Standard Operating Procedure for Sampling and Analysis of Formaldehyde Emissions from Composite Wood Products

SAS20
Revision 1.1

Northern Laboratory Branch
Monitoring and Laboratory Division

Approval Signatures	Approval Date
Manisha Singh, Ph.D., Chief Quality Management Branch	August 23, 2021
Michael Werst, Chief Northern Laboratory Branch	10/28/2021

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Table of Contents

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1 Introduction

This standard operating procedure (SOP) describes procedures for measuring formaldehyde emissions from composite wood products (CWPs) as required by the Airborne Toxic Control Measure to Reduce Formaldehyde Emissions from Composite Wood Products, April 18, 2008 (ATCM).

2 Summary of Method

A section of composite wood sized to meet airflow to surface area requirements is loaded into a small sampling chamber using procedures based on ASTM D6007-02: "Standard test method for determining formaldehyde concentrations in air from wood products using a small-scale chamber". The chamber air is sampled using 2,4-dinitrophenylhydrazine (DNPH) silica gel cartridges to capture the formaldehyde. During composite wood sampling, the formaldehyde (H2CO) reacts with the DNPH on the cartridge to form the hydrazone derivative. DNPH cartridges are eluted with acetonitrile (ACN) and the DNPH-derivative extract is then analyzed using a liquid chromatograph with an ultraviolet detector (HPLC-UV), a procedure based on ASTM D5197-03: "Standard test method for determination of formaldehyde and other carbonyl compounds in air (active sampler methodology)".

3 Acronyms and Definitions

Acronym or Term	Definition
ACN	Acetonitrile
Analytical Batch	A set of prepared samples (i.e., extracts) analyzed together as a group in an uninterrupted sequence.
Blank	A sample that has not been exposed to the sample stream in order to monitor contamination during sampling, transport, storage, extraction, or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value.
Calibration	Calibration refers to the act of evaluating and adjusting the precision and accuracy of measurement equipment using known values (i.e., standards).
CARB	California Air Resources Board

Acronym or Term	Definition
Cartridge Blank	A new DNPH cartridge from the same lot as those used for samples that is not exposed to the target analyte or sample matrix (i.e., does not go through the sampling process) but is carried through all extraction and analytical steps to determine any possible background contribution from the cartridge.
CHP	Chemical Hygiene Plan
COC	Chain of Custody
Composite Wood Products (CWP)	The complete item purchased (e.g., a box of flooring, a cabinet, a panel).
Conditioning Environmental Chamber	An environmental chamber used to bring samples to a similar temperature and relative humidity (RH) prior to sampling (APPENDIX A, Figure 1).
Control/check standard	A quality control (QC) standard prepared from a source different from the calibration standards. This QC, although the same solution, may also be separately identified as a control and a check standard.
DNPH	2,4-dinitrophenylhydrazine
Duplicate	Two aliquots taken from and representative of the same sample or product and carried through all steps of the sampling and analytical procedures in an identical manner. Duplicate samples are used to assess variance of the total method including sampling and analysis.
Eluted DNPH cartridge	A DNPH cartridge that has gone through the elution process.
Elution	The process of removing an adsorbed substance from an adsorbent by washing with a solvent.
Environmental Chamber	An enclosure with controlled temperature and humidity.
Extract	The product obtained from the elution of DNPH cartridge.
H&SC	Health & Safety Coordinator
H2CO	Formaldehyde
HPLC-UV	High Performance Liquid Chromatography with Ultraviolet Detector
LIMS	Laboratory Information Management System
NIST	National Institute of Standards and Technology
NLB	Northern Laboratory Branch
Preparation (extraction) Batch	A set of samples processed all in one group using the same equipment and reagents.
PTFE	Polytetrafluoroethylene

Acronym or Term	Definition
Purge Cartridge	DNPH cartridge attached to the small sampling chamber during a system purge. This cartridge is not analyzed and may be used multiple times for this purpose.
QC	Quality Control
QCM	Quality Control Manual
RH	Relative Humidity
Sample	The item that goes into the chamber for analysis, samples may be made from multiple specimens. Multiple samples may be analyzed for one product. Each sample has a unique sample number. One or more specimens may be sampled in a single small sampling chamber, as a single unit, in order to achieve air flow to surface area requirements.
Sample Batch	The samples that are conditioned together at the same time in the conditioning environmental chamber.
Sample Conditioning	To hold samples in an environmental chamber at specified temperature and humidity for a specified time prior to sampling (APPENDIX A, Figure 2).
Sampled DNPH cartridge	A DNPH cartridge that has gone through the sampling process, before going through elution.
Sampling Batch	The samples that are sampled together at the same time in the sampling environmental chamber.
Sampling Environmental Chamber	An environmental chamber used to hold small sampling chambers for sampling (APPENDIX A, Figure 3).
Small Sampling Chamber	An enclosure used to hold samples for collection of emissions while air is circulated at a specified flow rate around the sample inside (APPENDIX A, Figure 4). Multiple small sampling chambers fit into a single sampling environmental chamber.
Small Sampling Chamber Blank (Method Blank)	A blank used to monitor the laboratory preparation and analysis systems for interferences and contamination from glassware, reagents, sample manipulations, and the general laboratory environment. This blank is an analyte-free matrix to which all reagents are added in the same volumes or proportions as used in sample processing, and which is taken through the entire sample preparation and analysis process.
Solvent Blank	A sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps.
SOP	Standard Operating Procedure

Acronym or Term	Definition
Specimen	A unit that is cut from the CWP. Specimens can be put together to create the surface area necessary for one sample. A single piece of cut composite wood.

