



CARB 436:

**A Cautionary Tale of
Methods, Math, and
Miscalculations.**

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What Are the Problems?

- The calculations at the end of many promulgated methods are inaccurate.
- Laboratories and Testers need to verify the calculations given in the methods for accuracy.
- Regulators need to be aware of the possibility of errors within the promulgated method.
- CARB 436 is being used as an example. It is not the only method with egregious errors.
- This presentation will only look at the errors in data reduction for mercury in CARB 436. Similar errors are present for other metals in the method when mercury is a desired analyte.
- If Mercury is not a desired analyte, the calculations in CARB 436 are accurate.

Why Does CARB 436 Exist?

- CARB 436 last updated July 28, 1997
- Nearly identical to 40 CFR 60 Method 29 (multi-metals in stationary sources)
- M29 reports Front Half (particulate metals) and Back Half (gaseous metals) as two separate results.
- What if both results are non-detect?
- What if one is non-detect and one is a detectable amount?
- CARB attempted to resolve this problem by combining the Front and Back Half into one digestate.
- One digestate = one detection limit = eliminate problem...
- Unless mercury is a desired analyte.

How to Sample for Mercury Using CARB 436

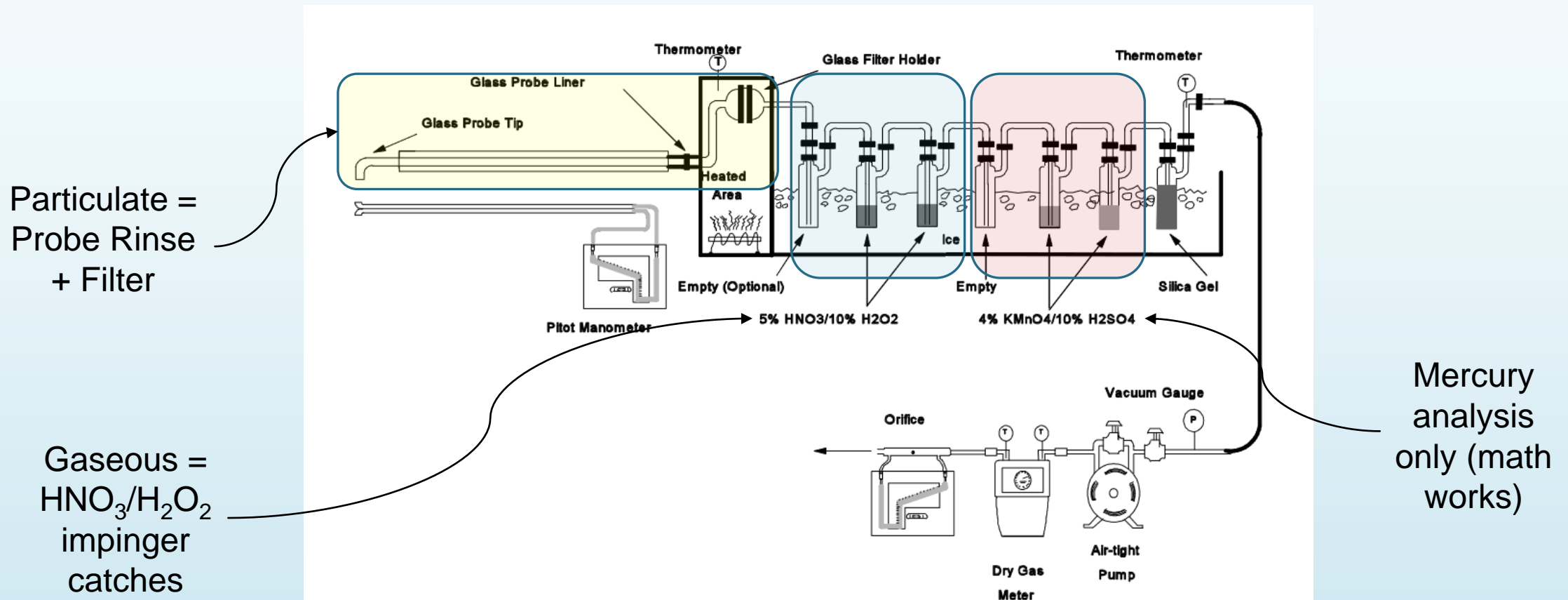
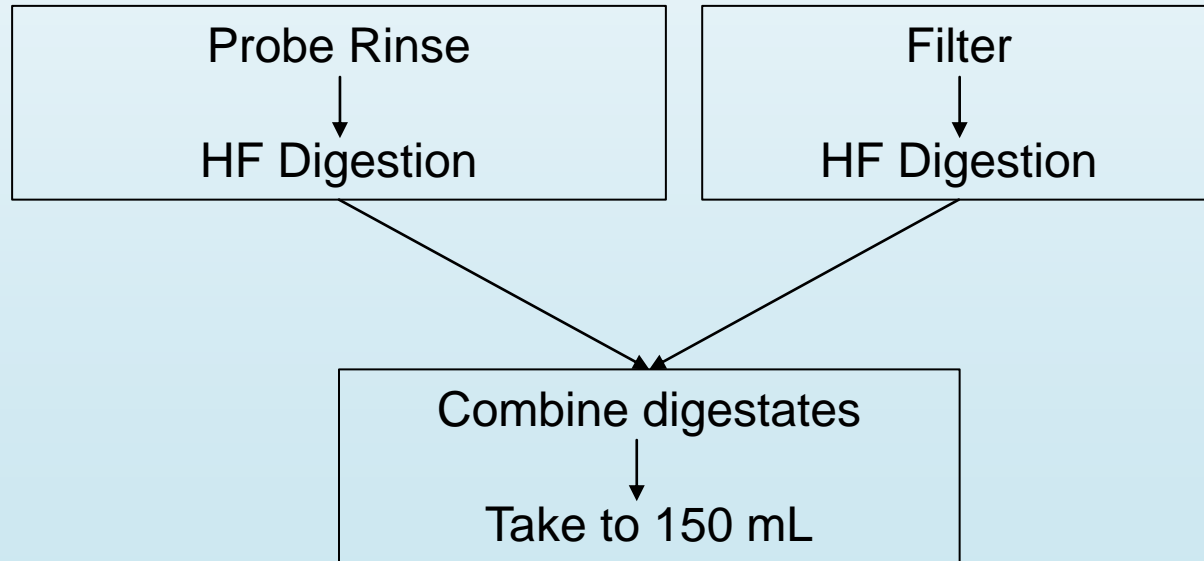
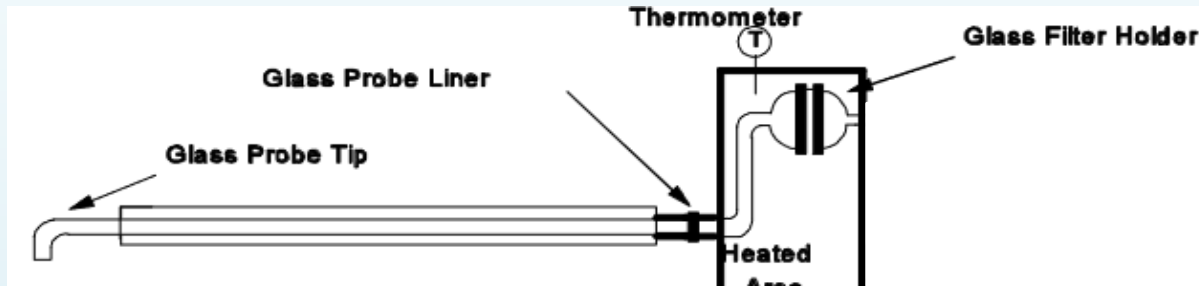


