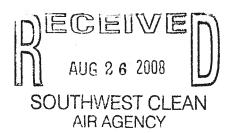
# HAP Emissions from the Drying of Hemlock and Douglas-fir Lumber by NCASI 98.01 and 105

Report to Hampton Affiliates

Report by

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May 22, 2007



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# VOC and HAP emissions from the drying of hemlock and Douglas-fir lumber

### I. Results Summary

Two charges, containing approximately 75 board feet of 2x4 lumber were dried in a small kiln at Oregon State University to less than 15% moisture content. The kiln dryand wet-bulb temperatures were based on schedules provided by Hampton. The maximum temperature was 180°F (82.2°C) for hemlock and 170°F (76.7°C) for Douglas-fir. The air velocity was 750 feet per minute (3.8 m/s). The kiln was indirectly heated with steam. There was no humidification. Regulating the amount of air entering the kiln controlled the humidity.

A JUM VE-7 total hydrocarbon analyzer was used to measure organic emissions following EPA Method 25A. A chilled impinger sampling trains were used to sample for methanol and formaldehyde following NCASI Method 105 and NCASI Method 98.01. The results are shown in Table 1.

**TABLE 1.** Summary of results. Both methods for HAP measurement were run simultaneously.

Methods 25A & 98.01	Initial MC %	Time <sup>a</sup> hr:min	VOC <sup>b</sup> lb/mbf	Methanol lb/mbf	Formaldehyde lb/mbf
Hemlock	7 102.3	49:27	7 0.14	0.083	0.00125 0.0013
Doug-fir	56.9	27:30	0.24	0.026	0.00080

Appears that initia moisture, drying time, voc results all swapped in this table

Method 105°	Methanol lb/mbf	Form- aldehyde lb/mbf	Acet- aldehyde lb/mbf	Propion aldehyde lb/mbf	Acrolein lb/mbf
Hemlock	0.075	0.0014	0.078	0.0020	0.0012
Doug-fir	0.024	0.0008	0.030	0.0004	0.0005

<sup>\*</sup> time is to 15% moisture content

as carbon from green to 15% moisture content

<sup>&</sup>lt;sup>c</sup> phenol was not detected so it is not included in table

### II. Lumber Source and Handling

Hemlock lumber was delivered to Oregon State on March 16 and Douglas-fir on April 20. The wood was delivered in a covered vehicle. Upon arrival at OSU the wood was wrapped in plastic and stored at 5°C until used. The charges were dried between March 19-21 and April 23-25, 2007

### III. Kiln Description and Operation

A schematic of the kiln is shown in Figure 1. The kiln box is approximately 4' by 4' by 4'. It is indirectly heated by steam. Four dry-bulb thermocouples and two wet-bulb thermocouples are located on the entering-air side of the load. The dry-bulb thermocouples are spaced in a grid. The two wet-bulb thermocouples are under a single sock at the center of the entering-air side of the load.

### **Humidity control**

A 200 L/min MKS mass flow meter controlled and measured the amount of air entering the kiln. It was factory calibrated and checked using a bubble meter. The amount of air entering the kiln is based on the wet-bulb temperature - if it is above setpoint, the airflow is increased and if it is below setpoint the airflow is decreased. This is analogous to venting for

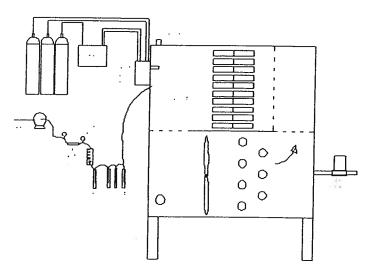


FIGURE 1. Schematic of kiln and sampling system.

a commercial kiln. A minimum of 8-12 L/min entered the kiln at all times, more than removed through the analyzer and impinger trains (< 3.2 L/min combined). Putting air into the kiln at a rate of 100 L/min causes the pressure in the kiln to be 60 to 130 Pa above ambient, depending on location in the kiln (high-pressure or low-pressure side). Thus, any fugitive leakage should be out of the kiln. Two additional flow meters can be manually set to provide additional airflow. One of these was used for small segments of the charges. The steam spray line is disabled, so no water vapor is added to the kiln atmosphere.

### Temperature control

Temperature in the kiln is controlled by indirect steam heating. When the average of the four dry-bulb thermocouples is below setpoint, the steam pressure in the coil is increased. When it is above setpoint, steam flow to the coil is reduced.

#### Schedules

The drying schedules used were based on drying conditions supplied by the mill and are shown in Table 2. The values in Table 2 are based on the entering-air temperature. This represents the highest temperature the wood would experience in a commercial kiln. The actual temperatures in the lab kiln are presented in Figure 2. These compare well with what the mill uses.

### Charge Sequence

After removing from the refrigerator and unwrapped, 2" were trimmed from each end of each board to give 44" samples. These were then weighed, placed in the kiln as shown in the photo to the right, and dried according to the one of the schedules in Table 2. Sampling for hydrocarbon and HAPs was done as described in section IV. At the end of drying the wood was weighed, oven dried, and reweighed so initial and final moisture contents could be determined by ASTM D4442 (oven-dry method).

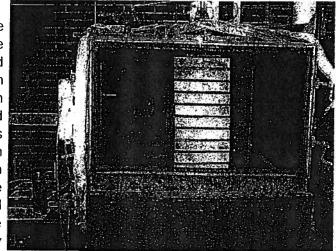


TABLE 2a. Drying schedule used for hemlock. Actual final moisture content was 14.7%.

Step time,	Ramp time,	Run time,	Dry-bulb,	Wet-bulb,
hr:min	hr:min	hr:min	°F	°F
0	-	-	110	95
8	8	8	180	165
42.27	0:30	50:27	180	150

 TABLE 2b. Drying schedule used for Douglas-fir. Actual final moisture content was 8.8%.

Step time, hr:min	Ramp time, hr:min	Run time, hr:min	Dry-bulb, °F	Wet-bulb, °F
0	-	-	90	80
0:30	0:06	0:30	120	110
49:30	11	50	170	140

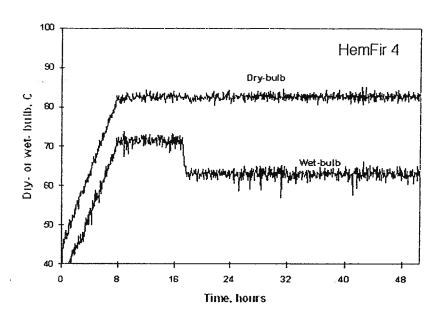
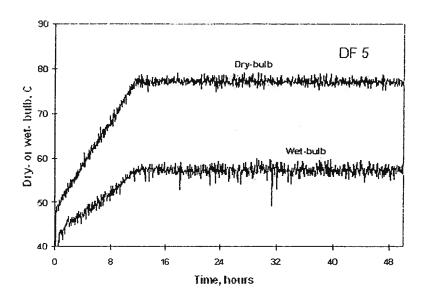


FIGURE 2a. Dry- and wet-bulb temperatures during hemlock drying. 15% moisture content was reached at 27.5 hours .



**FIGURE 2b.** Dry- and wet-bulb temperatures during Douglas-fir drying. 15% moisture content was reached at 49.45 hours.

### IV. Sampling Systems and Methodologies

Sampling for total hydrocarbon, methanol, and formaldehyde is done directly from the kiln as shown in Figure 1 (except there are three sets of impingers). The concentration obtained from the hydrocarbon analyzer and the amount of air entering the kiln allow the total hydrocarbon emissions to be calculated. The concentration obtained from the impingers, the amount of air flowing through the impingers, and the amount of air entering the kiln allow the HAP emissions to be calculated.

### Total hydrocarbon

Figures 3a and 3b show the hydrocarbon sampling system. Unlike stack testing, all necessary equipment is permanently mounted on the kiln and flows are controlled with valves. The sample is withdrawn from the kiln under the assumption that the gas in the kiln is well-mixed and that the composition in the kiln near the exhaust is the same as the composition of the exhaust. The THC sample was drawn from the kiln directly into a heated dilution/filter box mounted on the side of the kiln. The box was heated to 125°C. Heated dilution gas can be added to the hydrocarbon sample gas to lower the gas moisture content to the detector. Dilution air was used when the gas moisture content in the kiln was greater than 15% so that the air moisture content to the detector remained less than 15%. The sample line from the box to the analyzer was heated to 135°C. The valve at the back of the analyzer was heated to 145°C.

The fuel gas was hydrogen. The span gas was EPA Protocol 611 ppm propane in air, the mid-gas was EPA Protocol 300 ppm propane. The zero gas was 0.1 ppm air. Detailed sampling procedures are in Appendix 1 and a summary is presented below.

Leak checks were conducted before and after the charge was dried. Valves are closed and all components from just behind the probe tip to the valve at the back of the analyzer are placed under a 18-20 inHg vacuum. Less than one inHg pressure change during two minutes is acceptable and this was met.

Total flow and sample flow to the analyzer were checked using an NIST-traceable flow meter. Total flow is measured with the dilution gas off. Sample flow is measured with it on. This was done at the beginning and end of each sampling interval. The meter was attached to the system near the probe tip within the heated box. The valves were repositioned so that the sample came from the flow meter rather than the kiln. Readings of flow were made with the dilution gas both off and on. The flow readings were verified by observing the change in the analyzer reading for span gas with the dilution gas off and on. The dilution ratio calculated based on the analyzer readings was within 2% of that determined by the flow meter.

