduction

Mercury Toxicity

Mercury is distributed throughout the environment in a number of different forms. It is found as elemental mercury vapor in the atmosphere, while most of the mercury in water, soil, plants, and animals is found as inorganic and organic forms of the element. Natural sources of mercury come from volcanoes, forest fires and the weathering of mercury-bearing rocks. However, this is small compared to the vast amount of mercury which is generated from anthropogenic sources (human activities), such as fossil fuel combustion, solid waste incineration, mining and smelting, manufacture of cement and the use of mercury cells in the commercial production of chlorine.

Of all the anthropogenic activities, by far the largest polluters are coal-fired power plants, which release approximately 50 tons of elemental mercury into the atmosphere each year via the effluent generated by the combustion process. Once released, the mercury particulates fall back down to the ground and are either absorbed by soil/sediments or find their way into surface waters, such as lakes, rivers, wetlands, estuaries and the open ocean, where it is converted to organic mercury (mainly methyl mercury) by the action of anaerobic organisms that live in these aquatic systems. The methyl mercury bio-magnifies up the food chain as it is passed from a lower food chain level to a subsequently higher food chain level through predator feeding. Fish, which are at the top of the aquatic food chain, accumulate methyl mercury approximately 1 to 10 million times greater than dissolved methyl mercury concentrations found in surrounding waters.

Several instances of severe organic mercury poisoning through consumption of contaminated fish have occurred in recent times. Probably the most famous was the release of methyl mercury in industrial wastewater from the Chisso Corporation's acetaldehyde chemical factory in Minimata City, Japan, from 1932 to 1968. It bio-accumulated in shellfish and fish harvested from the local bay, which when eaten by the local population, produced quite horrifying results. It resulted in central nervous system effects such as loss of vision, impairment of motor coordination, loss of feeling, and, at high doses, seizures, very severe neurological impairment, and in many cases, death. It wasn't until 2001, after almost 1800 people had died, that the company officially accepted responsibility for this disaster.

As a result of this and other similar incidents, the EPA considers there is sufficient evidence for methyl mercury to be considered a developmental toxicant that can potentially change the genetic

material of an organism and thus increases the frequency of mutations above the natural background level. At particular risk are women of childbearing age because the developing fetus is the most sensitive to the toxic effects of methyl mercury. It has been proved that children who are exposed to methyl mercury before birth may be at increased risk of poor performance on neuro-behavioral tasks, such as those measuring attention, fine motor function, language skills, visual-spatial abilities and verbal memory.

Power Plant Emissions

By far the majority of power stations being operated today are based on the production of electricity by the combustion of a fossil fuel (coal, oil or gas). They all use a similar principle of burning the fossil fuel to heat a reservoir of water in order to generate steam to drive a turbine blade. This in turn is connected to the shaft of a generator rotor, which rotates at high velocity and produces electricity.

In the U.S., coal-burning power plants supply more than half of the electricity we use. Even though coal is a very cost-effective fossil fuel to use, it generates a great deal of harmful combustion products when burned. This is particularly the case with lignite and bituminous-type coals, which tend to be the most common coals used in power plants because it is relatively inexpensive. The problem with using these low-grade coals is that they are relatively high in pyrite content. However, one of the other major elemental contaminants in coal containing pyrite is elemental mercury. When burned, iron sulfide generates high levels of oxides of sulfur, which if not treated or cleaned will be expelled into the atmosphere. This is normally done by chemically leaching the coal or by passing the exhaust gases through scrubbers to remove the harmful components. These removal processes are very efficient at taking out the oxides of sulfur and nitrogen, but are not very effective in taking out the mercury. As a result about 70% of the mercury content of the coal will be expelled into the atmosphere in the form of elemental mercury vapor.