4 Interferences

Interferences can result from contaminants in solvents, reagents, glassware and other processing apparatus that can lead to discrete artifacts or elevated baselines. High levels of formaldehyde in background or supply air may contribute to elevated concentrations. A solvent blank, cartridge blank and small sampling chamber blanks (method blanks) must be analyzed with each batch of samples to detect any possible interference. Conditioning environmental chamber and room background levels are analyzed on a quarterly basis and must not exceed 20 ppb.

5 Personnel Qualifications and Training

5.1 Prior to performing this method, new personnel must be trained by staff with expert knowledge of this method. Personnel must be trained to understand the program's requirements per any applicable State and federal regulations and guidance, and this SOP. Personnel will also be trained on how to safely and properly operate the equipment needed to perform the method, the quality assurance components, and LIMS functionality pertaining to the program.

5.2 Personnel should provide an initial demonstration of capability prior to performing this method on real-world samples (i.e., data for record).

5.3 Training will be documented and maintained by the laboratory supervisor.

6 Safety Requirements

6.1 All personnel must follow the general health and safety requirements found in NLB's Chemical Hygiene Plan.

6.2 Ensure engineering controls are in place and operating (i.e., adequate ventilation).

7 Hazardous Waste

7.1 As formaldehyde is a carcinogen, the waste stream needs to be segregated and managed properly. Waste vials must be stored in a designated collection bucket that is separate from other solvent/vial waste streams. Any other liquid waste containing formaldehyde must be similarly managed. H&SC must be notified when waste bucket is ready for disposal.

7.2 Sample extracts are to be disposed of in the composite wood waste container in

the satellite hazardous waste accumulation area.

7.3 Waste generated by the instrumentation are to be collected in a satellite waste container and disposed of in accordance with the NLB Chemical Hygiene Plan.

8 Equipment, Supplies, and Chemicals

8.1 Conditioning Environmental Chamber (e.g., Caron model 6020-1 with Condensate Recirculator model CRSY102-1)

8.1.1 Temperature and humidity monitoring system (e.g., chart recorders)

8.1.2 Flow Meter

8.2 Sampling Environmental Chamber (e.g., Caron model 6020-1 with Condensate Recirculator model CRSY102-1)

8.2.1 Temperature and humidity monitoring system (e.g., chart recorders)

8.2.2 Mass Flow Controller

8.2.3 Small Sampling Chambers each with a volume of 0.021 m^3 (20.32 x 20.32 x 50.8 cm)

8.2.4 Sampling manifold (APPENDIX A, Figure 5)

8.2.4.1 Mass Flow Controllers

8.2.4.2 Vacuum Pump

8.2.5 Flow Meter

8.3 HPLC system with Multiple Wavelength Detector (MWD), capable of detecting 360 nm (e.g., Agilent 1260 Infinity Series)

8.3.1 Column: C-18 150 x 4.6 mm, 5 µm (e.g., Restek Allure)

8.3.2 Laboratory work station with software for data processing (e.g., ChemStation, OpenLab)

8.4 Software for data transfer and collection (e.g., BalanceTalk, Excel, LabX)

8.5 Laboratory Information Management System (LIMS)

8.6 Analytical Balance, capacity of at least 200 g x 0.00001 g readability (e.g., Mettler XP205 or Sartorius Genius)

8.7 Refrigerator/Freezer

8.8 Pipettors, various sizes

8.9 Transfer pipettes, disposable

8.10 Volumetric flasks, various sizes

8.11 2 mL autosampler vials with caps

8.12 Sample vials, 8 mL

8.13 Syringe, glass 10 mL

8.14 Task wipes (e.g., Kimwipes)

8.15 Gloves, non-powdered nitrile or suitable alternative

8.16 Clock or timer

8.17 DNPH cartridges (e.g., Sigma Aldrich)

8.18 Flex tape, Metallized Flexible Duct Tape (e.g., 3M™ Metallized Flexible Duct Tape 3350)

8.19 Ruler

8.20 Razor Blades, Single Edge

8.21 Reagents and Samples

8.21.1 Water, ASTM Type 1

8.21.2 Acetonitrile, >99.9%, HPLC grade or better

8.21.3 Calibration standard, Formaldehyde DNPH stock standard in ACN (e.g., Restek Formaldehyde-DNPH Standard, 500 µg/mL of formaldehyde, in acetonitrile)

8.21.4 Control/check standard, neat Formaldehyde DNPH (e.g., Sigma Aldrich Formaldehyde-2,4-DNPH, 100mg, Neat)

9 Procedure

9.1 Composite wood sample transfer

9.1.1 Transfer custody of composite wood samples

9.1.1.1 Samples arrive at the laboratory with COC forms. If the sample identification information does not match the COC record, the laboratory shall refuse to accept samples until the discrepancy is resolved.

