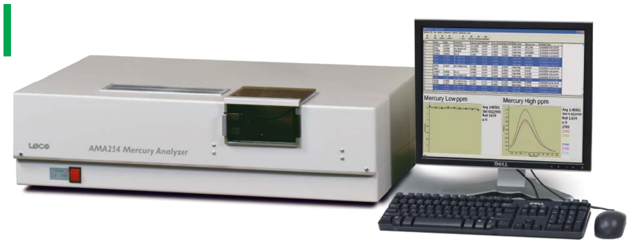
Mercury Determination in Sorbent Trap Material

LECO Corporation; Saint Joseph, Michigan USA

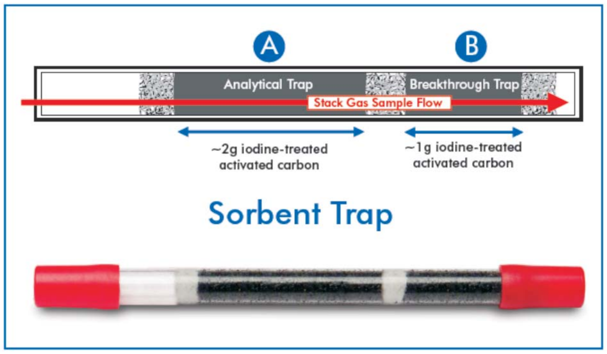
Instrument: AMA254



Background

The Environmental Protection Agency (EPA) issued a federal rule to permanently cap and reduce mercury emissions from coal-fired power plants. In order to comply with the EPA mercury emission standard, the power industry is required to determine the amount of mercury emitted from their power plants. One technique that may be utilized is described in EPA 40 CFR Part 75 Appendix K, and allows for sampling of the stack effluent and off-line analysis of mercury retained by sorbent traps (iodide-treated, activated carbon).

The method described here utilizes a direct combustion methodology based on ASTM Method D6722, "Total Mercury in Coal and Coal Combustion Residues by Direct Combustion Analysis". The sample preparation and handling methodology were modified so that the sorbent traps could be reliably and routinely analyzed with a minimum of sample handling. This approach requires sample homogenization. This homogenization provides the additional benefits of allowing replicate analysis of each sample, as well as enabling the possibility of saving retains of samples.



Sampling and Sample Preparation—Equipment

- Spex Mill 8000M® Mixer/Mill
- Spex mixing vial, 2-3/8 in. diameter x 3 in. vial body with screw on cap and O-ring
- Spex mix/mill balls, three 1/4 in. steel balls
- LECO AMA254 Mercury Analyzer

Sampling and Sample Preparation—Procedure

1. The sorbent tube is opened and the total weight of the carbon in both sections is determined and recorded. Section A is the analytical portion of the tube and section B is used to check for analyte break-through.
2. The front portion of section B is analyzed without grinding to check for analyte break-through. Only one analysis is made on this section unless the result is greater than five times the average blank measurement on the mercury analyzer, in which case a second determination is performed to confirm the result. Such a result would be indicative of analyte break-through and any results from the analytical portion (section A) are suspect.
3. Section A is divided into two relatively equal portions.
4. Each portion of section A is ground separately in a ball mill.[1] Place a portion of section A into the mixing vial with three 1/4 in. steel balls and screw the mixing vial lid on securely.
5. Place the mixing vial into the vial holder within the mixing mill and tighten the vial restraint.
6. Set the timer on the mill for two minutes. After the first two minutes of grinding allow the vial to sit for one minute.[2] Then set the timer for an additional two minutes of grinding.
7. Remove the mixing vial, unscrew the cap and remove the ground sample and mixing balls.
8. The other portion of Section A is also ground following steps 4–7.
9. The two ground portions of section A are then combined and thoroughly mixed by placing them together into the mixing vial with three 1/4 in. steel balls and screw the mixing vial lid on securely.
10. Place the mixing vial into the vial holder within the mixing mill and tighten the vial restraint.
11. Set the timer on the mill for one minute.
12. Remove the mixing vial, unscrew the cap and remove the ground sample and mixing balls.[3]
13. The total ground section A is weighed and recorded and sample loss from grinding is determined.[4]
14. Three determinations are then made on this ground and mixed material from section A. If the deviation of these three replicates is high, additional runs are added.[5]

[1] *Section A is split to avoid overloading the mixer mill.*

[2] *The one minute delay is used to keep the mill and material cool to avoid the possibility of analyte loss.*

[3] *The mixing vial and balls are rinsed with Ethanol between analyses.*

[4] *The sample loss observed for this sample handling and grinding step has been determined to be ~4% with a maximum loss of <8%.*

[5] *The calculated RSD of this procedure is 5%. In many cases it is better than 2%.*

Accessories

614-822-102 Small Nickel Boats

Note: Boats must be pre-baked at 400°C or analyzed without a sample prior to analysis of samples.