Under the 2005 EPA CAIR, the initial phase of mercury reductions from coal-fired utility power stations will primarily result as a co-benefit of reducing other pollutants like oxides of sulfur and nitrogen using existing control technology like chemical leaching or flue gas scrubbing systems. Under the specifications of the second phase of the plan, the EPA CAMR, it will result in greater reductions of mercury emissions, probably requiring new and improved mercury-specific control technology for power utilities. Let's take a more detailed look at the CAMR.

Clean Air Mercury Rule

The EPA CAMR of 2005 is the first ever federally-mandated requirements that coal-fired electric utilities reduce their emissions of mercury. Together the CAMR and the CAIR create a multi-pollutant strategy to reduce emissions throughout the United States. The major points of the rules are given below:

- The CAMR was built on EPA's CAIR to significantly reduce emissions from coal-fired power plants – the largest remaining sources of mercury emissions in the country. The goal of these rules regarding mercury is to reduce utility emissions of mercury from 48 tons a year to 15 tons, a reduction of nearly 70 percent.
- The CAMR establishes “standards of performance” limiting mercury emissions from new and existing coal-fired power plants and creates a market-based cap-and-trade program to reduce nationwide utility emissions of mercury in two distinct phases. The first phase cap is 38 tons by 2010. In the second phase, due in 2018, coal-fired power plants will be subject to a second cap, which will reduce emissions to 15 tons upon full implementation.
- New coal-fired power plants (“new” means construction starting on or after Jan. 30, 2004) will have to meet stringent new source performance standards in addition to being subject to the caps.

Coal Combustion Products

Besides knowing the mercury content of the coal, it is also critical to determine the level of mercury in the coal combustion products (CCP). These are the inorganic residues that remain after crushed coal is burned and are used for a variety of industrial/commercial purposes. During the combustion process, coarse particles (bottom ash and boiler slag) settle to the bottom of the combustion chamber, and the fine portion (fly ash) is removed from the flue gas by electrostatic precipitators or other gas-scrubbing devices. In addition, flue gas desulfurization (FGD) is a chemical process to remove sulfur oxides. The principle of the FGD process is to chemically combine the sulfur gases released in coal combustion by reacting them with a sorbent, such as limestone (calcium carbonate). As the flue gas comes in contact with the slurry of calcium salts, sulfur dioxide (SO₂) reacts with the calcium to form hydrated calcium sulfate, commonly known as gypsum. A typical breakdown of the major components of these coal combustion products are: fly ash – 60 %, FGD products – 20%, bottom ash – 15 %, and boiler slag – 5 %. From data taken in 1999/2000, the total quantity of these products together with their most common uses is given here:

- 57 million tons of fly ash produced - main uses were in concrete, structural fill and waste stabilization.
- 22 million tons of FGD material produced - used mostly in gypsum wallboard manufacture.
- 15 million tons of bottom ash produced - mainly used in structural fill, snow and ice control, road bases and concrete.
- 3 million tons of boiler slag produced - used predominantly in blasting grit and roofing applications.

Of all these by-products, fly ash is by far the largest component and probably has the broadest application. Its most common use is in the production of concrete and concrete products.

Experimental Discussion

The goal of this study was to evaluate a novel approach for the determination of total mercury in coal and coal combustion products and in particular, to assess its capabilities with aqueous calibration standards, when measuring standard reference materials (SRMs). It was also important to understand the achievable reproducibility, not only in evaluating the precision of the technique, but also to see if there were any significant differences in the homogeneity of the coal. The study was therefore split into two experiments. The first part of the study was to measure the mercury concentrations of a bituminous coal and fly ash SRM sample. The second part was a reproducibility study of two coals – one with a high mercury content and the other with a mercury content about an order of magnitude lower. To complete this experiment, the two samples were also analyzed by wet digestion/oxidation, and chemical reduction using a conventional atomic absorption-based mercury analyzer, for comparison purposes. For both experiments, aqueous standards made up in 10% nitric acid were used for calibration

