Formaldehyde Testing with Method 323

How to Avoid Common Testing Errors when Using US EPA Method 323 – Best Practices for Best Results

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Formaldehyde Methods

Method	Collection	Preparation	Analysis
Method 320	Heated Line	Direct	FTIR
Method 316	Lg. Aq. Impinger	Chromotropic Acid	Color
NCASI 98.01	Mig. Chilled Aq. Impinger	Acetylacetone	Color
NCASI 105.01	Mig. Aq. Impinger	BHA Derivative	GC
CARB M-430	Mig. Aq. Impinger	DNPH Derivative	LC
Method 0011	Lg. Aq. Impinger	DNPH Derivative	LC
Method 323	Mig. Chilled Aq. Impinger	Acetyl Acetone	Color

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Method 323 Sampling Train Preparation

- Clean and air dry and inspect train sampling lines
  - avoid contamination eliminate pre-sampling water from
    - Quartz or stainless steel probe
    - PFTE Tubing connection tubing

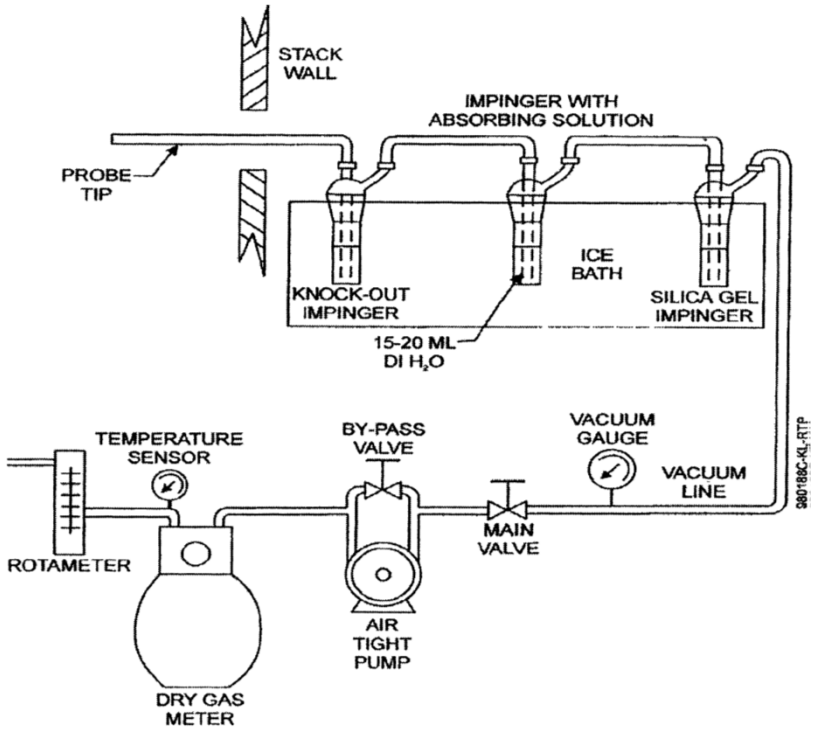

Figure 323-1. Chilled Impinger Train Sampling System

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Method 323 Sampling Topics

- Minimize the sample line length to enhance sample recovery
- Ensure the sample line has no upward or parallel sloped section where condensation can accumulate.

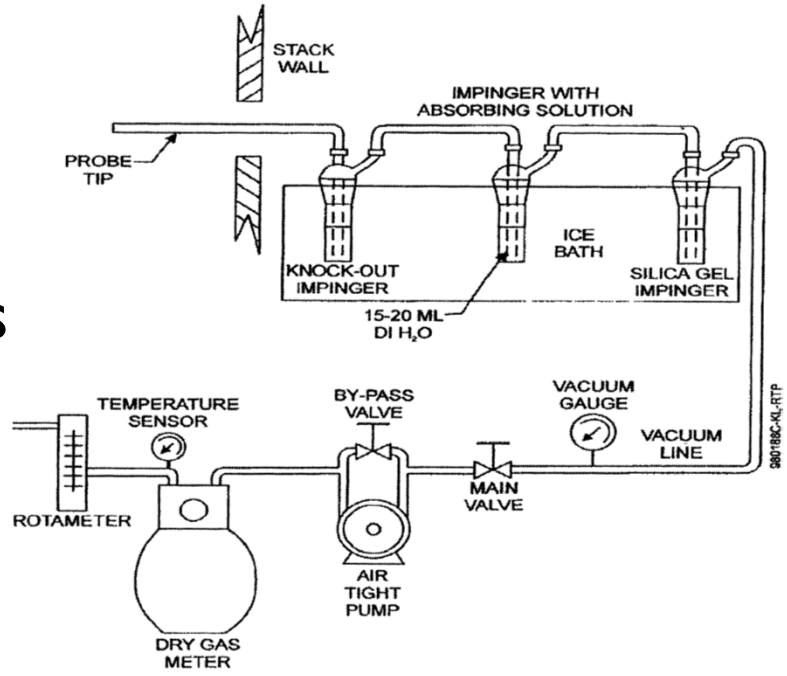

Figure 323-1. Chilled Impinger Train Sampling System

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Method 323 Sampling Topics

- Midget Impinger Style Sampling train
  - Do not use Method 5 impingers
    - This is a stack gas to impinger liquid detection limit issue
  - Do not exceed the nominal method flow
    - This is an impinger collection efficiency issue
    - You are using midget impingers (0.2 to 0.4 L/min)
    - Use maximum 0.4 L/min to reach minimum detection limits

