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Committee D05 on Coal and Coke
Subcommittee D05.29 on Major Elements in Ash and Trace Elements of Coal

Research Report D05-1026

Interlaboratory Study to Establish Precision Statements for ASTM D3684, Standard Test Method for Total Mercury in Coal by the Oxygen Bomb Combustion/Atomic Absorption Method, D6414, Standard Test Methods for Total Mercury in Coal and Coal Combustion Residues by Acid Extraction or Wet Oxidation/Cold Vapor Atomic Absorption, and D6722, Standard Test Method for Total Mercury in Coal and Coal Combustion Residues by Direct Combustion Analysis

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Research Report for the Determination of Mercury in Coal
D3684 Bomb Combustion CVAA
D6414 Acid Extraction-Wet Oxidation CVAA
D6722-01 Direct Combustion CVAA

Limitations of the Existing ASTM Method for Mercury

The original ASTM method approved for the determination of mercury in coal is ASTM D 3684 Bomb Combustion.

ASTM D 3684 Bomb Combustion CVAA involves igniting approximately 1 g of coal inside a sealed stainless steel bomb in an oxygen atmosphere. The bomb solution is treated to unify all mercury species into the elemental state. A concentrated cloud of the ground state atoms is introduced into a light path. These ground state atoms are irradiated with light at a characteristic wavelength for mercury. The amount of light absorbed is proportional to the amount of mercury present

Although the weight of coal can be lowered for high mercury coals, increasing the weight much beyond 1.3 g tends to result in incomplete combustion of the coal. Consequently, the lower limit of the method is constrained by the maximum weight of coal that can be burned in the combustion bomb. Samples that do not burn well can be a real problem for the bomb combustion method, and thus the method is generally unsuitable for ashes and other low-Btu materials. Coal samples that do not burn well fall into two categories: high moisture or high ash coals, and at the other end of the spectrum, highly swelling coals that can be ejected from the sample crucible during the combustion process. Some practitioners resort to the use of combustion aids or mediators to deal with ashes and difficult to burn coals, but these substances can introduce significant opportunities for contamination. The large internal volume and surface of the oxygen bomb, as well as the number of contact surfaces and valves, increase the risk of contamination or loss of mercury. The use of non-corrosion resistant bombs and crucibles can result in mercury being trapped in the bomb components, resulting in either low or erratic recoveries.

The precision and accuracy of ASTM D 3684 have been validated in two round studies for a range of 0.05 μg/g to 0.2 μg/g mercury in coal. However, these studies did not include coals, which represent a significant portion of the current thermal US coal production and which can have mercury contents of less than 0.05 μg/g.

Proposed Alternative Methods for Mercury in Coal

For the reasons cited above ASTM committee D05 initiated a study to establish the precision and accuracy of two proposed alternative methods for mercury in coal while simultaneously re-evaluating the precision and accuracy of method D 3684.

The two proposed alternative methods are

Acid Extraction Cold Vapor Atomic Absorption (CVAA)
Direct Combustion Cold Vapor Atomic Absorption (CVAA)

Description of the Acid Extraction Cold Vapor Atomic Absorption (CVAA) Procedure

The Acid Extraction CVAA procedure involves extracting up to 2 g of coal in a sealed plastic container. The solution is treated to unify all mercury species into the elemental state. The principle of detection is the same as for D 3684. The method can be adapted for high mercury samples by decreasing the weight of sample. The method is also suitable for ash materials.

Recovery of mercury can be a problem if the digestion bottles are not properly sealed. One of two scenarios can occur depending on the coal type: either mercury can be lost or the digestion environment may not be severe enough to extract all the mercury from the coal. It is essential that the seal on the digestion bottles is checked regularly.

The procedure uses inexpensive labware and common chemicals. Contamination is not a problem if good laboratory practice is followed. The procedure is readily amenable to batching.

Description of the Direct Combustion Cold Vapor Atomic Absorption (CVAA) Procedure

The Direct Combustion CVAA procedure involves igniting a milligram quantity of coal in a combustion train and capturing the mercury in its elemental state on gold amalgam.
The principle of detection is the same as for D 3684.

Because the weight of sample can be increased and successive aliquots can be ignited before releasing the mercury from the amalgam, the procedure is adequate for all U.S. thermal coals. The method is also suitable for ash materials. The method can be adapted for high mercury samples merely by decreasing the weight of sample.

Some samples can cause problems with uniform combustion depending on their moisture content or mineral composition. The physical properties of these samples may cause the sample to explode or "spark" in the combustion train, carrying material out of the combustion region before mercury is completely released.

Since the procedure involves very little handling of the sample and a limited number of reagents, loss of mercury and contamination should not be a serious problem if good laboratory practice is followed. Direct combustion systems can be constructed or purchased. Some manufactured systems are factory calibrated and can be difficult to re-calibrate. Analysis times are in the order of 10 minutes per sample.