Instrumentation

The SMS 100 mercury analyzer (PerkinElmer, Inc., Shelton, CT) was used for this study. This is a dedicated mercury analyzer for the determination of total mercury in solid and liquid samples using the principle of thermal decomposition, amalgamation and atomic absorption described in EPA Method 7473 and ASTM Method 6722-01. The SMS 100 uses a decomposition furnace to release mercury vapor instead of the chemical reduction step used in traditional liquid-based analyzers. Both solid and liquid matrices can be loaded onto the instrument's autosampler and analyzed without acid digestion or sample preparation prior to analysis. Because this approach does not require the conversion of mercury to mercuric ions, lengthy sample pretreatment steps are unnecessary. As a result, there is no need for reagents such as highly corrosive acids, strong oxidizing agents or reducing chemical, which means, no hazardous waste to be disposed of.

An additional benefit of this technology for coal-related samples is that it allows for the stack gas monitoring of mercury with sorbent traps, such as those described in the EPA methods, 40 CFR, Part 60, Appendix B, "Specification and Test Methods for Total Vapor Phase Mercury Continuous Emission Monitoring Systems in Stationary Sources" and 40 CFR Part 75, Appendix K, "Quality Assurance and Operating Procedures for Sorbent Trap Monitoring Systems".

Principles of Operation

A small amount of the coal or fly ash sample (0.05-1.00 gms, depending on the mercury content) is weighed into a sample boat (typically nickel). The boat is heated in an oxygen rich furnace, to release all the decomposition products, including mercury. These products are then carried in a stream of oxygen to a catalytic section of the furnace. Any halogens or oxides of nitrogen and sulfur in the sample are trapped on the catalyst. The remaining vapor is then carried to an amalgamation cell that selectively traps mercury. After the system is flushed with oxygen to remove any remaining gases or decomposition products, the amalgamation cell is rapidly heated, releasing mercury vapor. Flowing oxygen carries the mercury vapor through an absorbance cell positioned in the light path of a single wavelength atomic absorption spectrophotometer. Absorbance is measured at the 253.7 nm wavelength as a function of the mercury concentration in the sample. A

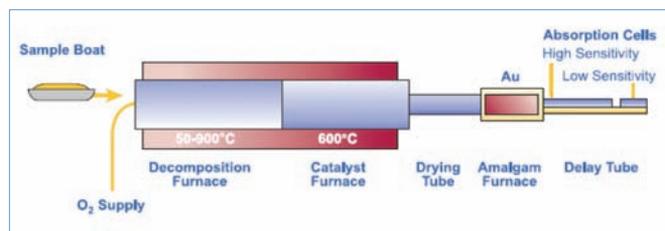


Figure 1. A schematic of the SMS 100 mercury analyzer.

detection limit of 0.005 ng (nanogram) of mercury is achievable with a 25 cm path length cell, while a 2 cm cell allows a maximum concentration of 20 µg (microgram) of mercury. A schematic of the SMS 100 is shown in Figure 1.

Operating Conditions

Table 1 shows the instrumental operating conditions for both the coal and fly ash samples.

Parameter	Setting
Sample Weight	0.500 gm (weighed accurately)
Sample Boat	Nickel
Drying Temp/Time	300 °C for 45 sec
Decomposition Temp/Time	800 °C for 150 sec
Catalyst Temp	600 °C
Catalyst Delay Time	60 sec
Gold Trap Temp	700 °C for 30 sec
Measurement Time	90 sec
Oxygen Flow Rate	300 mL/min

Calibration

Calibration graphs of 0-50 ng and 50-500 ng of mercury were generated from 0.1 and 1.0 ppm aqueous standards in 10% nitric acid respectively, by injecting different weights into a nickel sampling boat. The 0-50 ng calibration was obtained using the high sensitivity 25 cm optical path length cell, while the optional 2 cm cell was used for the 50-500 ng. The 0-50 ng calibration plot is shown in Figure 2, while the 50-500 ng plot is shown in Figure 3.