Calibration Samples

LECO 502-813 Fly Ash, LECO 502-499 (BCR 143r), LECO 502-649 Dry Sludge (NIST 2781), or other suitable reference material

Delivering the Right Results

Furnace Temperature 550°C

Analysis Time ~8 minutes

Method Parameters

Drying Time	60 seconds
Decomposition Time	200 seconds
Cuvette Clear Time	45 seconds
Dosing Delay Time	0 seconds
Cell Selection	Auto Select
Metric For Calculations	Peak Area

Procedure

1. Determine Blank.
    a. Enter Blank from the drop-down menu under the Name column.
    b. Click Analyze; the door will open and the nickel loop will be presented.
    c. Carefully place a 614-822-102 Small Nickel Boat into the nickel loop using clean tweezers.
    d. Click OK in the Load Sample window; the analysis sequence will start automatically.
    e. Repeat steps 1a through 1c two more times. Set blank as directed in the operator's instruction manual.
2. Calibrate/Drift Correct.
    a. Weigh various masses of each reference material in accordance with the absolute amount of mercury required to calibrate an appropriate dynamic range. The reference samples are weighed into a 614-822-102 Small Nickel Boat.
    b. Enter each reference material identification and mass using the Sample Login (F3) function.
    c. Click Analyze (F5); the furnace door will open and the nickel loop will be presented (if there is a boat in the nickel loop, remove it and save it for later use).
    d. Carefully place the boat, containing the reference sample, into the nickel loop using clean tweezers.
    e. Click OK in the Load Furnace window. The boat will be inserted into the furnace, the furnace door will close, and the analysis sequence will start automatically.
    f. Repeat steps 2a through 2e until all reference materials have been analyzed.

    NOTE: The result from the first analyzed sample after an extended delay should be discarded. This sample is considered a "conditioner" and should not be used for calibration.

    g. Complete the calibration by following the calibration procedure as outlined in the operator's instruction manual.
3. Analyze the samples as follows.
    a. Weigh ~0.01 to 0.1 gram of the sample into a 614-822-102 Small Nickel Boat (smaller masses are used for higher Hg concentrations, larger masses are used for lower Hg concentrations).
    b. Enter the sample identification and mass using the Sample Login (F3).
    c. Follow the procedure outlined in steps 2c through 2e.

Typical Results

Sample	Mass (g)	Mercury (ppm)	Mercury (ng)	Trap Mass (g)	Trap Total Hg (ng)
Sorbent #1	0.10220	0.1292	13.20	2.0378	263.3
	0.10440	0.1267	13.23	2.0378	258.2
	0.10220	0.1259	12.86	2.0378	256.5
	***X* =**	***0.1273***	***13.10***	—	***259.3***
	***s* =**	***0.0017***	***0.21***	—	***3.5***
Sorbent #2	0.02228	1.267	28.23	2.0402	2585
	0.02055	1.323	27.20	2.0402	2700
	0.02162	1.323	28.61	2.0402	2700
	***X* =**	***1.304***	***28.01***	—	***2662***
	***s* =**	***0.032***	***0.73***	—	***66***
Sorbent #3	0.02064	4.368	90.17	2.0988	9168
	0.02092	4.386	91.76	2.0988	9206
	0.02227	4.361	97.13	2.0988	9153
	***X* =**	***4.372***	***93.02***	—	***9176***
	***s* =**	***0.013***	***3.65***	—	***27***
Sorbent #4	0.01020	16.203	165.27	2.1785	35300
	0.01040	16.162	168.09	2.1785	35210
	0.01000	16.016	160.16	2.1785	34891
	***X* =**	***16.127***	***164.51***	—	***35134***
	***s* =**	***0.098***	***4.02***	—	***214***

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