9.1.1.2 The area and cut size of the sample submitted is dependent on the type of composite wood product and based on the flow to area (Q/A) ratio described in ASTM D6007-02. Measure the sample to ensure the dimensions meet the requirements. Several specimens may be submitted as one sample.

9.1.1.3 Ensure the prescreen levels are indicated on the COC when available.

9.1.1.4 Fill out the Transfer Record on the COC. Include any applicable fields indicating the persons involved in the transfer and the date of the transfer.

9.1.2 Store composite wood samples as received in separate packaging at room temperature in a locked cabinet.

9.1.3 Log composite wood samples into LIMS (see LIMS Manual: Sample Login)

9.2 Composite Wood Sample Preparation

9.2.1 Obtain a sample batch

9.2.1.1 Determine the number of samples in the sample batch, and obtain the samples and the COC paperwork.

9.2.1.2 Transfer custody of samples by filling out the transfer record on the COC.

9.2.2 Prepare composite wood samples for conditioning

9.2.2.1 Follow all instructions on the COC to achieve surface area requirements (e.g., test one specimen with both sides exposed, two specimens cut and arranged back-to-back, or specimens arranged in sequence).

9.2.2.2 Cover exposed edges with flex tape.

9.3 Composite Wood Sample Conditioning

9.3.1 Conditioning environmental chamber requirements

9.3.1.1 The temperature and relative humidity of the conditioning environmental chamber must be 24 ± 3°C and 50 ± 5%, and is continuously monitored and recorded to ensure that these parameters stay within the range.

9.3.1.2 Ensure air is flowing through the chamber.

9.3.1.3 Determine the conditioning environmental chamber background levels quarterly.

Attach one end of an approximately 10 ft. piece of PTFE tubing to a DNPH cartridge attached to the sampling manifold tubing within the sampling

environmental chamber. Place the other end of the tubing in the conditioning environmental chamber. Close the doors of both environmental chambers as tightly as possible. Turn on the sampling manifold and sample the empty chamber for 0.5 hour. Repeat with a second DNPH cartridge.

Elute the sampled DNPH cartridges, and analyze the extracts following procedures outlined in sections 9.6 - 9.8.

Calculate the conditioning environmental chamber background level by averaging the results.

The background formaldehyde levels shall not exceed the limit of 20 ppb.

9.3.1.4 Determine the room background levels quarterly.

Attach one end of an approximately 10 ft. piece of PTFE tubing to a DNPH cartridge attached to the sampling manifold tubing within the sampling environmental chamber. Place the other end of the tubing in the laboratory room. Close the sampling environmental chamber door as tightly as possible. Turn on the sampling manifold and sample the laboratory room for 0.5 hour. Repeat with a second DNPH cartridge.

Elute the sampled DNPH cartridges, and analyze the extracts following procedures outlined in sections 9.6 - 9.8.

Calculate the room background level by averaging the results.

The background formaldehyde levels shall not exceed the limit of 20 ppb.

9.3.2 Sample Placement

9.3.2.1 Place the composite wood samples in the conditioning chamber standing on edge and at least six (6) inches apart to ensure that the maximum surface area is exposed. This maximizes airflow around the samples (APPENDIX A, Figure 2).

9.3.2.2 Place samples in the conditioning chamber according to their formaldehyde prescreening concentrations when indicated on the COC. When a prescreen test indicates a high emitting sample, the high emitting samples (> 150 ppb H2CO) are not conditioned with low emitting samples (< 70 ppb H2CO) to avoid cross contamination. If no prescreen levels are indicated on the COC, and following analysis it is determined that high emitting samples were conditioned with low emitting samples, re-condition, re-sample and reanalyze the low emitting samples.

9.3.3 Sample Conditioning

9.3.3.1 Condition the composite wood samples for 24 hours ± 3 hours prior to sampling.

9.3.3.2 Record the date, time, temperature, and RH at the beginning of the conditioning period.

9.3.3.3 Record the date, time, temperature, and RH at the end of the conditioning period.

9.3.3.4 Remove the composite wood samples from the conditioning environmental chamber and immediately transfer them to the sampling environmental chamber placing each in its own small sampling chamber as specified in section 9.4.4.2.

9.4 Composite Wood Sample Emission Sampling

9.4.1 Sampling environmental chamber requirements

9.4.1.1 The temperature and relative humidity of the sampling environmental chamber is maintained at 25 ± 1°C and 50 ± 4% and is continuously monitored and recorded to ensure that these parameters stay within the range.

9.4.1.2 Small sampling chambers are located inside the sampling environmental chamber.

Each small sampling chamber has a volume of 0.021 m^3 (20.32 x 20.32 x 50.8 cm). The airflow is 0.06 m^3/hour (1.0 L/min) and is maintained using a sampling manifold that includes a pump and flow controllers (APPENDIX A, Figure 5).