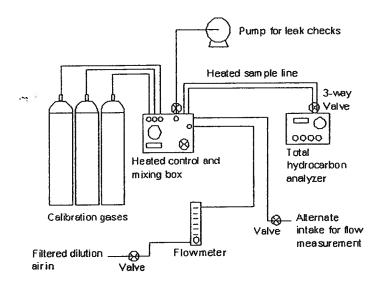


FIGURE 3A. Schematic of heated filter box with air dilution system, heated sample line, and analyzer. Sample enters heated box from back of drawing (box is attached to kiln).



FIGURE 3B. Photo of VOC sampling system showing heated sample box (with white insulation), valves and flow meter for calibration gases (upper left), on/off valve for calibration gas (3 at upper center right), heated sample line to analyzer (green tube, center left), valve for sample (2 at center), toggle valve to vacuum pump (near calibration gas valves).

Calibration of the zero and span of the detector was done at the beginning of each measurement interval (about every three to six hours). The calibration gas was introduced by setting the valves so the calibration gas entered the system near the probe tip at ambient pressure. The calibration was checked at the end of each run with no adjustments made to the zero or span during the run. The span drift was always less than five percent of full scale for a run and generally less than one percent. The zero drift was minimal during entire drying cycles.

### **HAPs** sampling

The sampling train for NCASI Method 105 (modified to have an extra impinger) is shown in Figure 4. The impingers were in a glycol solution maintained at -1 C. Prior to each sampling interval, the impingers were laboratory-washed and 10 to 15 mL of BHA solution were added to each impinger. The fourth impinger was not used. The system was then assembled and a vacuum check was performed with the valves at each end closed. Less than 1" Hg of pressure change over 2 minutes was acceptable. This was met. The flow rate through the system was then measured by taking four flow readings by attaching the probe tip to a Gilibrator flow meter. This was approximately 500 mL/min. The probe tip was then inserted into the kiln and the sampling interval begun. The collection interval time varied from 2 to about 3 hours, depending on the condensation rate of water.

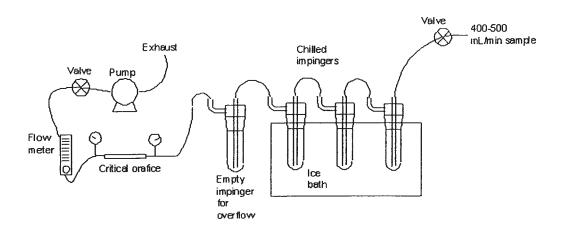


FIGURE 4. Sampling train for the methanol and formaldehyde.

At the end of each interval, the flow rate was again measured. The sampling line(s) was rinsed. The fluid in the three impingers was weighed, placed in a vial. The impingers were than rinsed with 10 mL of water followed by 3 to 5 mL of hexane. The rinses were also placed in the vial and it was sealed. Samples were kept refrigerated and in the dark until lab analysis was done. Lab analysis was done within two weeks after sample collection. The local airport altimeter setting and the lab temperature were recorded at the beginning and end of each interval so the flow rates could be adjusted to standard conditions.

Sampling by the NCASI Method 98.01 was the same as described above for NCASI 105 with the following exceptions. The first impingers were filled with 15 and 10 mL of water, respectively, instead of BHA solution. No water was put in the third impinger. There is no water rinse or hexane rinse after sample collection.

### Lab analysis for aldehydes (105)

The aldehyde standard was prepared by the volumetric dilution of neat aldehydes into a solution of ortho-benzylhydroxylamine hydrochloride (BHA) and water (30g BHA per liter of water). The BHA solution was vigorously agitated and allowed to sit for 15 minutes to allow for derivatization of the aldehydes into aldoximes. The derivatized aldehyde solution was extracted with three aliquots of hexane and brought to volume to make 1000 mg/L. A standard curve was prepared by volumetric dilution in hexane at a range from 1 to 100 mg/L as aldehydes into autosampler vials with 100 mg/L of nitrobenzene as an internal standard.

The samples were prepared by extraction in a separatory funnel with three aliquots of hexane for a total hexane volume of approximately 25 mL. The volumes of the two phases were calculated from their weights. A 1 mL aliquot of the hexane fraction was transferred to an autosampler vial and spiked with internal standard.

The analytical instrument was a Shimadzu GC model 2010 with a flame thermionic detector (FTD), the Shimadzu equivalent of a nitrogen phosphorous detector (NPD). The column was a 105-meter Restek RTX-5 capillary with a 0.25 mm outside diameter and a stationary phase thickness of .25 µm. The oven schedule was: 2 minutes at 120°C, 2°C/min ramp to 160°C, 40°C/min ramp to 220°C and 6.5 minutes at 220°C. The column flow was 25 cm/sec, with 3 mL/min septum purge, and a 1:10 split ratio with a glass wool packed split injection liner. The detector make up He was set to 20 mL/min and the  $H_2$  was set to 3 mL/min. The air was set to 140 mL/min, and the source current was set to 2 pA. The He and  $H_2$  gases were grade 5 and the air was grade 0.1. The injector temperature was 200°C and the detector temperature 280°C. An AOC-20i autosampler was used to perform 1 µL injections using a 10 µL syringe with a steel plunger.

### Lab analysis for alcohols (105)

The methanol standard was prepared by the volumetric dilution of neat methanol into water. The phenol standard was prepared by the gravimetric addition of solid phenol to a known volume of water. The alcohol mixed standard was prepared by volumetric addition of methanol to a gravimetrically prepared phenol standard. The mixed standard was prepared at a concentration of 1000 milligrams per liter (mg/L). A standard curve was prepared by the volumetric dilution of the mixed standard at a range from 5 mg/L to 1000 mg/L into autosampler vials.

Samples were prepared by transferring aliquots of the previously hexane extracted aqueous fractions into autosampler vials.

The analytical instrument was a Shimadzu GC model 2010 with a FID detector. The column was a 60-meter Restek Stabilwax capillary with a 0.53 mm outside diameter and a stationary phase thickness of 1.5 µm. The oven schedule was: 3 minutes at 80°C, 10°C/min ramp to 240°C, and 10 minutes at 240°C. The column flow was 30 cm/sec, with 3 mL/min septum purge, and a 1:10 split ratio with a glass wool packed split injection liner. The detector make up He was set to 25 mL/min and the H<sub>2</sub> was set to 50 mL/min. The air was set to 500 mL/min. The He and H<sub>2</sub> gases were grade 5 and the air was grade 0.1. The injector temperature was 175°C and the detector temperature 250°C. An AOC-20i autosampler was used to perform 1 µL injections using a 10 µL syringe with a PTFE plunger.

### Lab analysis for methanol (98.01)

Methanol solutions in varying concentrations were prepared by dilution, 1 gram of HPLC grade methanol to 1000 grams with distilled water (at 20°C). This stock solution was further diluted to provide methanol solutions in the 1 ppm to 150 ppm range for use as standards.

Autosample vials for GC analysis were prepared by adding 2mL of the impinger sample or standard to a 2mL vial. These were crimp sealed and refrigerated until tested.

The GC was an Shimadzu 2010 with a 60-meter Restek Rtx-624 fused capillary column. A FID was the detection device. The column had a internal diameter of 0.53 mm and a stationary phase thickness of 3  $\mu$ m. The oven schedule was: 7 minutes at 10°C, 20°C/min ramp to 200°C, and 5.5 minutes at 200°C. The column flow was 6 mL/min of He (48.1 Pa head pressure), 3 mL/min septum purge, and a 1:4 split ratio (24 mL/min through the split vent purge). The detector make up He was set to 25 mL/min and the H<sub>2</sub> was set to 50 mL/min. The air was set to 500 mL/min. The He and H<sub>2</sub> gases were grade 5 and the air was grade 0.1. The injector temperature was 150°C and the detector temperature 250°C. An AOC-20i autosampler was used to perform 1  $\mu$ L injections.

### Lab analysis for formaldehyde (98.01)

Formaldehyde solutions in varying concentrations were prepared by diluting 2.703 grams of formalin to 1000 grams with distilled water at 20°C. This stock solution was further diluted to provide methanol solutions in the 0.25 ppm to 7.5 ppm range for use as standards.

An acetylacetone reagent was prepared by dissolving 15.4 g of ammonium acetate in 50 mL of water. To this, 0.2 mL of acetylacetone and 0.3 mL of glacial acetic acid were added. This was then diluted to 100 mL and stored in the dark in a refrigerator.

A 2.0 mL aliquot of the impinger catch or standard was placed in a test tube and 2 mL of the acetylacetone reagent was added. Once mixed, the test tube was placed in a 60°C water bath for 10 minutes. The vials were allowed to cool to room temperature, then the solution was transferred to a cuvette and absorbance measured at 412 nm. For each impinger catch, two replications of this procedure were done.

#### V. Data Reduction and Treatment

The "FlowCalc" worksheet in the Excel file "Kiln, RunName.XLS" in Appendix 2 shows the calculations for each 3-minute interval during the charges (RunName="Hampton, DF4" or "Hampton HF4"). Column A is a reading number. Columns B and C are the clock and charge times, respectively. Columns D and E are the average dry- and wet-bulb temperatures. Column F is the vapor pressure of water at the wet-bulb temperature. The absolute humidity is shown in column G and the molal humidity in column H. These are calculated based on the dry-bulb temperature, wet-bulb temperature, vapor pressure.