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Method 323 Sample Recovery Topics

- Moisture that accumulates in the sampling line is part of the sample and should be added to the first (knock out) impinger.
  - This moisture is part of the sample and must be completely recovered.
  - Stack Moisture is hard to measure with this sampling train
    - Low volume of water collected
    - Bias from wet impinger surface

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Method 323 Sample Recovery Topics

- Use sufficient water to ensure full sample recovery
  - Longer sampling lines may need more than 10 mL for complete recovery
  - Could require more than 40 mL recovery vial
  - Recovery volume affects detection limit
  - There should be no headspace loss in bigger recovery vessels.
  - Consider the need for antibacterial a.k.a. Method 316

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Method 323 Analysis Topic

- Careful attention to the spectrometer instrument calibration factor to avoid a 2X error:
  - Calibration curve is performed in ug/mL
  - Sample analysis is performed on a total of 2.0 mL aliquot
  - Equation 325-5 corrects for the total and aliquot volume.

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Method 323 Quality Control Topics

- Field Duplicate train is Required and:
  - Trains should be completely independent including:
    - Independent probes
    - Sampling lines
    - Impinger Trains
    - Pumps
    - Flow meters
  - Should agree within 20 percent of the duplicate train average.

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Method 323 Quality Control Topics

- One set of Laboratory Duplicate Analyses
  - Two aliquots of one sample from each source test (a minimum of one pair of aliquots for every 10 samples)
  - Acceptable agreement ± 10 percent of duplicate mean result.

- Matrix Spike/Matrix Spike Duplicate Analysis is required
  - Three aliquots of one sample
    - One native analysis
    - One MS spike analysis
    - One MSD spike analysis
    - Acceptable spike recovery is ± 20 percent

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TRI-fold Best Practices Brochure for Method 323

- Available online: *www.epa.gov/nscep*
- *Will be posted on the EPA TTN EMC website soon.*

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For More Information
To download or print more copies of this brochure:
www.epa.gov/nscep

To access a Technical Report that provides additional information on the recommendations in this brochure:
Visit www.regulations.gov and search for Document ID "EPA-HQ-OAR-2008-0708-0467"

To view the full text of EPA Method 323:
Visit www.epa.gov/ttn/emc/methods/method323.html

Still have questions on this method?
Contact the EPA expert Ray Merrill at merrill.raymond@epa.gov

Background
EPA has found that many Method 323 emission tests are not performed in accordance with the method. Inaccurate measurements may be obtained due to common test method deviations, irregularities, and errors.

This brochure summarizes best practices to minimize human error during preparation, sampling, and data analysis in performing Method 323. This guidance applies when using Method 323 to measure emissions from both engines with post-combustion controls (e.g., oxidation catalysts) and engines with no controls.

Preparation

1. Minimize the sample line length where possible, and ensure the sample line configuration directs flow downward toward the first impinger.
Condensation may accumulate in sections where the sample line configuration is parallel, sloped upward, or looped. Sample losses may result where condensate containing formaldehyde is allowed to accumulate, leading to inaccurate measurement.

2. Inspect and clean sampling lines before conducting test.
Pre-test inspection and cleaning will remove contaminants that may be present. Flushing the sampling lines with air will remove any moisture.

3. Make sure to configure the sample train with midget impingers.
Method 323 Section 6.3 specifies three midget impingers are required for sample collection. You should avoid using Greenburg-Smith impingers or larger impingers since the added volume of the impingers and associated recovery rinses would raise the detection limit of the method.

Sampling Procedures

4. Do not exceed the test method maximum sampling rate of 0.4 L/min.
It is critical that you do not sample at a flow rate higher than 0.4 L/min. Sampling at higher flow rates may reduce formaldehyde collection efficiency resulting in measured formaldehyde concentrations that are less than the actual concentrations.

5. Make sure to thoroughly rinse the probe and sampling line during sample recovery, even if more than 10 mL of water is required.
Method 323 Section 8.3 states: “In general, combined rinse volumes should not exceed 10 mL.” However, in cases where a long, flexible extension line must be used to connect the sample probe to the sample box, sufficient water must be used to rinse the connecting line to recover any sample that may have collected. The volume of the rinses during sample recovery should not be excessive, as this may result in your having to use a larger-than-40 mL VOA bottle.

6. Be aware that accurately measuring moisture with Method 323 may be challenging.
Make sure to thoroughly dry the outside of the impingers before weighing. Avoid allowing condensate to collect in the sampling line, as described in recommendation #1 in this brochure. Moisture that accumulates in the sampling line should be added to the first (knock out) impinger and included in the moisture determination. Since moisture may collect in a common sampling line feeding duplicate sampling trains, the duplicate trains must be independent, including independent sample probes and lines.

QA/QC and Data Analysis

7. Ensure that you review and follow the Quality Control requirements for Method 323.
Method 323 Section 9 lists QA/QC requirement categories, acceptance criteria, and corrective actions.

8. When calculating mass emissions of formaldehyde using Method 323 Equation 323-5, ensure that K_c, the spectrophotometer calibration factor, has been correctly developed.
Method 323 Section 12.1 defines K_c as: “spectrophotometer calibration factor, slope of the least squares regression line, µg/absorbance.” It should be noted that the value of micrograms, µg, used in developing the regression line to calculate K_c, should be per 2-mL aliquot. Equation 323-5 includes a division factor of 2 to account for this; if K_c is not developed on the basis of a 2-mL aliquot, formaldehyde mass emissions will be under-estimated by a factor of 2.

QUESTIONS