9.4.2 Purging the small sampling chambers prior to method blank collection

9.4.2.1 For each small sampling chamber, attach a DNPH cartridge (a previous cartridge blank is acceptable) between the small sampling chamber outlet and the sampling manifold tubing (APPENDIX A, Figure 6). This cartridge is a “purge cartridge” and may be used for this purpose multiple times, but should be replaced monthly. The purge cartridge is not analyzed.

9.4.2.2 Turn on the sampling manifold to purge the small sampling chambers for 0.5 hour.

9.4.3 Collecting the small sampling chamber blanks (method blanks)

9.4.3.1 For each small sampling chamber being used, replace the purge cartridge with a new labeled DNPH cartridge. Label and do not discard cartridge packaging.

9.4.3.2 Labels shall identify the sampling chamber to which they correspond, and the date.

9.4.3.3 Turn on the sampling manifold and sample the empty chamber for 0.5 hour.

Record the date, time, temperature, and RH at the start of the method blank sampling period.

9.4.3.4 Turn off the sampling manifold and remove the sampled DNPH cartridge(s) at the end of the sampling period.

Record the date, time, temperature, and RH at the end of the method blank sampling period.

9.4.3.5 Store the sampled DNPH cartridge method blanks in the original cartridge packaging under conditions specified by the cartridge manufacture until elution.

9.4.4 Purging the small sampling chamber prior to collecting emissions from the sample

9.4.4.1 Reattach the purge cartridges to the small sampling chambers.

9.4.4.2 Transfer each conditioned composite wood sample from the conditioning environmental chamber to a small sampling chamber (APPENDIX A, Figure 4) after purging the small sampling chambers and collecting method blanks.

9.4.4.3 Turn on the sampling manifold to purge the small sampling chambers for 0.5 hour to allow the small sampling chamber conditions to equilibrate.

9.4.5 Collecting emissions from the sample(s)

9.4.5.1 Replace the purge cartridge(s) with new, labeled DNPH cartridge(s). Label and do not discard cartridge packaging.

Labels shall include the composite wood sample ID number, date, and identify the small sampling chamber to which they correspond.

9.4.5.2 Turn on the sampling manifold and sample the chambers for 0.5 hour.

Record the date, time, temperature, and RH at the start of the sampling period.

Flow rates must be recorded at the start and end of each sampling period and must not vary by more than 0.05 L/min for the sample to be considered valid.

9.4.5.3 Turn off the sampling manifold and remove the sampled DNPH cartridge(s) at the end of the sampling period.

Record the date, time, temperature, and RH at the end of the sampling period.

Flow rates must be recorded at the start and end of each sampling period and must not vary by more than 0.05 L/min for the sample to be considered valid.

9.4.5.4 Store the sampled DNPH cartridges in their original packaging under refrigeration until elution.

9.4.6 Collecting a duplicate from one composite wood sample per sampling batch

9.4.6.1 Replace one of the sampled DNPH cartridges with a new DNPH cartridge labeled for the duplicate. Label and do not discard cartridge packaging.

Labels shall include the composite wood sample ID number, date, and identify the small sampling chamber to which they correspond.

Replace the remaining sampled DNPH cartridges with the purge cartridges.

9.4.6.2 Turn on the sampling manifold and sample the chamber for 0.5 hour.

Record the date, time, temperature, and RH at the start of the sampling period.

Flow rates must be recorded at the start and end of each sampling period and must not vary by more than 0.05 L/min for the sample to be considered valid.

9.4.6.3 Turn off the sampling manifold and remove the sampled DNPH cartridge at the end of the sampling period.

Record the date, time, temperature, and RH at the end of the sampling period.

Flow rates must be recorded at the start and end of each sampling period and must not vary by more than 0.05 L/min for the sample to be considered valid.

9.4.6.4 Store the sampled DNPH cartridge for the duplicate in the original packaging under refrigeration until elution.

9.4.7 Repeat section 9.4.4 to 9.4.7 as necessary for additional samples.

9.5 Hold time of sampled DNPH cartridges

Storage of sampled DNPH cartridges must not exceed 30 days. If this hold time prior to elution is exceeded, results may be biased low and shall be flagged on the report to the client.

9.6 DNPH Cartridge Elution

9.6.1 Bring the sampled DNPH cartridges and a new DNPH cartridge (cartridge blank) to room temperature before elution.

9.6.2 Elute the H2CO-DNPH derivative from the sampled DNPH cartridge with 10 mL acetonitrile.

9.6.2.1 Collect the extract in a 10 mL volumetric flask.

9.6.2.2 Bring the volumetric flask up to volume with acetonitrile.

9.6.2.3 Cap and mix by inversion.

9.6.3 Transfer approximately 2 mL of the extract to a 2 mL autosampler vial and cap. Transfer the remainder into a sample vial and cap.

9.6.4 Repeat sections 9.6.1 to 9.6.3 for all samples, duplicates, method blanks, and a cartridge blank.

9.6.5 Prepare an acetonitrile solvent blank in a 2 mL autosampler vial and cap.

9.7 Hold time of extracts

Extracts may be stored under refrigeration, but must be analyzed within 180 days of elution. If this hold time is exceeded, results may be biased low and shall be flagged on the report to the client.

