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# *Mercury Measurement Using EPA Method 30B*

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# Acceptable Reference Methods

- Originally, the Ontario Hydro method (ASTM D6784-02) and EPA Method 29 were the only acceptable reference methods.
- August 22, 2007, EPA released a direct and final rule that allowed two other reference methods.
  - EPA Method 30A – Instrumental reference method (IRM)
  - EPA Method 30B – Sorbent trap method
- Both methods were promulgated November 2007.

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# EPA Method 30B

***Determination of Total Vapor-Phase Mercury Emissions from Coal-Fired Combustion Sources Using Carbon Sorbent Traps***

- Sample point selection
- Analytical procedures
- Measurement system performance tests
- Sampling procedures
- Sampling handling
- QA/QC

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# Sorbent Traps as a Reference Method and for Appendix K

- Both are sorbent trap methods
- Both are procedural not proscribed methods

**But:**

- A reference method is designed to certify or prove another method is working properly. In this case, a CMM.
- Appendix K is a CMM.

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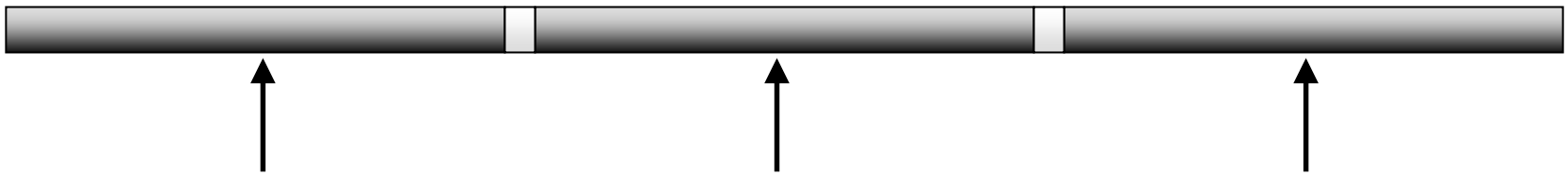
# Differences Between Method 30B and Appendix K Carbon Traps

## Appendix K Trap



**Section 1**

Primary Section

**Section 2**

Secondary Section

**Section 3**

Spiked Section

## EPA Method 30B Trap

**Section 1**

Primary Section (Spiked for Field Recovery Test)

**Section 2**

Secondary Section

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# Sample Point Selection

- Do a Long-line traverse for the RATA or,
- Conduct a 12-point mercury stratification test prior to the RATA.

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# Analytical Procedures

- Modified EPA Method 1631 Digestion Procedures followed by analysis using cold-vapor atomic fluorescence (CVAF)
- Thermal desorption – Ohio Lumex RA-915+ Hg analyzer with RP-324 attachment
- Thermal combustion – Leeman, Leco, Milestone

# Measurement System Performance Tests

- Determination of minimum mass of Hg to be collected
- Analytical matrix test (wet analysis method)
- $Hg^0$ and $HgCl_2$ analytical bias test (instrumental analysis method)
- Field recovery test


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# Determination of Minimum Mass of Hg to Be Collected

- Perform a multipoint calibration of the analyzer at a minimum of three points (the linear coefficient $r^2$ must be ≥0.99).
- All field samples analyzed must fall within the range of the calibration curve.
- Lowest point in your calibration curve must be ≥10, the minimum detection limit of your instrument (MDL).
- Select a calibration check standard that is >2 times the lowest concentration in your calibration curve.
- Minimum sample time is 30 minutes.

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# $Hg^0$ and $HgCl_2$ Analytical Bias Test

- This test defines the bounds within which the field samples must be to be valid.
- Only done once for each sorbent type or instrument.
- Analyze the front section of three sorbent traps spiked with $Hg^0$ at the lower and upper concentrations (must be spiked with vapor-phase $Hg^0$).
- Analyze the front section of three sorbent traps spiked with $HgCl_2$ at the lower and upper concentrations (liquid standards may be used).
- To be valid, the average recovery of each set of three samples must be between 90% and 110% of the known value.

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# Analytical Bias

| $Hg^0$ Spike, ng | Recovery, % | $Hg^0$ Spike, ng | Recovery, % |
|---|---|---|---|
| 500 | 91.6 | 500 | 102.6 |
| 500 | 83.6 | 500 | 100.0 |
| 500 | 92.0 | 500 | 99.6 |
| 500 | 80.6 | 20 | 105.0 |
| 500 | 84.2 | 20 | 95.0 |
| 200 | 78.5 | 20 | 100.0 |
| 200 | 84.0 | | |
| 200 | 87.5 | | |
| 200 | 90.5 | | |
| 25 | 92.0 | | |
| 25 | 100.0 | | |
| 25 | 104.0 | | |

# Field Recovery Test

- Done once for each unit tested.
- Requires three sets of dual-train tests using one $Hg^0$-spiked trap (first section) paired with a nonspiked trap.
- Based on the Hg mass to be collected on the first section of the trap, the spike must be within 50% to 150% of this mass.

