



## The Determination of Total Mercury in Soils and River Sediments Using Thermal Decomposition and Amalgamation Coupled with Atomic Absorption

### Summary

Mercury has long been recognized as a serious global pollutant that has a significant impact upon our ecosystem. Unlike most other pollutants, it is highly mobile, non-biodegradable, and bio-accumulative and as a result has to be closely monitored to ensure its harmful effects on local populations are minimized. Approximately 50 tons of mercury particulates are emitted into the atmosphere every year by a variety

of different man-made and natural sources including coal-fired power plants, solid waste incineration plants, volcanoes and forest fires. When the mercury falls back to earth it is deposited on the land and gets into the soil, river sediments and water ecosystems, where it is converted into the highly toxic organo mercury compound, methyl mercury ( $\text{CH}_3\text{Hg}^+$ ). This toxicant enters both the plant and aquatic system food chain, and eventually ends up in the crops, vegetables and seafood we consume.

This application note will focus on a rapid test method for determining mercury directly in soils and river sediments 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 soil or sediment sample in less than five minutes, which is significantly faster than the traditional wet chemical reduction method.

## Introduction

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, sediments, 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<sup>1</sup>. Once released, the mercury particulates fall back down to the ground and get absorbed by soils, where they eventually get into commercial farming crops and vegetables. Mercury also enters surface waters, such as lakes, rivers, wetlands, estuaries and the open ocean, where it is converted to organic mercury (mainly methyl mercury – CH<sub>3</sub>Hg<sup>+</sup>) by the action of anaerobic organisms. The methyl mercury biomagnifies up the aquatic food chain as it is passed from a lower food chain to a subsequently higher food chain level through feeding and eventually finds its way into the fish we eat.

As a result of this, 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<sup>2</sup>. 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 proven that children 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.

For that reason the EPA initiated the Clean Air Interstate Rule (CAIR)<sup>3</sup> and the Clean Air Mercury Rule (CAMR)<sup>4</sup> in March 2005, which is a two-phase plan to reduce the amount of mercury emission from coal-fired power stations from 48 tons to 15 tons by the year 2018, requiring new and improved mercury-specific control technology for power utilities.

## Study

The goal of this study was to evaluate a novel approach for the determination of total mercury in an SRM (standard reference material) soil and an SRM river sediment directly in the solid material using aqueous calibration standards. The SRM soil was NIST 2709, while the SRM river sediment was NIST 8406.

## Instrumentation

The SMS 100 mercury analyzer (PerkinElmer, Inc., Shelton, CT) was used for the study. This is a dedicated mercury analyzer for the determination of total mercury in solid and liquid samples using the principles of thermal decomposition, amalgamation and atomic absorption described in EPA Method 7473 (5) and ASTM Method 6722-01<sup>6</sup>. 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.

## Principles of Operation

A small amount of the solid material (0.05-1.00 gms, depending on the mercury content) is weighed into a nickel sample boat. 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 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.

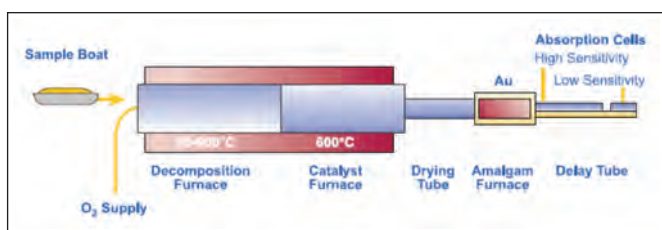


Figure 1. A schematic of the SMS 100 mercury analyzer.

## Operating Conditions

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

**Table 1. The SMS 100 operating conditions for both the SRM soil and sediment.**

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

The SMS 100 measurement process involves the thermal generation of mercury vapor from the sample, which means the instrument can either be calibrated with aqueous standards or directly with solid certified reference materials. However, it is not critical that the calibration standards are of a similar matrix to the sample, because under similar operating conditions, different sample matrices generate similar absorbance values. This is shown by the straight line calibration graph in Figure 2 obtained from different concentrations of mercury in widely different samples, such as oyster tissue, dogfish, sediment and coal<sup>7</sup>.

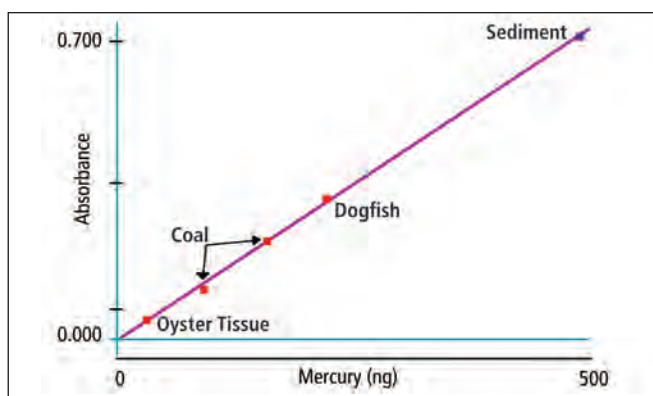


Figure 2. Under similar operating conditions, different sample matrices generate similar absorbance values as shown by the straight line calibration graph obtained from different concentrations of mercury in widely different samples.