#### Flow calculations

The volumetric dry gas flow rate in column I is the flowmeter reading adjusted for the meter calibrations and the molar humidity of the entering gas. This is in standard (at 0°C) liters per minute. In column J this has been converted to a mass flow rate in kg/min and in column K is the same information is expressed as a molal flow rate. These values are for the dry gas vented from the kiln.

#### Moisture calculations

The water removal rate in g/min (column L) is calculated from the humidity (column G) and the gas flow (column J). The total water (column M) is an integration of column L over time.

The moisture content of the wood at each time interval in the event (column N) was determined by reducing the MC of the wood from the previous time interval by accounting for the amount of water leaving the kiln during the interval. This amount has been adjusted by adjusting the wet-bulb temperature to make the ending moisture content match.

### Total hydrocarbon calculations

The original total hydrocarbon analyzer reading is shown in column O. In column P this has been corrected to compensate for the range setting switch on the analyzer and scaling between the analyzer reading and the computer reading. Also in column P, the THA data between sampling runs has been adjusted to the average of the data during the 12-minute period before the analyzer testing and calibration time. The dilution THA (column Q) is the corrected THA reading divided by the dilution ratio (from column Y). In column R we have the opportunity to compensate for the effect of moisture on the JUM detector. This was not done so column R equals column Q. Finally in column S, the hydrocarbon concentration is converted to a dry gas basis concentration using the molar humidity (column H).

In column T, the hydrocarbon flow rate in  $g_{carbon}$ /min is calculated in a manner analogous to the water flow rate using the dry gas flow rate from column K and the hydrocarbon concentration from column S. Column U is the integral of column T over time, the cumulative hydrocarbon release up to that point in the schedule. Column V is the cumulative unit emissions, that is, column U divided by the oven-dry weight of the wood in the kiln.

Column X indicates the hydrocarbon sampling run and column Y is the dilution ratio during that run. The next two columns, Z and AA, are the cumulative dry gas and water during the kiln cycle. These are used obtain the average gas moisture contents. The uncorrected wood moisture content is shown in column AC. This is the MC in column N before adjustment of the wet-bulb to make the beginning and ending MCs match the ovendry test. The kiln air and analyzer air moisture contents (based on volume) are shown in columns AD and AE.

At the end of the FlowCalc spreadsheet (below the data) are summaries by run of the flow data for the total hydrocarbon run intervals. Further down are summaries by impinger interval. These are the tables that appear in the body of the report. The other pages in the files "Kiln, RunName.XLS" are graphs of the data in the FlowCalc page.

Moisture content and board weight data are in the files named "Weights, RunName.XLS."

### HAP calculations (105)

Data from the lab analysis for HAPs is shown in Appendix 3. The laboratory data reduction for the HAPs (from the field data sheets and lab analysis) is shown in electronic form in the file named "HAPs, RunName.XLS" in Appendix 2. Within this file the summary page presents the data by run interval. The "Field Data" page is the data from the field data sheets (samples of actual sheets included in Appendix 3 and PDF versions are included in Appendix 2) and includes the ambient pressure, lab temperature, flow rate through the impingers, and run start and stop times. The "Laboratory Data" page includes the results of the lab analyses on the impinger catch or hexane fraction. The lab data sheets are included in Appendix 2. On the "Impinger Calculations" page, the field data is manipulated to give a dry gas flow rate through the impingers (columns J and K) and the mass HAPs in the impingers (columns L to Q).

The "Kiln Calculations" page uses a ratio of the dry gas flow through the kiln (calculated in the spreadsheets named "Kiln, RunName.XLS") to the dry gas flow rate through the impinger to scale up the quantities and obtain the mass of each compound leaving the kiln (columns I to N).

On the "Emission" page, the amount of a HAP leaving the kiln is divided by the mass (in kg) or volume of wood (in mbf) to express the emissions on a per kg (columns B-G) or per mbf basis (columns H-M). Concentrations leaving the kiln are given in columns N to Y.

The "Quality Assurance" page presents information on the spikes, duplicates and blanks. For each spike a % recovery is calculated based on the mass of a HAP recovered divided by the amount added. The difference for each duplicate is calculated as a percentage from the difference between the impingers divided by the average mass collected.

The remaining pages in "HAPs, RunName.XLS" are for graphing purposes.

### HAP calculations (98.01)

The laboratory data reduction for the HAPs (from the field data sheets and lab analysis) is shown in electronic form in the file named "Methanol and Formaldehyde, RunName.XLS" in Appendix 2. Within this file the summary page presents the data by run interval. The "Field Data" page is the data from the field data and includes the ambient pressure, lab temperature, flow rate through the impingers, and run start and stop times. The field data sheets are presented electronically in Appendix 2. The "Concentrations" page includes the results of the lab analyses on the impinger catch. The lab data sheets are included in Appendix 2. On the "Impinger Calculations" page, the field data is manipulated to give a dry gas flow rate through the impingers (columns J and K) and the mass of methanol and formaldehyde in the impingers.

The "Kiln Calculations" page uses a ratio of the dry gas flow through the kiln (calculated in the spreadsheets named "Kiln.XLS") to the dry gas flow rate through the impinger to scale up the quantities and obtain the mass of each compound leaving the kiln (column I-M). The unit emissions in columns K-N are obtained by dividing the total emissions by either the volume or mass of wood in the kiln.

### VI. Sampling Results

### Hydrocarbon

The hydrocarbon emissions are summarized graphically here. All emission data is presented in detail in electronic form in Appendix 2. The time to 15% moisture content was estimated by interpolation and the emissions are reported from green to 15% moisture content.

Figure 5 shows total hydrocarbon concentration (left scale) and dry gas vent rate (right scale) versus time. Profiles are similar in replicate charges.

The total hydrocarbon concentration is very dependent on the venting early in the schedule with a high vent rate resulting in a low hydrocarbon concentration and vice versa. Once the venting increases, the total hydrocarbon concentration decreases. In the lower-temperature schedules, the total hydrocarbon concentration remains low until the venting starts to decrease. In the higher-temperature schedules, the total hydrocarbon decreases, probably because the drying rate decreases, then increases as the vent rate decreases.

Note that total hydrocarbon concentration is not indicative of the amount of hydrocarbon emissions unless one also considers the vent rate. These two factors combined determine the emissions.

Figure 6 shows the cumulative hydrocarbon emissions and the rate of emissions versus time. The cumulative emissions is the emissions up to any point in time in the schedule. The rate of emissions is how much is coming out per unit time. The maximum emission rates occur early in the schedules.

Figure 7 shows the wood moisture content versus time. The estimated moisture content should most accurately represent the MC-time relationship because the initial and final moisture contents match the oven-dry test. The initial moisture contents and final moisture contents based on the oven-dry method are shown on each plot.

Figure 8 shows the cumulative hydrocarbon emissions versus moisture content. The hydrocarbon emissions for drying to any moisture content can be read from this graph. In agreement with past studies, there is a fairly linear relationship between the emissions and the decrease in moisture content.

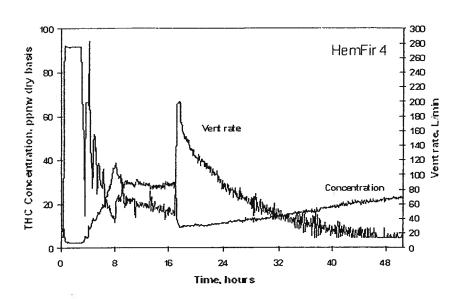


FIGURE 5a. Hydrocarbon concentration and vent rate versus time for the Douglas-fir charge.

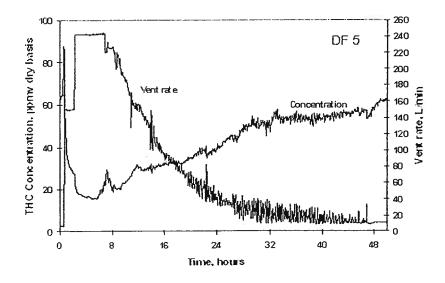
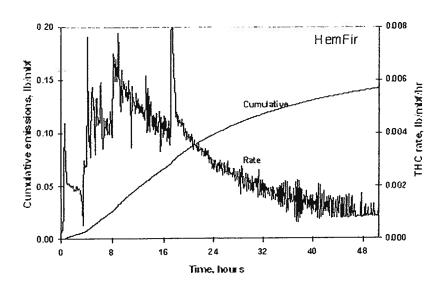


FIGURE 5b. Hydrocarbon concentration and vent rate versus time for the hemlock charge.



**FIGURE 6a.** Cumulative and rate of emissions versus time (as carbon) for the Douglas-fir charge.

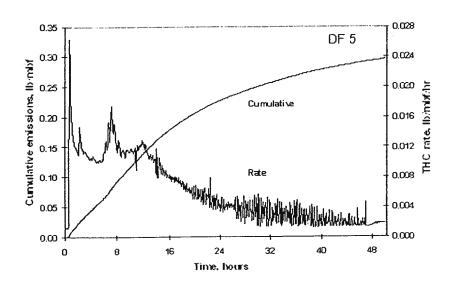


FIGURE 6b. Cumulative and rate of emissions versus time (as carbon) for the hemlock charge.

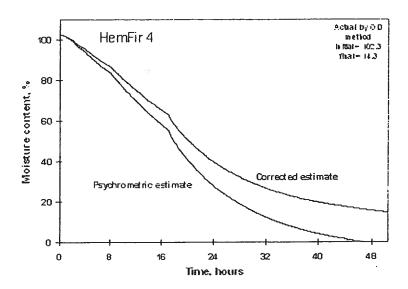


FIGURE 7a. Moisture content versus time for the Douglas-fir charge.