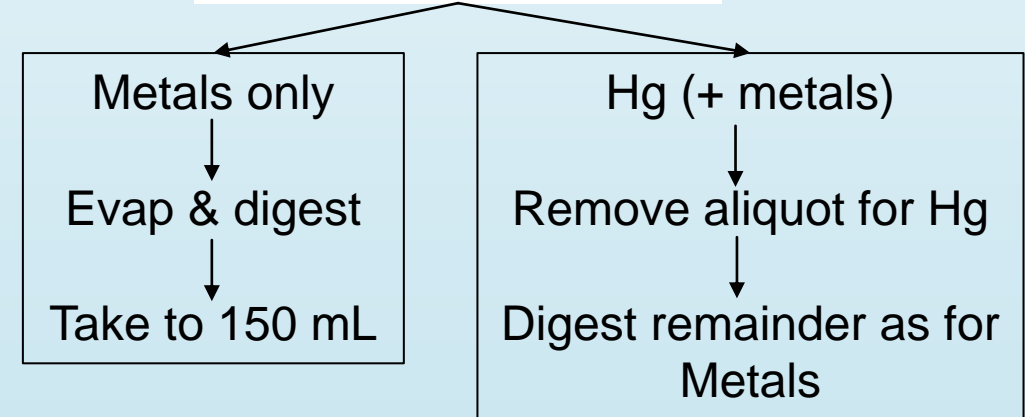
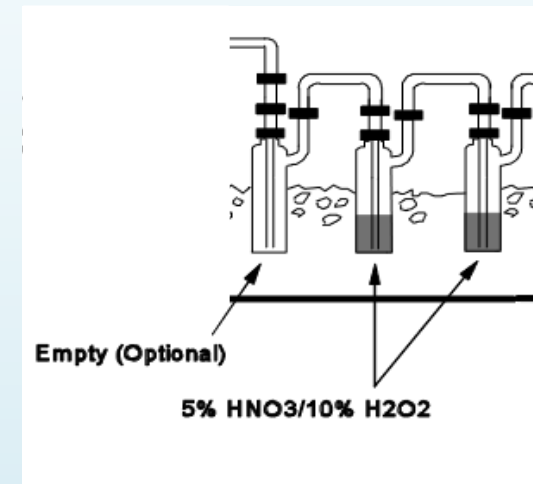
Figure 1. Sampling train.

How to Digest for Mercury Using CARB 436

Front Half (Particulate)



Back Half (Gaseous)



Problem the First

6.1.3 Container No. 3 (Impingers 1-3)

Measure and record the total volume of this sample (Fraction 2) to within 0.5 mL. Remove an aliquot equal in volume to Analytical Fraction 1B for mercury analysis and label as Fraction 2B.

Equal in volume.

Legally, volume = volume. 15 mL = 15 mL.

Volume \neq Percentage.

FH digestate has a known value of 150 mL, therefore 15 mL = 10% of FH digestate.

BH has, at a minimum, 300 mL. 15 mL \neq 10% of BH. 15 mL = 5% maximum of BH.

This is a problem because...

Problem the Second

Fraction 2A is combined with Fraction 1A to form Analytical Fraction A and analyzed using ICP or AAS for all metals except Hg. Fraction 2B is combined with Fraction 1B to form Analytical Fraction B and analyzed using CVAAS to determine front half mercury.

2B ($\leq 5\%$ BH) + 1B (10% FH) = ??? % of total sample.

Example A:

15 mL of 150 mL FH digestate = 10% of FH sample

15 mL of 500 mL BH "as received" = 3% of BH sample

$$10\% + 3\% = 13\%$$

15 mL FH + 15 mL BH = 30 mL sample aliquot

150 mL FH + 500 mL BH = 650 mL total sample volume

$$30 \text{ mL} / 650 \text{ mL} = 4.6\%$$

$$13\% \neq 4.6\%$$

Maybe We Can Proportion the Result?