9.8 Extract Analysis

9.8.1 Bring extracts to room temperature prior to analysis.

9.8.2 Prepare calibration standards.

9.8.2.1 Prepare a working standard from the formaldehyde DNPH stock standard solution at 10 µg/mL of free formaldehyde in ACN. Note the equation for converting between free formaldehyde concentration and its hydrazine derivative in section 12.

9.8.2.2 Pipette 0.5 mL of the stock standard into a 25 mL volumetric flask and bring to volume with acetonitrile. Alternative volumes may be prepared with the same final concentration.

9.8.2.3 Store under refrigeration.

9.8.2.4 Prepare calibration standards from the 10 µg/mL working standard at the following concentrations in ACN: 0.05, 0.10, 0.20, 0.50, 1.00, and 2.00 µg/mL.

Pipette the working standard into 10 mL volumetric flasks as follows:

Volume of Standard	Calibration Standard Concentration
0.05 mL	0.05 µg/mL
0.10 mL	0.10 µg/mL
0.20 mL	0.20 µg/mL
0.50 mL	0.50 µg/mL
1.00 mL	1.00 µg/mL
2.00 mL	2.00 µg/mL

Alternative volumes may be prepared with the same final concentration.

9.8.2.5 Store under refrigeration.

9.8.3 Prepare Control/check Standard

9.8.3.1 Prepare a 1.0 mg/mL control/check standard stock solution by weighing 10 mg of neat formaldehyde DNPH in a 10 mL volumetric flask and bring to volume with acetonitrile.

9.8.3.2 Prepare the working control/check standard at 1.4 µg/mL of formaldehyde DNPH which is equivalent to 0.20 µg/mL of formaldehyde in ACN. Intermediate standards may be used.

9.8.3.3 Prepare intermediates stock solutions using the C1xV1=C2xV2 formula, where C stands for concentration and V for volume. See table below for 5 mL final volume examples.

Final Concentration (µg/mL)	Volume of standard	Volume of ACN (mL)
100	0.5 mL of 1.0 mg/mL stock	4.5
10	0.5 mL of 100 µg/mL stock	4.5
1.4	0.7 mL of 10 µg/mL stock	4.3

9.8.3.4 Alternative volumes may be prepared with the same final concentration.

9.8.3.5 Store under refrigeration.

9.8.4 Prepare the HPLC Instrument

9.8.4.1 Turn on the following components of the HPLC system: Pump, Autosampler, Column Heater, and UV Detector.

9.8.4.2 Prepare the mobile phases, ensuring there is enough for the analytical run.

Mobile phase A: 60% ACN / 40% Water

Mobile phase B: 100% ACN

9.8.4.3 Start the HPLC pumping mobile phase A at a minimum of 0.2 mL/min. The baseline should stabilize after approximately 40 minutes. Once the baseline has stabilized, prepare for the analytical run.

9.8.4.4 Verify the following method parameters:

Quaternary Pump Flow Rate	1.000 mL/min
Injection Volume	5.00 µL
Column Temperature	35.0°C
Stop Time	15 min
Detector Signal	Wave length 360 nm, band width 4

Gradient Program Timetable:

Time (min)	%A	%B
0.0	100.0	0.0
4.5	100.0	0.0
5.0	0.0	100.0
10.0	0.0	100.0
10.5	100.0	0.0

9.8.4.5 Save the method and sequence table using the analysis date as a part of the name. The sequence should be in the following order with a maximum of ten samples between control and check standards, and ending with a check standard:

Solvent Blank, Calibration Standards, Solvent Blank, Control, Solvent Blank, Cartridge Blank, Small Sampling Chamber Blanks, Samples, and Solvent Blank, Check Standard.

Add additional solvent blanks and check standards as necessary.

9.8.5 Analysis

9.8.5.1 Place the 2 mL autosampler vials in the autosampler, matching the vial location in the sequence.

9.8.5.2 Run the sequence.

9.8.5.3 Verify quality control criteria in section 10 are met.

9.8.5.4 Print and review the chromatograms and the calibration curve.

9.9 Data upload to LIMS

9.9.1 Enter batch information (refer to LIMS Manual: Batch Information Login)

9.9.2 Enter batch results (refer to LIMS Manual: Formaldehyde Results and QC Data)

9.10 Report generation

Generate a report (refer to LIMS Manual: Formaldehyde Results Report)

9.11 Data Review

Submit the data set for peer and management review. The NLB QCM outlines the review process and criteria.

10 Quality Control

10.1 Table of Quality Controls

QC Type	Frequency	Criteria	Corrective Action
Solvent Blank	Before the calibration, before and after the control standard, before and after each check standard, except at the end of the analytical batch in which the solvent blank is only analyzed before check standard.	Must be free of interferences that may affect the formaldehyde peak, and less than the lowest calibration standard.	If criterion is not met, results are invalid. The affected sample(s) shall be re-sampled and reanalyzed.