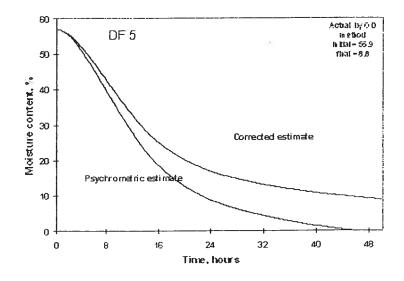
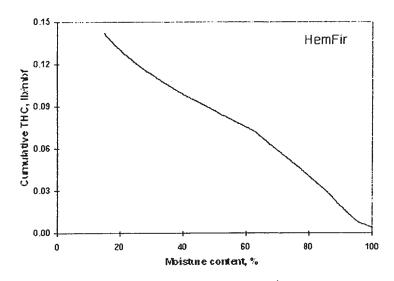


FIGURE 7b. Moisture content versus time for the hemlock charge.



**FIGURE 8a.** Cumulative emissions versus moisture content (as carbon) for the Douglas-fir charge.

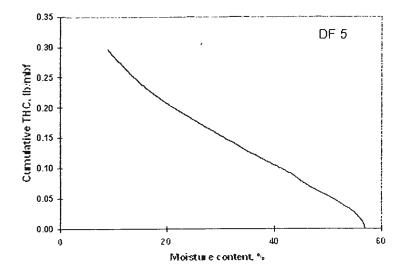


FIGURE 8b. Cumulative emissions versus moisture content (as carbon) for the hemlock charge.

Table 3 shows the VOC results by run for the charges. A run is an interval between analyzer calibrations, about three to four hours of data. The interval time periods shown in the table include the times between sampling and mass calculations are adjusted to account for these. Sampling occurred for approximately 95% of the drying time. Sample copies of field sampling sheets, including dilution system and heated component data are given in Appendix 3 with full PDF format versions in Appendix 2.

**TABLE 3a.** Summary of sample runs for analysis of total hydrocarbon for the Douglas-fir charge.

Sample	Time	Cumu	lative	Average	Dry Flow	THC mass		THC		Av	erage N	AC.
Run		Dry Gas	Water	Humidity	Rate @68	as C	wet conc	as C	as C	Wood	Air	Anal
	hrs	kg	kg	kg/kg	I/min	g	ppmv	ibs/mbf	lb#r/mbf	%	%_	%
1	3.90	67.43	3.39	0.050	239.0	0.26	3.5	0.008	0.0020	99.5	7.5	7.5
2	4.05	31.35	4.36	0.139	107.0	0.61	14.6	0.018	0.0045	91.0	18.3	18.3
3	2.85	14.66	4.21	0.287	71.1	0.56	21.0	0.017	0.0059	82.8	31.6	12.5
4	3.55	16.02	4.74	0.296	62.4	0.57	19.4	0.017	0.0049	73.9	32.3	12.9
5	5.90	48.66	9.73	0.200	114.0	0.90	13.5	0.027	0.0046	60.4	24.4	10.0
6	4.15	33.47	5.60	0.167	111.5	0.45	8.5	0.013	0.0032	44.0	21.2	8.7
7	2.60	15.18	2.50	0.164	80.7	0.23	9.6	0.007	0.0027	36.2	20.9	12.0
8	3.45	15.88	2.67	0.168	63.6	0.26	10.2	0.008	0.0022	31.1	21.3	12.1
9	3.50	12.20	2.02	0.165	48.2	0.22	11.4	0.007	0.0019	26.4	21.0	12.0
10	3.95	10.38	1.73	0.167	36.3	0.21	12.7	0.006	0.0016	22.7	21.2	12.1
11	5.70	10.52	1.76	0.167	25.5	0.25	14.9	0.007	0.0013	19.2	21.2	12.1
12	4.90	6.48	1.09	0.168	18.3	0.17	16.6	0.005	0.0011	16.5	21.3	12.1
13	1.20	1.39	0.23	0.164	16.0	0.04	17.8	0.001	0.0010	15.2	20.9	12.0
Sum	49.70	283.6	44.0			4.7		0.142				
Average				0.177	76.4		13.4		0.0028			

**TABLE 3b.** Summary of sample runs for analysis of total hydrocarbon for the hemlock charge.

Sample	Time	Cumu	lative	Average	Dry Flow	THC mass		THC		Av	erage N	1C
Run		Dry Gas	Water	Humidity	Rate @68	as C	wet conc	as C	as C	Wood	Air	Anal
	hrs	kg	kg	kg/kg	1/min	g	ppmv	lbs/mbf	lb/hr/mbf	%	%	%
1	3.05	33.57	1.84	0.055	152.1	1.24	36.8	0.034	0.0111	55.8	8.1	8.1
2	3.65	68.82	4.60	0.067	260.6	1.45	15.2	0.040	0.0109	49.9	9.7	9.7
3	4.80	74.41	6.85	0.092	214.3	2.17	20.4	0.059	0.0124	39.8	12.9	12.9
4	4.25	42.59	4.94	0.116	138.5	1.60	25.2	0.044	0.0103	29.4	15.7	9.8
5	4.15	26.38	3.02	0.115	87.9	1.06	27.2	0.029	0.0070	22.7	15.€	9.8
6	3.50	14.83	1.71	0.115	58.6	0.68	30.9	0.019	0.0053	18.7	15.6	9.8
7	3.30	9.71	1.11	0.114	40.7	0.50	35.1	0.014	0.0042	16.3	15.6	9.8
8	0.80	1.95	0.22	0.113	33.8	0.11	37.7	0.003	0.0037	15.2	15.3	9.9
Sum	27.50	272.3	24.3			8.8		0.241				
Average				0.098	123.3		28.6		0.0081			

### HAP results (105)

Results of the lab analyses for methanol and formaldehyde are summarized in Table 4 and complete results are in Appendix 2. Table 5 shows a summary of the methanol and formaldehyde analyses by run during the charge.

The HAPs released are plotted as a function of time in Figure 9. In Figure 9, acetaldehyde and methanol are plotted with bold lines and correspond to the axis with larger values. The other HAPs are plotted on the smaller-scale axis.

The total HAPs released is a nonlinear function of moisture content (Figure 10), with the rate increasing with decreasing moisture content.

TABLE 4a. Results of NCASI 105 laboratory analyses for the hemlock charge.

Aq	<u>ueous concenti</u>	rations	l I		Hexane	concentrations		
Sample	Methanol	Phenol	Sample	Formaldehyde	Ac etal dehyde	Propionaldehyde	Acrolein	Mass
Run	μg√mL	µg/mL	Run	µg/mL	µg∕mŁ	µg/mL	μg/mL	g
1	1.7	00.0	1	0.2	41 D	0.8	0.1	11.42
2	3.9	000	2	0.4	55.7	1.2	0.3	13.84
3	13.6	000	3	0.7	103.9	2.7	1.5	13.04
4	22.5	000	4	1.8	82.B	2.5	1.8	12.53
5	18.9	00.0	5	1.4	46 B	1.4	1.0	12.58
8	11.7	000	6	0.6	27 D	0.8	0.8	14.82
7	16.3	000	7	0.9	36.4	1.1	0.8	12.83
8	18.6	000	8	1.0	30.1	0.8	0.7	14.66
9	23.1	000	9	0.8	31.3	0.9	0.7	14.28
10	29.5	00.0	10	1.4	40.1	1.1	1:1	14.67
- 11	34.2	000	11	1.4	43.4	1.3	1.2	13.35
12	41.1	000	12	1.7	51.3	1.5	1.4	13,39
13	47.8	000	13	1.8	50.3	1.8	1.5	14.27

**TABLE 4b.** Results of NCASI 105 laboratory analyses for the Douglas-fir charge.

Aq	uecus concen	trations			Hexane	concentrations		
Sample	Methanol	Phenol	Sample	Formaldehyde	Acetal dehyde	Propionaldehyde	Acrolein	Mass
Run	µg/m L	µg/mL	Pun	μg/mL	μg/mL	µg/mL	µg/mL	g
1	4.3	0.00	1	0.3	38.7	0.2	0.0	15.08
2	3.8	00.0	2	0.3	16.1	0.2	0.0	13.79
3	4.2	00.0	3	0.5	16.9	0.1	0.0	13.76
4	8.1	0.00	4	0.7	17 ወ	0.2	8.0	15.00
5	9.5	00.0	5	1,1	24.9	0.4	1.4	12.10
6	18.5	000	8	1.0	23 ß	0.5	1.3	11.75
7	14.9	00.0	7	0.8	16.9	0.4	0.0	15.37
8	22.0	00.0	8	1.0	21.6	0.5	1.0	14.13
9	31.0	000	9	1.4	29.9	0.8	1.2	16.79
10	27.1	000	10	1.5	27.4	0.8	1.2	13.89
11	31.3	00.0	11	1.5	28.9	0.8	1.2	13.19
12	29.4	00.0	12	1.4	24.1	0.9	2.3	13.42
			<u>                                    </u>					

TABLE 5a. Summary of NCASI 105 sample runs for HAPs for the hemlock charge.