Assumptions:

- 10% of FH + 3% of BH (13% total sample)
- Filter/Probe Rinse contains 3 mg of Hg in 150 mL of digestate (20 mg/L)
- HNO₃/H₂O₂ contains 7 mg of Hg in 500 mL liquid, as-received by the laboratory (14 mg/L)
- Entire sample, combined = 10 mg Hg in 650 mL total volume (15.38 mg/L)
- The laboratory recovers exactly 100%

Example A:

“True value” of FH = 0.3 mg/15 mL

“True value” of BH = 0.21 mg/15 mL

“True value” of 13% total sample = 0.51 mg/30 mL = 17 mg/L

17 mg/L ≠ 15.38 mg/L (10% RPD)

Our sample is an unknown, no way to know what percent Hg came from FH or BH.
But we can show that the result is incorrect.

Problem the Third

10.5.1 Front-Half Hg; Analytical Fraction B

Calculate the amount of Hg collected in the filter and probe rinse combined with impingers 1 through 3 to form Analytical Fraction B of the sampling train by using Equation 436-10:

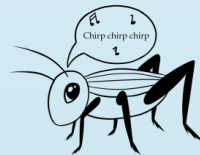
$$Hg_{fh} = \frac{Q_B}{V_B} (V_{soln,B}) \quad \text{Eq. 436-10}$$

“True value” of 13% sample = 17 mg/L (we already know this is wrong)

$V_{soln,B} = 30 \text{ mL}$ (15 mL FH + 15 mL BH)

Total Hg per sample = 17 mg/L Hg \div dil factor if any $\times 0.03 \text{ L} = 0.51 \text{ mg Hg}$

Where does Eq. 436-10 take into account that this result only represents 13% of the total sample volume?



Total Hg per sample = 17 mg/L Hg $\times 0.03 \text{ L} \div 0.13 = 3.923 \text{ mg Hg/Sample}$.

“Reported Value” total Hg per sample = **0.51 mg Hg**, “Known Value” = **10 mg Hg**.

Only 5.1% of the Hg present in the sample is being reported for regulatory purposes.

Problem the Fourth

Remember this?

6.1.3 Container No. 3 (Impingers 1-3)

Measure and record the total volume of this sample (Fraction 2) to within 0.5 mL. Remove an aliquot equal in volume to Analytical Fraction 1B for mercury analysis and label as Fraction 2B.

Equal in volume.

Legally, volume = volume. 15 mL = 15 mL (I checked with an attorney!)

Problems the Fifth/Sixth/Seventh/Eighth

Problems:

5. Figures are not enforceable. To be legally defensible, the method must be run following the “equal in volume” text in section 6.1.3.
6. Since the “10%” given in Figure 3 is not contained in the normative text, a laboratory is in jeopardy of having its data thrown out if it follows Figure 3 and not the normative text.
7. A laboratory is also in jeopardy of having its data thrown out if it does not follow equation 436-10, which we know only reports a small fraction of the total Mercury in the sample %, as there is no multiplier in the equation to back-calculate from $\leq 10\%$ of the sample to 100% of the sample.
8. A laboratory is in double jeopardy of having its data thrown out if it does follow equation 436-10, because we are aware that the amount of mercury reported will likely be $\leq 10\%$.

What Can a Person Do To Avoid This Issue?

**CHECK THE MATH!
THEN HAVE SOMEONE ELSE CHECK THE MATH!**

When errors are found:

Laboratories must discuss the issue with their client before work is started. The final report to the client must contain any knowledge of inaccurate data, no matter what the cause, describe why the data is inaccurate, and what, if anything, the laboratory did to mitigate the problem.

Stationary Source Testers must discuss this issue with the Regulator. No matter what the regulator requires or allows, get it in writing. Attempt to educate the Regulator.

Regulators need to have open, professional and science/math-based discussions with the Testers and Labs. Regulators need to be cognizant that they have far greater ability to fix errors in methods than either the Testers or the Labs.

QUESTIONS?



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