QC Type	Frequency	Criteria	Corrective Action
Method Blank	One per small sampling chamber per day	The concentration of formaldehyde must not exceed 20 ppb.	If criterion is not met, sample results from that small chamber are invalid. The affected sample(s) shall be re-sampled and reanalyzed.
Cartridge Blank	One per extraction batch	Must not contain formaldehyde greater than 0.15 µg/cartridge	If criterion is not met, results are invalid. The affected sample(s) shall be re-sampled and reanalyzed.
Calibration	Each analytical batch	$R^2 \geq 0.999$	If criterion is not met, reanalyze the calibration curve or make new calibration standards. Reanalyze the analytical batch after successful calibration.
Control/check Standard	The control/check standard is analyzed after the calibration and after every ten or fewer samples and at the end of the analytical sequence.	Warning and control limits set at ± 8 and ± 10 percent difference respectively from the target value.	If an analysis is outside of the control limits, the affected sample results are invalid. Take action to bring the system back into control and reanalyze the control/check and any samples not bracketed by successful control/check standards. Three consecutive control standards falling between the warning and control limits require investigation and corrective action as described in the QCM.

QC Type	Frequency	Criteria	Corrective Action
Duplicate	Minimum of one per sampling batch.	Relative percent difference within 20 percent.	Evaluate the cause of the discrepancy (i.e., inadequately set cartridge, loose sampling line, or other mechanical issues, issues with the analytical system, etc.) and make appropriate corrections. Samples are re-sampled and/or reanalyzed as necessary (e.g., if the cause of the discrepancy is due to an issue in the sampling process, samples are resampled and reanalyzed. If the cause of the discrepancy is the result of an issue within the analytical process, extracts are reanalyzed, but samples don't necessarily need to be resampled).
Background (Conditioning Environmental Chamber and Room)	Quarterly	The concentration of formaldehyde must not exceed 20 ppb	Discontinue conditioning/sampling until background levels are below the 20 ppb limit. Investigate the source of the contamination and/or contact facilities about the building air quality.
Conditioning Environmental Chamber	All conditioning batches	Temperature must be 24 ± 3°C. RH must be 50 ± 5%.	If any criteria are not met, discontinue conditioning. Bring system back into compliance prior to restarting the sample conditioning.

QC Type	Frequency	Criteria	Corrective Action
Sample Conditioning	All conditioning batches	Samples must be conditioned for 24 hours ± 3 hours immediately prior to transferring to the small sampling chambers for equilibration and emission sampling.	If any criteria are not met, discontinue conditioning. Bring system back into compliance prior to restarting the sample conditioning.
Sampling Environmental Chamber	All sampling batches	Temperature must be 25 ± 1°C. RH must be 50 ± 4%.	If any criteria are not met, discontinue sampling. Bring system back into compliance prior to restarting the sample batch.
Sample Emission Sampling	All sampling batches	Flow rates must not vary by more than 0.05 L/min. Samples must be sampled for 0.5 hour.	If any criteria are not met, discontinue sampling. Bring system back into compliance prior to restarting the sample batch.
Sampled DNPH Cartridge Hold Time	All sampled DNPH cartridges	Store the sampled DNPH cartridges under refrigeration. Storage of sampled DNPH cartridges must not exceed 30 days.	If hold time is exceeded, results may be biased low and shall be flagged on the report to the client.
Extract Hold Time	All extracts	Store the extracts under refrigeration. Storage of extracts must not exceed 180 days.	If hold time is exceeded, results may be biased low and shall be flagged on the report to the client.

10.2 Equipment Requirements

10.2.1 Environmental Chambers must be verified for temperature and RH on a quarterly basis using a NIST traceable temperature/humidity/dew point meter.

10.2.2 Mass flow controllers must be calibrated or have calibration verified at least annually against NIST traceable standards, where feasible, by an outside vendor or by CARB's Standards Laboratory.

11 Sample and Data Management

11.1 Data management consists of samples logged into the LIMS, documentation of unusual occurrences and their resolutions, creation of data packages (monthly, amendments, and special projects) for peer review and management approval,

submittal of data to clients, and archival procedures for sample media and respective chains of custody. Program and maintenance notebooks and/or logbooks are to be kept with the instrumentation at all times.

11.2 The LIMS Manual describes data management procedures as they pertain to LIMS for this SOP. LIMS performs the functions of data storage, data processing, and report generation.

11.3 Final reports generated by LIMS and submitted for review and approval as outlined in the QCM will include the following:

11.3.1 Conditioning information: date, time, temperature, humidity, duration, conditioning background level

11.3.2 Sampling information: date, time, temperature, humidity, air flow rate, duration, testing background level

11.3.3 Analytical results: sample identification, wood type, analysis date

12 Calculations

12.1 Standard stock solution concentrations are given either as free formaldehyde concentration or as hydrazine derivative (H2CO-DNPH). To convert between these concentrations use the following equation:

$$C_{H2CO} = C_{H2CO\text{-}DNPH} \times \frac{MW_{H2CO}}{MW_{H2CO\text{-}DNPH}}$$

Where:

C_{H2CO} = concentration of H2CO

$C_{H2CO\text{-}DNPH}$ = concentration of H2CO-DNPH

MW_{H2CO} = molecular weight of H2CO = 30.031 g/mol

$MW_{H2CO\text{-}DNPH}$ = molecular weight of H2CO-DNPH = 210.15 g/mol

12.2 The total amount of formaldehyde emissions collected from a sample (W) in µg, is calculated as:

$$W = C_{H2CO}\ (\mu g/mL) \times 10\ mL \text{ of total collected sample}$$

Where:

C_{H2CO} = concentration of formaldehyde in the extract

12.3 Molar volume (V_m), using ideal gas law approximation (PV = nRT) at sampling

conditions:

$$V_m = \frac{V}{n} = \frac{RT}{P} = \frac{\left(0.082057\ \left(\frac{L \times atm}{K \times mol}\right) \times 298.15\ K\right)}{1\ atm} = 24.465\ L/mol$$

Where:

P = 1 atm

T = 25°C = 298.15K

R = 0.082057 ((L x atm)/(K x mol))

12.4 Volume of air passed over the sample in the small sampling chamber during the sampling period (V_a):

$$V_a(L) = \text{air flow (L/min)} \times \text{time (min)}$$

12.5 The concentration of free formaldehyde in ppm (C_{H2CO}) is calculated according to:

$$C_{H2CO}\ (ppm) = \frac{W(\mu g) \times V_m\left(L/mol\right)}{V_a(L) \times MW_{H2CO}\left(g/mol\right)}$$

Where:

W = the amount of H2CO in an aliquot (µg)

V_m = molar volume at sampling temperature (L/mol)

V_a = volume of air (L) passed over the sample in the small sampling chamber during the sampling period

MW_{H2CO} = molecular weight of H2CO = 30.031 g/mol

12.6 To convert from ppm to ppb:

$$1\ ppm = 1000\ ppb$$

12.7 Relative Percent Difference (RPD) shall be calculated as follows:

$$RPD = \frac{|(Y-X)|}{((Y+X)/2)} \times 100$$

Where:

X = the sample result

Y = the duplicate result

13 References

13.1 ASTM D6007-02 Standard Test Method For Determining Formaldehyde Concentration in Air From Wood Products Using a Small Scale Chamber

13.2 ASTM D5197-03 Standard Test Method for Determination of Formaldehyde and Other Carbonyl Compounds in Air (Active Sampler Methodology)

13.3 NLB Laboratory Quality Control Manual, September 17, 2018

13.4 MLD076 Standard Operating Procedure Preparation of Northern Laboratory Branch's Standard Operating Procedures, Revision 0.0

13.5 NLB Chemical Hygiene Plan (June 2019, or most current version)

13.6 Composite Wood Products Database Special Analysis Section (Oracle Database and Applications Manual for LIMS)

14 Revision History

	Date	**Updated Revision**	**Original Procedure**
1	**Description:** Revision 1		
	November 2012	Unknown	Unknown
2	**Description:** Revision 1.1		
	October 28, 2021	SAS20 Revision 1.1. Reviewed for grammar and content, and compliance with the most recent versions of the QC Manual and MLD076 Revision 0.0.	Revision 1