			Ma	ass		
Sample	Methanol	Phenol	Form-	Acet-	Propion-	Acrolein
RunID	MICLIANU	FIICHU	aldehyde	aldehyde	aldehyde	AUUIBIN
	lb/mbf	lb/mbf	lb/mbf	lb/mbf	lb/mbf	lb/mbf
1	0.0022	0.0000	0.0001	0.0122	0.0002	0.00004
2	0.0036	0.0000	0.0001	0.0113	0.0002	0.00006
3	0.0060	0.0000	0.0001	0.0111	0.0003	0.00016
4	0.0076	0.0000	0.0002	0.0091	0.0003	0.00018
5	0.0109	0.0000	0.0003	0.0103	0.0003	0.00022
6	0.0070	0.0000	0.0001	0.0060	0.0002	0.00013
7	0.0076	0.0000	0.0001	0.0048	0.0001	0.00011
8	0.0063	0.0000	0.0001	0.0034	0.0001	0.00008
9	0.0052	0.0000	0.0001	0.0026	0.0001	0.00006
10	0.0062	0.0000	0.0001	0.0027	0.0001	0.00007
11	0.0051	0.0000	0.0001	0.0020	0.0001	0.00005
12	0.0042	0.0000	0.0001	0.0015	0.0000	0.00004
13	0.0029	0.0000	0.0000	0.0009	0.0000	0.00003
SUM	0.075	0.0000	0.0014	0.078	0.0020	0.0012

		(	Concentratio	on in dry qa	S		Ì	C	oncentrati	on in wet	gas	
Sample Run ID	Methanol	Phenol	Form- aldehyde	Acet- aldehyde	Propion- aldehyde	Acrolein	Methanol	Phenol	Form- aldehyde	Acet- aldehyde	Propion- aldehyde	Acmiein
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
1	1.11	0.00	0.03	4.42	0.05	0.01	1.03	0.00	0.03	4.11	0.05	0.01
2	3.03	0.00	0.07	6.99	0.11	0.03	2.54	0.00	0.06	5.87	0.09	0.02
3	9.34	0.00	0.13	12.57	0.25	0.14	6.41	0.00	0.09	8.63	0.17	0.10
4	12.63	0.00	0.32	11.07	0.25	0.17	8.59	0.00	0.22	7.52	0.17	0.12
5	8.47	0.00	0.26	5.82	0.13	0.10	6.44	0.00	0.20	4.42	0.10	0.08
6	5.92	0.00	0.13	3.70	0.08	0.06	4.66	0.00	0.10	2.91	0.07	0.05
7	9.89	0.00	0.16	4.57	0.11	80.0	7.80	0.00	0.13	3.60	0.08	0.07
8	12.23	0.00	0.23	4.70	0.10	0.09	9.63	0.00	0.18	3.70	80.0	0.07
9	14.93	0.00	0.20	5.41	0.12	0.10	11.81	0.00	0.16	4.28	0.09	0.08
10	17.52	0.00	0.28	5.61	0.12	0.12	13.81	0.00	0.22	4.42	0.09	0.09
11	21.00	0.00	0.28	5.87	0.13	0.13	16.55	0.00	0.22	4.63	0.10	0.10
12	24.11	0.00	0.32	6.37	0.14	0.13	18.97	0.00	0.25	5.01	0.11	0.11

TABLE 5b. Summary of NCASI 105 sample runs for HAPs for the Douglas-fir charge.

†E			Ma	ass .		
Sample	Methanol	Phenol	Form-	Acet-	Propion-	Acrolein
RunID	MCHIANG	- I HEHOI	aldehyde	aldehyde	aldehyde	ACIOICIII
	lb/mbf	lb/mbf	lb/mbf	lb/mbf	lb/mbf	lb/mbf
1	0.0024	0.0000	0.0001	0.0075	0.0001	0.00000
2	0.0028	0.0000	0.0001	0.0057	0.0001	0.00000
3	0.0042	0.0000	0.0002	0.0058	0.0000	0.00000
4	0.0048	0.0000	0.0002	0.0048	0.0001	0.00022
5	0.0041	0.0000	0.0001	0.0030	0.0001	0.00017
6	0.0030	0.0000	0.0001	0.0018	0.0000	0.00010
7	0.0020	0.0000	0.0001	0.0012	0.0000	0.00000
8	0.0010	0.0000	0.0000	0.0004	0.0000	0.00002
SUM	0.024	0.0000	0.0008	0.030	0.0004	0.0005

		Concentration in dry gas							Concentration in wet gas						
Sample Run ID	Methanol	Phenol	Form- aldehyde	Acet- eidehyde	Propion- aldehyde	Acrdein	Methanoi	Phenoi	Form- aldehyde		Propion- aldehyde	Acrolein			
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm			
1	2.67	0.00	0.07	6.04	0.03	0.00	2.45	0.00	0.07	5.55	0.03	0.00			
2	1.36	0.00	0.05	2.06	0.02	0.00	1.23	0.00	0.05	1.87	0.02	0.00			
3	1.84	0.00	0.08	1.86	0.01	0.00	1,61	0.00	0.07	1.63	0.01	0.00			
4	3.39	0.00	0.15	2.47	0.03	0.09	2.86	0.00	0.12	2.08	0.02	0.07			
5	5.26	0.00	0.19	2.83	0.04	0.13	4.44	0.00	0.16	2.38	0.03	0.11			
6	6.75	0.00	0.19	2.91	0.05	0.13	5.69	0.00	0.16	2.45	0.04	0.11			
7	6.63	0.00	0.20	3.02	0.05	0.00	5.64	0.00	0.17	2.54	0.04	0.00			
8	11.15	0.00	0.20	2.88	0.05	0.11	9.44	0.00	0.17	2.44	0.04	0.09			

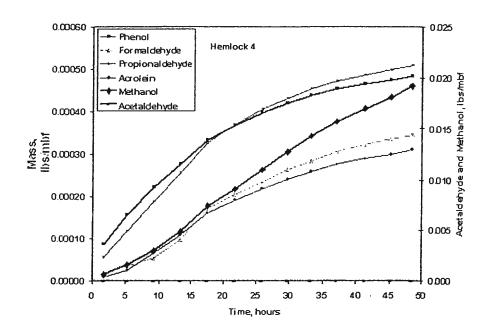


FIGURE 9a. Cumulative HAP emissions versus time for the hemlock charge (105).

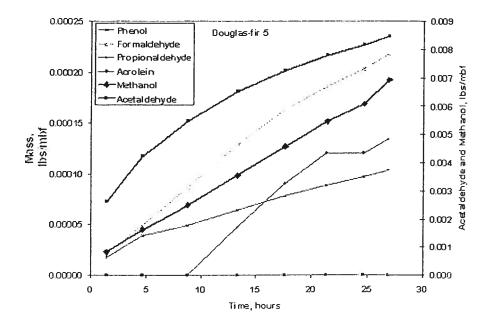


FIGURE 9b. Cumulative HAP emissions versus time for the Douglas-fir charge (105).

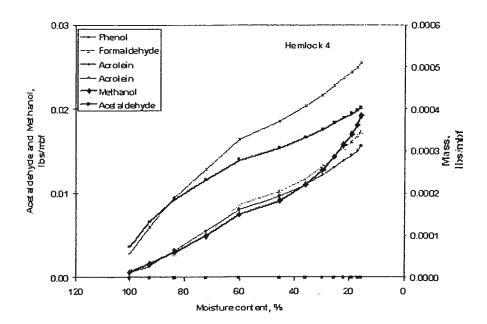
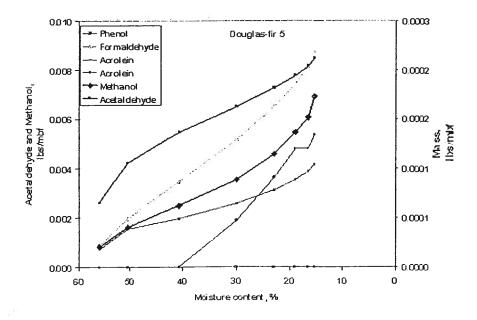


FIGURE 10a. Cumulative HAP emissions versus wood moisture content for the hemlock charge (105).



**FIGURE 10b.** Cumulative HAP emissions versus wood moisture content for the Douglas-fir charge (105).

### Methanol and formaldehyde (98.01)

Results of the lab analyses for methanol and formaldehyde are summarized in Table 6 and complete results are in Appendix 2. Table 7 shows a summary of the methanol and formaldehyde analyses by run during the charge.

The total emissions released as a function of time are shown in Figure 11. Figure 12 shown total emissions as a function of moisture content.

**TABLE 6.** Results of laboratory analyses for Douglas-fir (left) and hemlock impinger samples.

Impin	Impinger liquid concentrations									
Sample	Methanol	Formaldehyde								
Run	mg/L	mg/L								
1	3.9	0.06								
2	6.9	0.15								
- 3	21.3	0.32								
4	27.0	0.33								
5	20.3	0.28								
6	16.8	0.35								
7.	24.3	0.45								
8.	28.9	0.48								
950	33.9	0.48								
10	47.1	0.58								
	58.5	0.72								
12	64.7	0.73								
13	78.8	0.82								

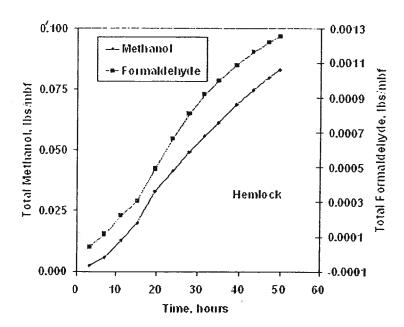
Impin	Impinger liquid concentrations									
Sample	Methanol	Formaldehyde								
Run	rng/L	mg/L								
1	7.5	0.15								
2	3.8	0.00								
3	5.2	0.00								
. 4	9.5	0.35								
5	14.6	0.28								
6	20.6	0.52								
7	20.3	0.47								
> 8	32.3	0.10								
學 9	43.2	0.38								
10	46.7	0.76								
11	54.5	0.79								
12	559	0.78								
. 13	54.2	0.69								

TABLE 7A. Summary of sample runs for methanol and formaldehyde for hemlock.