- Sample the stack gas and analyze traps using the same sampling procedures and analytical methods as for the standard field samples

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# Field Recovery Test

- The average of the percentage of the spike recovered must be between 85% and 115% to begin the RATA.
- It is acceptable to perform the field recovery test concurrent with the actual test run using a quad probe.
- It is also acceptable to use field recovery test data as part of the RATA if the difference between the spiked and unspiked samples after subtracting out the spike has a RD of ≤10%.

# Field Recovery Tests

| Sample* | Spike Recovery, % | | | |
|---|---|---|---|---|
| 1 | 98.0 | 94.7 | 105.0 | 100.5 |
| 2 | 59.0 | 86.9 | 89.8 | 90.4 |
| 3 | 11.3 | 106.3 | 98.5 | 86.9 |
| 4 | 54.5 | | | |
| 5 | 112.5 | | | |
| 6 | 101.7 | | | |

*Spiked field recovery samples used (100 ng).

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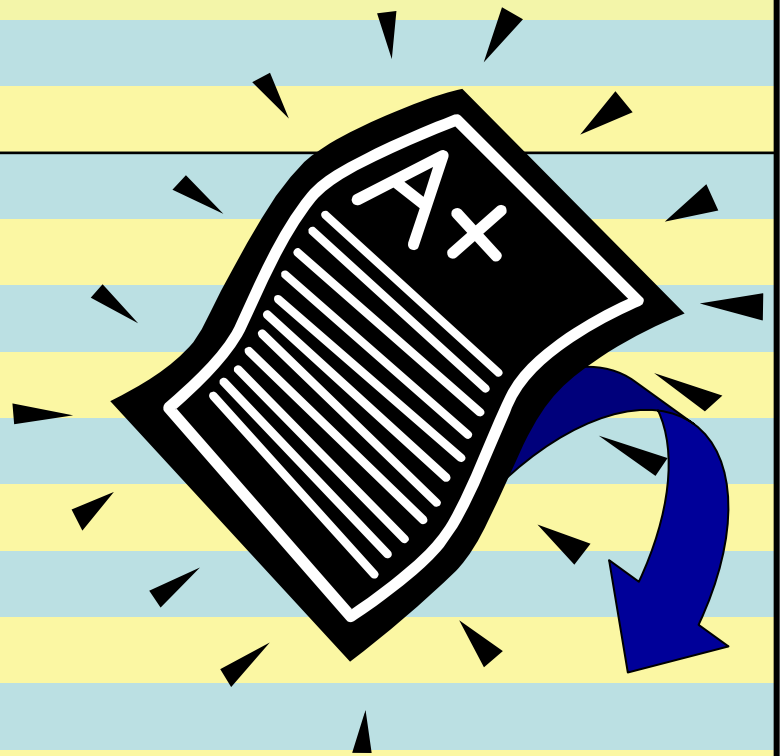
# RATA Data

| Sample | Sorbent Traps, µg/m³ | CMM, µg/m³ | RD, % | d | d² | Std Dev. | $t_{0.975}$ | cc | Bar d | RA, % |
|---|---|---|---|---|---|---|---|---|---|---|
| 1* | 2.90 | 3.04 | 0.79 | -0.14 | 0.020 | | | | | |
| 5* | 3.50 | 3.65 | 4.61 | -0.15 | 0.021 | | | | | |
| 6* | 3.77 | 3.74 | 0.68 | 0.03 | 0.001 | | | | | |
| 8 | 4.20 | 3.75 | 4.70 | 0.45 | 0.203 | | | | | |
| 9 | 3.86 | 3.72 | 1.19 | 0.14 | 0.020 | | | | | |
| 10 | 3.85 | 3.70 | 2.26 | 0.14 | 0.021 | | | | | |
| 11 | 3.55 | 3.59 | 3.79 | -0.04 | 0.002 | | | | | |
| 12 | 3.65 | 3.70 | 0.70 | -0.04 | 0.002 | | | | | |
| 13 | 3.64 | 3.80 | 1.46 | -0.16 | 0.026 | | | | | |
| 14 | 3.74 | 3.94 | 3.57 | -0.20 | 0.039 | | | | | |
| 15 | 3.74 | 3.88 | 2.57 | -0.14 | 0.019 | | | | | |
| 16 | 3.88 | 3.88 | 6.81 | 0.00 | 0.000 | | | | | |
| 17 | 3.73 | 3.88 | 0.42 | -0.15 | 0.023 | | | | | |
| | 3.69 | 3.71 | | -0.25 | 0.396 | 0.181 | 2.179 | 0.109 | -0.019 | 3.47 |




* Spiked samples (90 ng).

# EERC Recommendations

- Carefully read EPA Method 30B and fully understand the requirements before testing.
- If you have a wet stack, you will have to shroud your probe and provide extra heat. In addition you may have to reduce your flow rate (requiring more sample time) because of potential plugging.
- There are enough things that can go wrong that it is essential that the results are obtained quickly. Most likely will require analysis in the field.
- Although optional in the method, you must do blank samples.

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# EERC Recommendations

- Talk to your vendor about obtaining the carbon sorbent in bulk for doing check standards.
- Make sure you have good communication with the CMM operator when doing the RATA.
- Most likely, it will be necessary to have a high and low calibration curve.

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