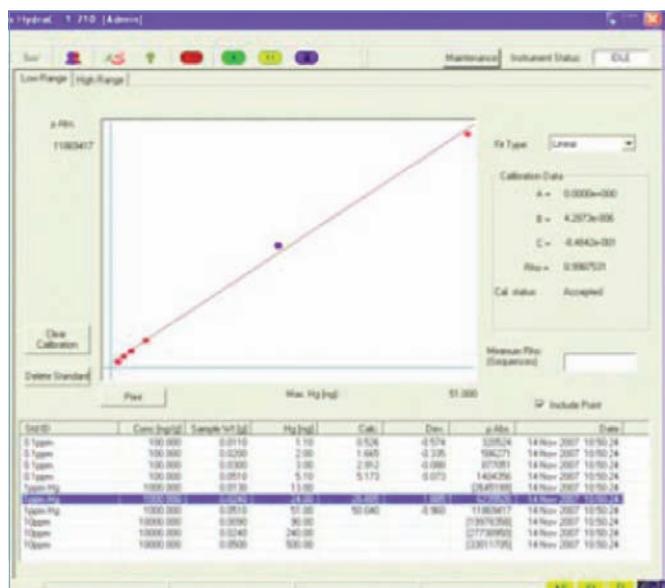


Figure 2. 0-50 ng mercury calibration plot.

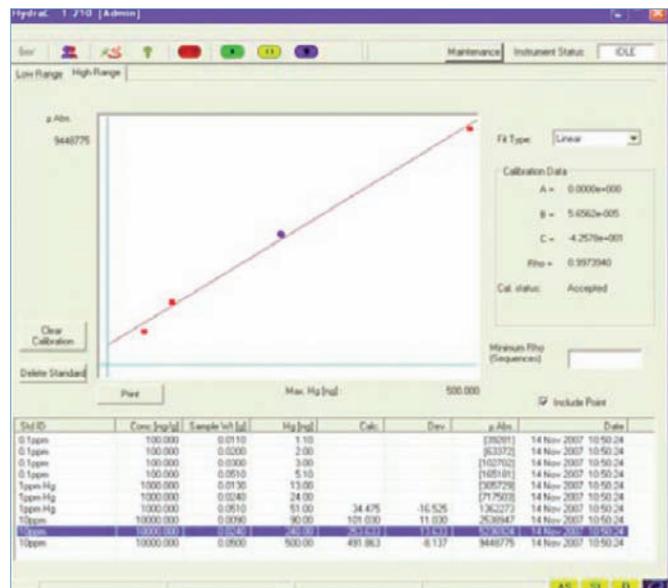


Figure 3. 50-500 ng mercury calibration plot.

Analytical Methodology

These aqueous calibration plots were then used for the two separate thermal decomposition experiments shown below, using the SMS 100 instrument operating parameters described in Table 1.

1. The determination of total mercury in the bituminous coal SRM: HC-35150 and fly ash SRM: NIST 1633b.
2. Reproducibility study by analyzing five separate portions of two different coal samples (one with a high and one with a low mercury content) and comparing precision values with the traditional wet digestion, chemical reduction, atomic absorption technique for the determination of mercury in coal samples using ASTM Method D6414-99 described below

Wet Digestion/Chemical Reduction

For this part of the investigation, five separate portions of both coal samples were prepared by placing approximately one gram (weighed accurately) of each into 50 mL polypropylene tubes followed by 2 mL of 15N nitric acid and 6 mL of 12N hydrochloric acid. All the tubes were held at 80 °C for one hour. Next, 36.5 mL of deionized water was added to each tube followed by 5 mL of 5% potassium permanganate. After allowing ten minutes for oxidation, each tube was examined to ensure that there was an excess of oxidant (purple color). Finally, 0.5 mL of a 12% sodium chloride/12% hydroxylamine mixture was added to remove the excess oxidant and complete the digestion. The calibration standards and samples were then loaded into the autosampler of the mercury analyzer where stannous chloride was used as the reducing agent to generate the free mercury vapor, where it was detected by atomic absorption.