Hemlock	Collection	Adjusted	Dry gas	Average	Molar	Mois	sture	M	ess	Conce	ntration	Conce	ntration
Sample	Interval	Interval	mass	Dry gas	Humidity	Cor	tent	1000 bo	erd feet	in dr	y gas	in we	t gas
RuniD				flow rate		Mid	End	MeOH	СНОН	MeOH	СНОН	MeOH	снон
	hours	hours	kg	kg/min	mol/moi	%	%	lb/mbf	lb/mbf	ppm	ppm	ppm	ppm
1:	3.10	3.35	€0.577	0.301	0.076	100.1	96.7	0.0025.	0.00004	1.23	0.02;	£1.15	0.02
: 2	3.20	3.80	35.406	0.155	0.191	92.4	88.4	0.0033	0.00007	2.80	40.0	2.35	0.06
. 3	3.20	4.10	19.347	0.079	0.456	83.2	77.5	0.0070	0.00011	1095	018	7 52	0.12
4	2.90	4.05	18.093	0.074	0.471	72.1	67.0	0.0072	0.000003	1193	0.16	8.11	0.11
. 5	3.05	4.35	38.841	0.149	0.317	60.1	51.8	0.0131	0.00018	10.16	0.15	7.71	0.11
. 6	3.10	4.20	35.724	0.142	0.269	45.5	40.0	0.0086	0.00018	7.25	016	5.72	
7	2.95	4.00	23.050	0.096	0.268	36.0	32.4	0.0076	0.0001.4	9.97	0.20	7.87	0.16
. 8	2.80	3.65	15.632	0.071	0.270	29.6	27.2	0.0065	0.00011	12.52	0.22	9.86	0.18
9	2.45	3.30	10.583	0.053	0.264	25.4	23.7	0.0054	0,00008,	15 47	0.24	12.23	0.18
10	2.95	4.40	10.694	0.041	0.269	21.9	20.2	0.0075	0.000093	21141	0,28	16.66	0.22
11	2.90	4.05	7.301	0.030	0.269	18.9	17.8	0,0060	0.00007	2475	0.32	19.51	0.26
1 12	3.05	3.75	5.250	0.023	0.271	16.9	16.0	0 0049	0,00000	2831	034	22 28	0.27
. 13	3.05	2.70	3.114	0.019	0.269	15.5	15.0	0.0034	0.00003	3265	036	25.73	<u>0.28</u>
SUM			·					0.083	0.00125				

TABLE 7B. Summary of sample runs for methanol and formaldehyde for Douglas-fir.

Doudlas-fir	Collection	Adjusted	Dry gas	Average	Molar	Moi:	sture	M	5SS	Conce	tration	Conce	ntration
Sample	Intervai	Interval	mass	Drygas	Humidity	Cor	tent	1000 bo	and feet	in dr	zap y	in we	et gas
Run ID				flowrate		Mid	End	MeOH	СНОН	МеОН	СНОН	MeOH	СНОН
	hours	hours	kq	kg/min	mol/mol	%	%	lb/mbf	ib/mbf	ppm	ppm	ppm	ppm
a 1 a s	2.65	2.85	29.806	0.174	0.088	56.0	54.1	0.0023	0.00005	251	,0.05	231	0.06
2 .	3.10	3.55	66.913	0.314	0.106	50.5	46.5	0.0024	0.00009	119	0.05	1.07	0.04
3	3.65	4.70	75.275	0.267	0.144	40.7	34.9	0.0037	0.00024	1.62	20.11¥	1.42	0.10
4	3.10	4.55	46.631	0.171	0.186	29.9	25.6	0.0046	0.00017	326	0.133	275	0.11.
5	3.10	4.00	25.904	0.108	0.185	22.9	20.5	0.0040	0 00008	1012	0.10	432	0.09
6	2.90	3.40	14.836	0.073	0.185	18.9	17.5	0.0034	0.00009	7.69	0.21	6,49	0.17
7.	2.45	3.20	9.800	0.051	0.185	16.5	15.6	1. 1. 1.	0.00010.	1379	0.34	£164	0,29
8	3.25	1.25	3.110	0.041	0.181	15.3	150	0.0011	0.00000	1206	<b>80 049</b>	1021	0.03
SUM								0.026	0.00080		4 mary 4	F-0.	W. 200



**FIGURE 11A.** Cumulative methanol and formaldehyde emissions versus time for hemlock (98.01).

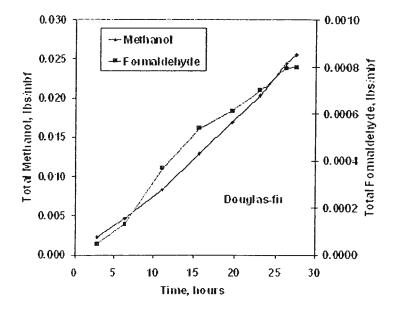


FIGURE 11B. Cumulative methanol and formaldehyde emissions versus time for Douglas-fir (98.01).

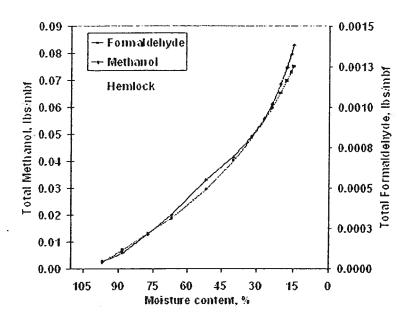


FIGURE 12A. Cumulative methanol and formaldehyde emissions versus wood moisture content for hemlock (98.01).

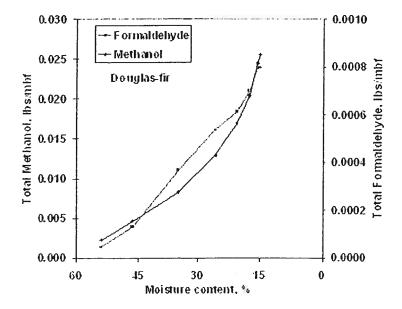


FIGURE 12B. Cumulative methanol and formaldehyde emissions versus wood moisture content for Douglas-fir (98.01).

#### Discussion of results

### Total hydrocarbon

The average values for the total hydrocarbon emissions in this study were 0.14 lbs<sub>c</sub>/mbf (pounds as carbon per thousand board feet) for hemlock and 0.24 lbs<sub>c</sub>/mbf for Douglas-fir. The total hydrocarbon value for hemlock is a little low, but consistent with past work. For example, the correlation in Milota and Mosher (Forest Product Journal, May 2006) would predict total hydrocarbon emissions of 0.2 to 0.25 lbs<sub>c</sub>/mbf for the hemlock tested. In February, we measured 0.18 lbs<sub>c</sub>/mbf for hemlock from Hampton. For Douglas-fir, past studies have measured total hydrocarbon emissions from 0.49 (Milota, Forest Product Journal, July 2006) to 1.19 lbs<sub>c</sub>/mbf (Wu and Milota, Forest Products Journal, June, 1999), higher than in this study. In February, we measured 0.65 lbs<sub>c</sub>/mbf for Douglas-fir from Hampton dried at the same temperatures. The Douglas-fir in this study had a slightly lower initial moisture content, 56%, compared to 80% for that dried in February.

#### **HAPs**

The two methods, NCASI 105 and NCASI 98.01, had surprisingly good agreement (See Table 1, page 1) for the methanol and formaldehyde. We expected the NCASI 105 method to give a lower value for formaldehyde based on past work, but this was not the case.

Methanol - The methanol emitted from hemlock, an average of 0.079 lb/mbf, was twice that measured in February, but lower than would be predicted by Milota and Mosher (Forest Product Journal, May 2006), approximately 0.15 to 0.2 lb/mbf. The methanol emitted from Douglas-fir averaged 0.025 lb/mbf. This is very consistent with the work for Hampton last February (0.024 lb/mbf) and also with 0.023 lb/mbf predicted by Milota, 2006 (Forest Product Journal, July 2006).

Phenol - Phenol was not detected. This is consistent with past results.

Formaldehyde - The formaldehyde emitted from hemlock, 0.0013 lb/mbf, was higher than the 0.0005 lb/mbf measured for Hampton in February but consistent with that predicted by Milota and Mosher (Forest Product Journal, May 2006), approximately 0.0018 lb/mbf. The formaldehyde emitted from Douglas-fir, 0.0008 lb/mbf, was higher than the 0.0005 lb/mbf measured for Hampton in February but consistent with that predicted by Milota (Forest Product Journal, July 2006), approximately 0.001 lb/mbf.

Acetaldehyde - The acetaldehyde emissions for hemlock, 0.078 lb/mbf, were lower than those reported for Rosboro lumber earlier in the year (0.13 lb/mbf). The acetaldehyde emissions did, however, exceed the methanol emissions. The acetaldehyde emissions

for Douglas-fir, 0.030 lb/mbf, were lower than the average reported for Rosboro lumber earlier in the year (0.057 lb/mbf) but within the range of that data (0.043 to 0.071 lb/mbf). The acetaldehyde emissions did also exceed the methanol emissions.