APPENDIX A

Figures

Figure 1: Conditioning Environmental Chamber

Figure 2: Samples in Conditioning Environmental Chamber

Figure 3: Sampling Environmental Chamber with Small Sampling Chambers Inside

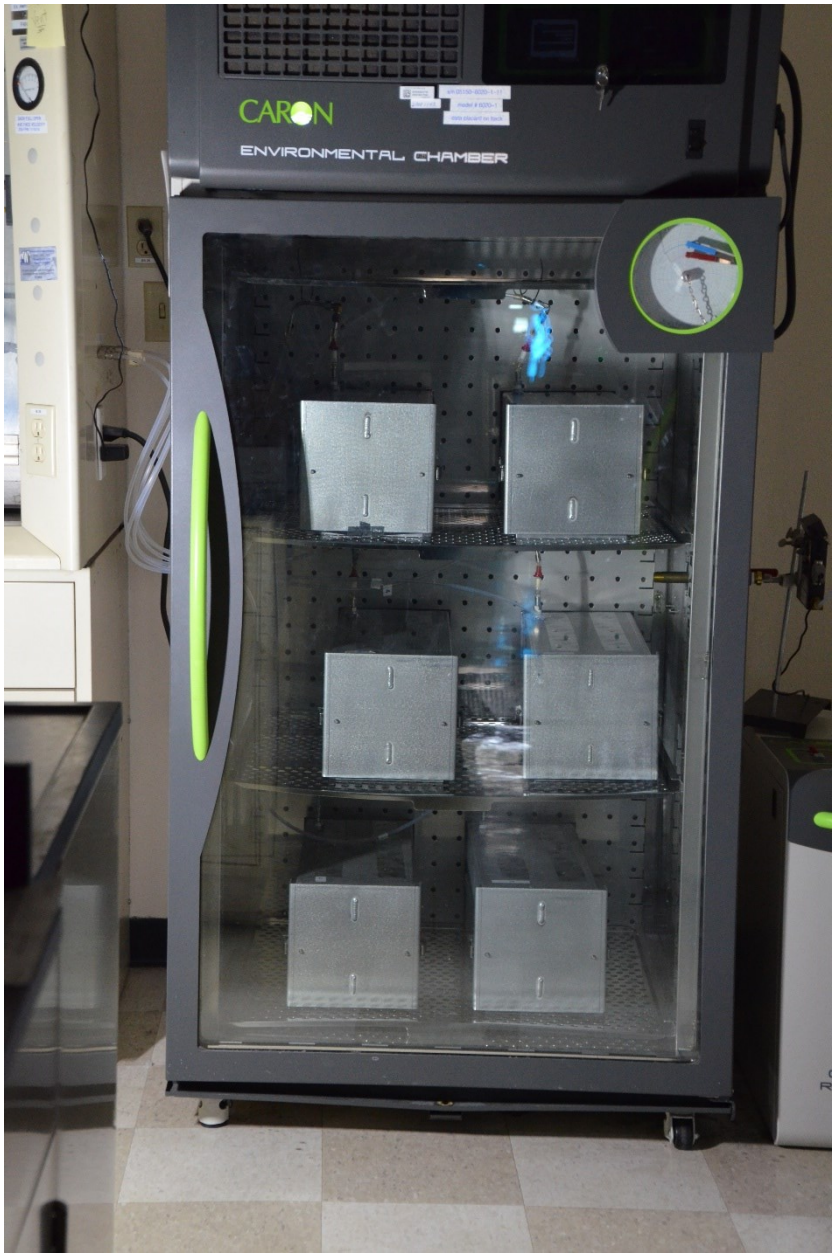

Figure 4: Taped Sample in a Small Sampling Chamber

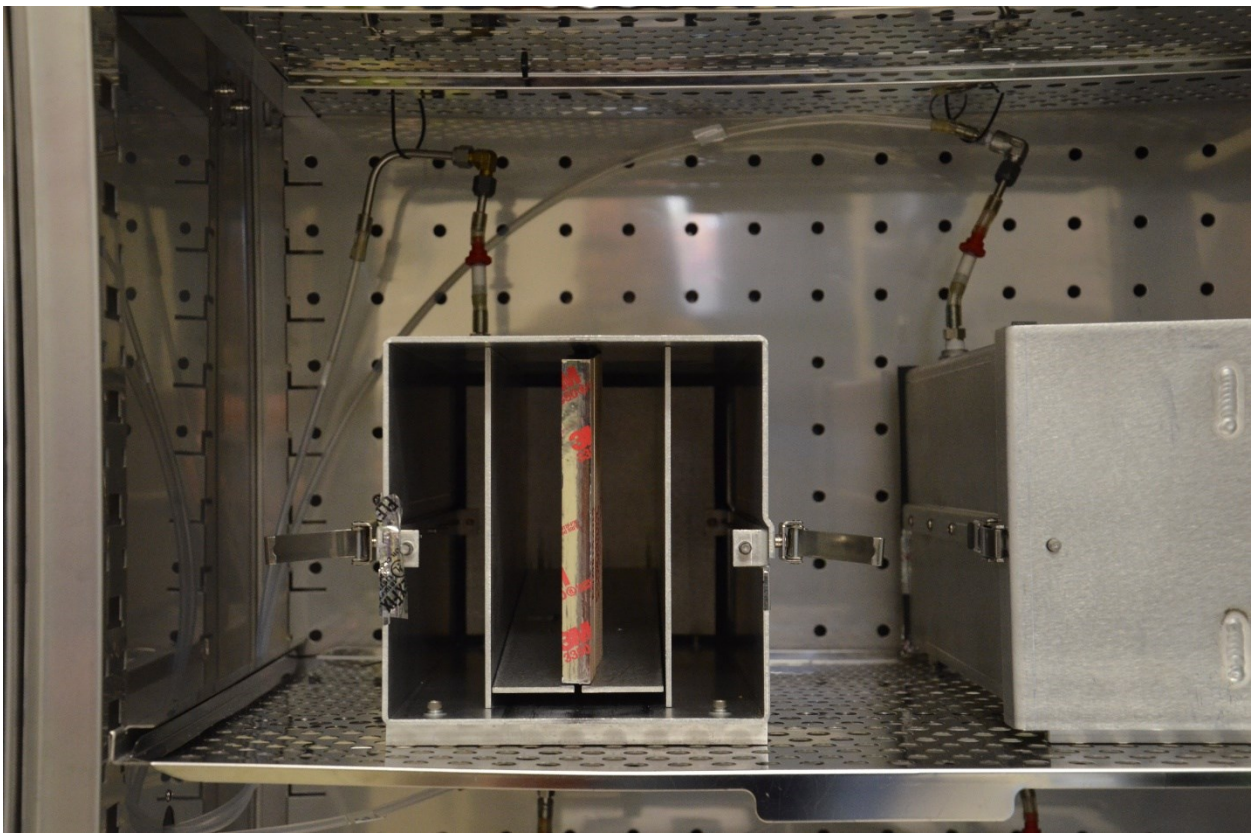

Figure 5: Sampling Manifold

Figure 6: DNPH cartridge Between the Small Sampling Chamber and Sampling Manifold Tubing