Results

The SMS 100 results for experiment 1 are shown in Table 2.

Table 2. Measurement of mercury in an SRM coal and fly ash sample using the SMS 100.

Sample	SRM	Mercury Certificate Value (µg/g)	Mercury Measured Value (µg/g)	% Recovery
Bituminous Coal	HC-35150	0.176	0.177	100.6
Bituminous Fly Ash	NIST 1633b	0.143	0.132	92.3

The SMS 100 results for experiment 2 are shown in Table 3, while the wet chemical data for the same coal samples using the traditional wet digestion and chemical reduction/atomic absorption technique (ASTM Method D6414-99) are shown in Table 4.

Table 3. Determination of mercury in five separate portions of two different coal samples (with precision data), using the SMS 100.

Portion #	Sample 1 (ng of mercury)	Sample 2 (ng of mercury)
1	80.4	3.1
2	77.5	2.8
3	84.1	2.4
4	77.1	2.5
5	75.0	2.3
Average	78.8	2.6
Std Dev	3.54	0.32
% RSD	4.5	12.3

Table 4. Determination of mercury in five separate portions of two different coal samples (with precision data), using the traditional wet digestion and chemical reduction/atomic absorption technique. (Note: ND = Not Detected)

Portion #	Sample 1 (ng of mercury)	Sample 2 (ng of mercury)
1	81.5	ND
2	85.0	ND
3	75.2	ND
4	79.0	ND
5	81.3	ND
Average	80.4	ND
Std Dev	3.62	ND
% RSD	4.5	ND

It's worth noting that mercury in Sample 2 using a conventional atomic absorption- based mercury analyzer, was not detected. This is not surprising because the wet digestion/oxidation sample preparation process resulted in a 50-fold dilution of the sample, whereas no sample dilution occurs with the thermal decomposition technique. In addition, with the SMS 100, the mercury is pre-concentrated on the gold amalgam tube, helping to lower detection limits for mercury in coal-related samples even further.

Conclusion

The first part of the study shows that the thermal decomposition, amalgamation and atomic absorption technique gives excellent correlation with standard reference materials for the determination of mercury in coals and coal fly ash samples. The fact that a sample can be analyzed in approximately 5 minutes, means the lengthy sample preparation steps associated with traditional wet chemical-based mercury analyzers can be avoided.

The second part of the study confirms that the reproducibility of this approach is equivalent to the wet chemical technique, keeping in mind that coal samples are notorious for not being homogeneous in their chemical composition. The added benefit of the SMS 100 for coal-related samples is that because the analysis is done directly on the solid, the detection capability is significantly lower than with traditional atomic absorption based mercury analyzers.

Further Reading

The following Internet references will be very useful to learn more about the subject matter described in this Application Note.

EPA Clean Air Interstate Rule

<http://www.epa.gov/CAIR/>

EPA Clean Air Mercury Rule

<http://www.epa.gov/oar/mercuryrule/>

EPA Method 7473

<http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/7473.pdf>

ASTM Method D6722-01

<http://www.astm.org/Standards/D6722.html>

Mercury in Fish

<http://www.epa.gov/waterscience/fish/advice/mercupd.pdf>

Mercury in Coal

http://energy.er.usgs.gov/health_environment/mercury/mercury_coal.html

Methyl Mercury

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

Minamata Disaster

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

Fossil Fuel Power Plants

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

Coal Combustion Products

<http://pubs.usgs.gov/fs/fs076-01/fs076-01.html>

Methods 40 CFR, Part 60/Appendix B

http://www.epa.gov/camr/pdfs/camr_final_preamble.pdf

Methods 40 CFR, Part 75/Appendix K

http://www.epa.gov/camr/pdfs/camr_final_preamble.pdf

EPA Method 245.1

<http://www.epa.gov/EPA-WATER/1999/June/Day-08/w14220.htm>

ASTM D6414-99

<http://www.astm.org/DATABASE.CART/HISTORICAL/D6414-99.htm>