Propionaldehyde - The propionaldehyde emissions for hemlock, 0.0020 lb/mbf, were higher than those reported for Rosboro lumber earlier in the year (0.009 lb/mbf) The propionaldehyde emissions for Douglas-fir, 0.0004 lb/mbf, were consistent with that reported for Rosboro lumber earlier in the year (0.0005-0.0006 lb/mbf)

Acrolein - The acrolein emissions. 0.0012 lb/mbf for hemlock and 0.0005 lb/mbf for Douglas-fir were within the range of the work for Rosboro.

### Comparison to past work

A comparison of the total hydrocarbon and methanol and formaldehyde emissions from this study to past work is shown in Table 8.

 TABLE 8. Comparison of results to past work.

	<b>-</b>	Dry-bulb	voc	Methanol	Formaldehyde	
Species <sup>A</sup>	Tested by	Temperature °F	lb <sub>c</sub> /mbf	lb/mbf		
Hemlock (this work)	osu	180	0.14	0.079	0.0013	
Hemlock (for Hampton in Feb. 2007)	OSU	180	0.18	0.038	0.0005	
Hemlock (for Hampton in Sept. 2004)	osu	200	0.20	0.057	0.0014	
Hemlock (for Hampton in August, 2004)	OSU	180	0.16	0.031	0.0008	
Hemlock (for Hampton in May, 2004)	osu	215	0.34	0.138	0.0043	
Hemlock (for Hampton in	0011	215	0.34		-	
April, 2004)	OSU	180	0.40	-		
Hemlock (for Hampton in Feb. 2002)	osu	180	0.12	-	-	
Southern pine	OSU/NCASI	235	3.6	0.265	0.019	
White fir	OSU	240	0.61	0.420	0.0160	
White fir	OSU	180	0.24	0.122	0.0028	
Ponderosa pine	OSU	180	1.38	0.065	0.0029	
Lodgepole	OSU	230	1.08	0.060	0.004	
Douglas-fir (this work)	osu	170	0.24	0.024	0.0008	
Douglas-fir (for Hampton in Feb. 2007)	osu	170	0.49	0.023	0.0010	

<sup>&</sup>lt;sup>A</sup> Lodgepole, and ponderosa to 12% moisture content. Other species to 15%.

### VII. Quality Assurance

#### Leak checks

Leak checks were performed on the VOC system before and after drying and on the impinger sample train before each run.

#### Calibration

Data for the calibration gases are given in Appendix 4. The mid gas was not named because the analyzer was within tolerance without naming.

### **Detection limits (105)**

The instrument detection limits were -

Methanol - 0.66 μg/mL in the aqueous phase Phenol - 0.76 μg/mL in the aqueous phase Formaldehyde - 0.12 μg/mL in the hexane phase Acetaldehyde - 0.19 μg/mL in the hexane phase Propionaldehyde - 0.19 μg/mL in the hexane phase Acrolein - 0.48 μg/mL in the hexane phase

All samples were present in the aqueous or hexane phase at concentrations above the instrument detection limits except acrolein.

For hemlock, acrolein concentrations in the first two samples were below the instrument detection limit. Calculating the acrolein emissions with  $\frac{1}{2}$  the instrument detection limit for these samples changes the acrolein emissions from 0.0012 lb/mbf to 0.0013 lb/mbf. Calculating the acrolein emissions with the full detection limit of 0.48 ppm for these samples changes the acrolein emissions from 0.0012 lb/mbf to 0.0014 lb/mbf.

For Douglas-fir, acrolein concentrations in four samples were below the instrument detection limit. Calculating the acrolein emissions with ½ the instrument detection limit for these samples changes the acrolein emissions from 0.0005 lb/mbf to 0.0007 lb/mbf. Calculating the acrolein emissions with the full detection limit of 0.48

ppm for these samples changes the acrolein emissions from 0.0005 lb/mbf to 0.0010 lb/mbf.

The method detection limit varies with gas flow through the impingers and the amount of water collected. We have calculated these for each sample in each charge by using the instrument method detection limit to calculate the concentration in the kiln gas) and averaged them below:

#### Hemlock:

Methanol - mean = 0.32 ppmvd standard deviation = 0.05 ppmvd Phenol - mean = 0.12 ppmvd standard deviation = 0.02 ppmvd Formaldehyde - mean = 0.024 ppmvd standard deviation = 0.004 ppmvd Acetaldehyde - mean = 0.026 ppmvd standard deviation = 0.005 ppmvd Propionaldehyde - mean = 0.020 ppmvd standard deviation = 0.004 ppmvd Acrolein - mean = 0.052 ppmvd standard deviation = 0.009 ppmvd

#### Douglas-fir:

Methanol - mean = 0.40 ppmvd standard deviation = 0.06 ppmvd Phenol - mean = 0.16 ppmvd standard deviation = 0.02 ppmvd Formaldehyde - mean = 0.024 ppmvd standard deviation = 0.003 ppmvd Acetaldehyde - mean = 0.025 ppmvd standard deviation = 0.003 ppmvd Propionaldehyde - mean = 0.019 ppmvd standard deviation = 0.003 ppmvd Acrolein - mean = 0.050 ppmvd standard deviation = 0.007 ppmvd

#### **Detection limits (98.01)**

No samples were near the detection limits for this method.

#### Spikes, duplicates, and blanks

Spikes were run by putting a known quantity of water containing methanol, phenol, formaldehyde, acetaldehyde, propionaldehyde, and acrolein into the first impinger of a duplicate sampling train. Both trains were run simultaneously and the difference between the recovered chemicals and the expected recovery without the spike was calculated. The results are shown in Table 7 and 8.

Methanol had spike recoveries of 90.7, 97, 104.3, and 84.2 for Method 105 and 96, 102, and 69% for Method 98.01, The one low value (>70% and <130% is acceptable) was spiked with a relatively low concentration.

Formaldehyde had spike recoveries of 63, 75, 68, and 85 for Method 105. These are lower than for Method 98.01 but within the acceptable range of 50% to 150% for concentrations less then 0.5 ppmvd. For Method 98.01 the spike recoveries were 98 and 101% (>70% and <130% is acceptable). The formaldehyde spike associated with Douglas-fir run 2 did not work due to clouding of the sample as noted in the anomalies section below.

Acetaldehyde had spike recoveries of 72, 72, 86, and 89%. The range of 70% to 130% is acceptable for gas concentrations greater than 1.5 ppmvd. It should be noted that these are all towards the low end suggesting that some acetaldehyde is not being recovered.

Propionaldehyde had spike recoveries of 71, 71, 87, and 84. The range of 50% to 150% is acceptable for gas concentrations less than 0.5 ppmvd. Again, these are all towards the low end suggesting that some propionaldehyde is not being recovered.

Acrolein had spike recoveries of 60, 59, 73, and 84%. The range of 50% to 150% is acceptable for concentrations less then 0.5 ppmvd. Again, these are all towards the low end suggesting that some acrolein is not being recovered.

Duplicate sample runs were made for each charge. These results of these are shown in Tables 7 and 8. All values under 30% are acceptable for methanol and acetaldehyde and 50% for the other compounds.

The difference between duplicates in Method 105 was 13 and 27% for methanol. In Method 98.01 the differences were 9, 4, and 21%

The difference between duplicates in Method 105 was 5 and 1% for formaldehyde. In Method 98.01 the differences were 42 and 21%. The high

value (42%) was on a duplicate early in a charge when the concentrations are lower.

The difference between duplicates for acetaldehyde was 2 and 1%

The difference between duplicates for propional dehyde was 3 and 9%

The difference between duplicates for acetaldehyde was 6%. In the second duplicate run, one sample was a "no detect" so a second recovery could not be calculated.

The NCASI 98.02 (chilled impingers with no BHA) gave similar results for the overall methanol and formaldehyde emissions as measures by Method 105.

Field blanks (samples of the impinger water) indicated the water used in the impingers was clean. Lab blanks of the water used for formaldehyde analysis indicated that it contained no formaldehyde.

#### **Anomalies**

There were no anomalies during the schedule that would significantly affect the total hydrocarbon data.

Formaldehyde 98.01 samples two and three for the Douglas-fir clouded when exposed to the acetylacetone reagent. A repeat of the test yielded the same results - a cloudy solution on which the attenuation of visible light cannot be determined. We therefore use the formaldehyde released during the first interval for the second. For the third interval we used the formaldehyde value from the fourth interval.

In run 8 of the hemlock, the student did not record the weight of the spike. He was very consistent at filling the impingers, so we estimated the spike mass. There was a second spike for that charge so we are not depending on run 8 to validate the results.

TABLE 9a. Summary of quality assurance for the hemlock charge (NCASI 105).

		Alcohol Spike (105)														
Г		Massini	ss in impinger li		Corrected mass		Spke	Spike concentrations		Spike recoverie						
ı	Run	Methanol	Ph enol	flow	Methanol	Phenol	mass	Methanol	Phenol	Methano	Phenol					
L		R4	μg	mL/min	μg	μg	Я	pg/mL	ug/mL	%	%					
Г	8	1284.5	0.0	431.3	1234.2	0.0	100 <sub>E1</sub>	4,3,0	4 S. E.S	4.57	- 5					
	108	4407.0	0.0	420.9	4407.0	0.0	3.5	1000.0	0.0	90.7	#DIV/0!					