For this study, the soil and river sediment were calibrated against standards made up in dilute nitric acid. 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 3, while the 50-500 ng plot is shown in Figure 4. The low calibration plot was then used to determine mercury in the SRM river sediment, while the high calibration plot was used for the SRM soil.

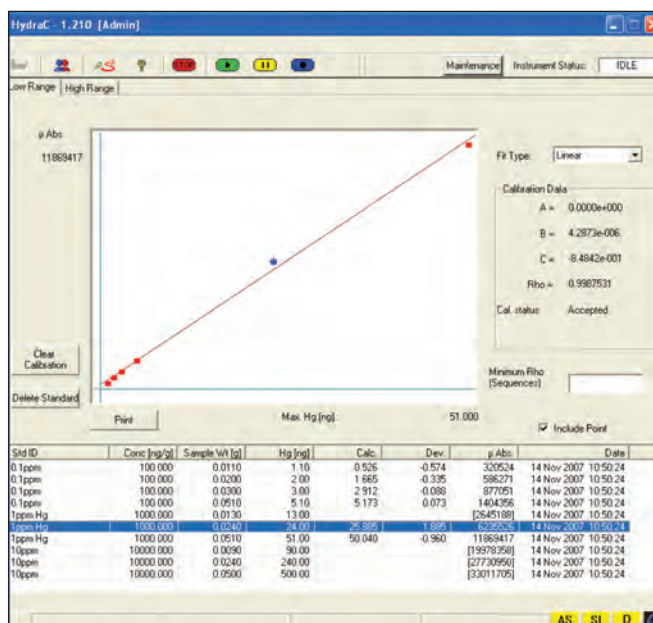


Figure 3. 0-50 ng mercury calibration plot in 10% nitric acid.



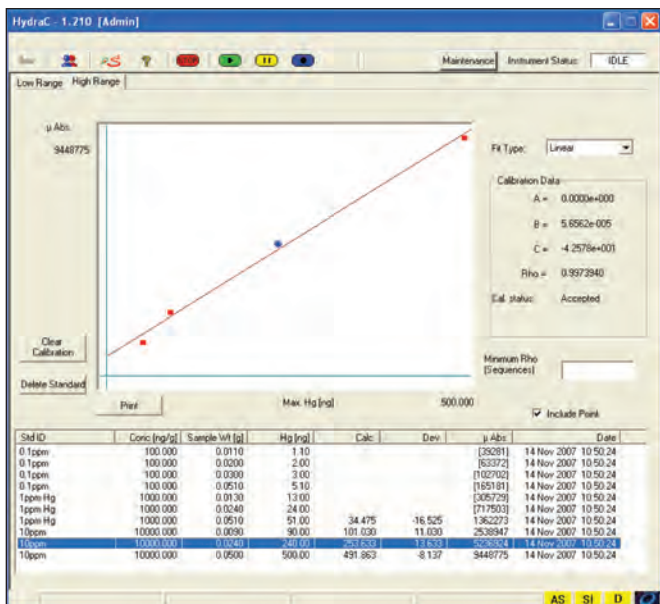


Figure 4. 50-500 ng mercury calibration plot in 10% nitric acid.

## Results

The SMS 100 results for the SRM soil and sediment are shown in Table 2.

**Table 2. Determination of mercury in NIST SRM 2709 soil and SRM 8406 river sediment using the SMS 100.**

Sample Matrix	SRM	Mercury Certificate Value (µg/g)	Mercury Measured Value (µg/g)	% Recovery
Soil	NIST 2709	1.4	1.52	108.6
River Sediment	NIST 8406	0.060	0.061	101.7

## Conclusion

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 an SRM soil and river sediment. The fact that a sample can be analyzed in approximately 5 minutes using aqueous calibration standards, means the lengthy sample preparation steps associated with traditional wet chemical-based mercury analyzers can be avoided.

## References

1. Pollution from FF Power Plants: [http://en.wikipedia.org/wiki/Fossil\\_fuel\\_power\\_plant](http://en.wikipedia.org/wiki/Fossil_fuel_power_plant)
2. Effects of Methyl Mercury: <http://en.wikipedia.org/wiki/Methylmercury>
3. EPA Clean Air Interstate Rule (CAIR) – <http://www.epa.gov/CAIR/>
4. EPA Clean Air Mercury Rule (CAMR) – <http://www.epa.gov/oar/mercuryrule/>
5. EPA Method 7473: <http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/7473.pdf>
6. ASTM Method D6722-01: <http://www.astm.org/Standards/D6722.html>
7. Determination of Total Mercury in Coal and Fly Ash Using Thermal Decomposition and Amalgamation Coupled with Atomic Absorption. PerkinElmer LAS Application Note # 008646\_01: URL address if posted on your website.