(estimated spike amount)

		,	Ndehyde S	Spike						
		Mass in	impinger		Impinger	Mass corrected for flow				
Run	Form- al dehyde	Acet- alde hyde	Propion- aldehyde	Acrolein	crolein flaw		Acet- al dehyd e	Propion- aldehyde	Acroleir	
	μΩ	рg	βď	ьa	ml/min	μΩ	рц	μg	μg	
8	22.4	659.1	18.9	15.9	431.3	21.9	653.1	18.4	15.6	
108	54.7	4427.7	55.5	47.0	420.9	54.7	4427.7	55.5	47.0	
		Spike con	centrations		1897 E. C		Spike re	coveries		
Spike mass	Form	Acet-	Propion-	Acrolein		Form	Acet-	Propion-		
	aldehyde	aldehyde	ald ehy de	Actoletti	100	ald ehyd e	al dehyd e	aldehyde	Acroleir	
g	. µg/mL	µg/mL	µg/mL	μg/mL	灵"。	%	%	%	%	
3.5	15.0	1500.D	15.0	15.0		62.6	71.9	70.6	59.9	

	D up licate											
Run	Mass in impinger											
	Methanol	Ph eno l	Form- aldehyde	Acet- aldehyde	Propion- aldehyde	Acrolein	tmpinger tlow					
	рg	μg	ρg	μģ	ЬB	pq	mVmin					
в	708.3	0.0	142	606.9	18.1	12.9	449.4					
108	762.8	0.0	14.1	564.5	18.8	11.5	424,9					
Difference, %	12.9	#DIV/0!	4.5	1.6	3.1	58	10000					

		Field bla			
Methanol	Phenol	Form- aldehyde	Acet aldehyde	Acet Propion- aldehyde aldehyde	
ppm	ppm	ppm	ppm	ppm	ppm
0.0	0.0	0.0	0.0	0.0	0.0

				Alcohol 9	Spke (105	)				
	Mass in	imp ing er	Impinger Corrected mass			Spike	Spike con	centrations	Spike recoveries	
Run	Methanol	Ph eno l	flow	Methanol	Phenol	mass	Methanol	Phenol	Methano	Phenol
	μg	pg	mL/min	рд	μg	g	ug/mL	μg/mL	%	%
13	3372.3	0.0	457.2	3291.5	0.0		S 140 W	P. 1948	100	M.74.
113	8849.0	0.0	430.9	8849.0	0.0	5.73	1000.0	0.0	97.0	#DIV/0!

			Ndehyde S	ipik e							
		Mass in	impinger		Impines i		Mass corrected for flow				
Run	Form- aldehyde	Acet- alde hyde	Propion- aldehyde	Acrolein	Impinger flow	Form- aldehyde	Acet- aldehyde	Propion- aldehyde	Acro lei ı		
	PЯ	μŊ	Ŕď	μg	mU/min	μg	hδ	มด	μg		
13	34.0	1089.5	34.D	33.4	457.2	32.1	1026.8	32.1	31.5		
113	96.2	7232.D	92.7	82.4	430.9	96.2	7232.0	92.7	82.4		
-		Spike con	centrations		.00	L	Spike re	cov eri es			
Spike mass	Soiles mars   Corm   Aget   Proping		Acrolein	St. 1	Form-	Acet-	Propion-	Acroleir			
	aldehyde	alde hv de	ald ehy de	ACIOIGIN		aldehyde	aldehyde	aldehyde	Poroleii		
а	ЬВ	μg	ья	μg		%	%	%	%		
5.73	15.0	1500 D	15.D	15.0	(m) (d)	74.8	72.2	70.5	59.3		

TABLE 9b. Summary of quality assurance for the Douglas-fir charge (NCASI 105).

					Alcohol	Spike (105	)				
١		Mass in	impinger	Impinger	Correct	zted mass Spike		oke Spike concentrations		Spike recoveries	
1	Run	Methanol	Phenol	flow	Meth anol	Phenol	mass	Methanol	Phenol	Methano	Phenol
ı	23 27	рg	- µg	mL/min	μg	ñй		pg/mL	µg/mL	%	%
1	3 "	253.7	0.0	441.3	253.8	0.0	3	1 1	14 July 19		20.8
Į	103	4681.B	QΩ	441.5	4581.8	0.0	4.13	1000.0	QΟ	104.3	#DIV/O!

		,	Ndehyde S	Spike							
		Mass in	impin ger		,	Mass corrected for flow					
Run	Form- aldehyde	Acet- ald ehy de	Propion aldehyde	Acrolein	Impinger flow	Form- aldehyde	Acet- aldehyde	Propion- aldehyde	Aa ole ir		
	Ьď	рg	μg	μg	mL/min	ьbа	рg	Ьď	μg		
3	10.7	353.1	2.9	0.0	441.3	10.7	353.2	2.9	0.0		
103	52.8	5700.4	56.6	52.2	441.5	52.8	5700.4	56.6	52.2		
	1	Spke con	rentrations		54 34 13		Spke re	roveries.			
Spike mass	Snike mass Form And Proving		Acrolein		Form- aldehyde	Acet-	Propion- aldehyde	Aaoleir			
g	ug/mL	μg/mL	μg/mL	μg/mL		%	%	%	%		
4.13	15.0	1500 D	15.0	15.D	1.5	87.9	86.3	86.7	84.3		

		,	Duplical	e			
Run	Meth anol	Phenol	Form- aldehyde	Acet- ald ehyde	Propion- al dehyde	Acrolein	Impinger flow
	μg	μα	μΩ	μg	μg	ըց	πιUmin
7	633.8	0.0	18.2	393.3	8.5	0.0	452.1
107	782.1	QQ	17.0	363.1	8.8	16.7	419.8
Difference, %	27.3	#DIV/0!	1.0	0.8	8.9	200.0	500

		Field bla	nk		
Methanol	Phenol	Form- ald ehyde	Acet- ald ehyde	Propion- aldehyde	Acrolein
ppm	ppm	ppm	ppm	ppm	ppm
0.0	0.0	0.0	0.0	0.0	0.0

Ī		Alcohol Spke (105)												
Į		Mass in	impinger	Impinger Corrected mass		Spike	Spike Concentrations		Soke recoveries					
]	Run	Meth anol	Phenol	flow	Methanol	Phenol	mass	Methanol	Phenol	Methano	Phenol			
		рg	μg	mL/min	ьa	P.Я	Я	μg/mL	μg/mL	%	%			
-	13	1302.0	αo	419.8	1302.4	0.0		1 W.		1	4.			
	113	3660.7	۵٥	421.0	3660.7	0.0	2.8	1000.0	ΩO	84.2	#DIVA!			

		- 1	Adehyde S	Spike						
		Mass in	i mpin ger		l,	Mass corrected for flow				
Run	Form- aldehyde	Acet- ald ehyde	Propion- aldehyde	Acrolein	Impinger flow	Form- aldehyde	A cet- ald ehyde	Propion- aldehyde	Aa ole ir	
	ьa	PΩ	ЬB	pg	mL/min	Pβ	หน	P P P	րց	
8	22,0	462.5	10.8	21.7	419.6	22.1	464.1	10.9	21.8	
109	57.8	4199.0	46.2	52.5	421.0	57.8	4199.0	46.2	52.5	
		Spike con	centrations				Spkere	coveries		
Spike mass	Spike mass Form- Acet- Propion Acet- aldehyde aldehyde aldehyde		Acrolein		Form- aldehyde	Acet- aldehyde	Propion- aldehyde	Aa oleir		
. <u> </u>	μg	ьū	μg	рq		%	%	%	%	
2.8	15.0	1500.0	15.0	15.0	**	84.9	88.9	84.1	73.3	

TABLE 10a. Summary of quality assurance for the hemlock charge (NCASI 98.01).

	Spike									
Methanol	Mass in	Impinger	Corrected	Mass	Spike	Spike	Mass	Recovery		
Run	impinger	flow	mass	difference	mass	Concentration	in Spike	] [		
	μg	m L/min	μg	рg	Я	рргпш	PA	7		
7	1088.7	432.1	1088.8	2.8	1 1 5 5	U &		874		
71	3987.8	423.4	3987.8	20010	3.00	1000	3000	98.7		

	Spike Spike									
Formal dehyde	Mass in	Impinger	Corrected	Mass	Spike	Spike	Mass	Pecovery		
Run	impinger	flow	mass	difference	mass	Concentration	in Spike	1		
	μg	m L/min	μg	μg	g	ppmw	hā	*		
7	20:2	432.1	19.8	11144	100	50 D	(6(3))			
71	84:1	423.4	64.1	443	3.00	15	45	98.4		

	Duplicate									
Methanol	Mass in	Impinger	Corrected	Mass						
Run	impinger	flow	mass	difference						
	Ьà	mL/min	ьà	%						
2	33339	434.6	318.75	1.00						
21	350.1	414.9	350.1	8.0						

Field bl	Field blank						
Concentrations							
Methanol	Formald.						
ppm	ppm						
0.0	0.0						

	Duplicate									
Formal dehyde	Mass in	Impinger	Corrected	Mass						
Run	impinger	flow	mass	difference						
	ΡB	mL/min	ht	%						
2	7.4	434.8	7.1	7 20 40 -						
21	12.2	414.9	12.2	41.9						

TABLE 10b. Summary of quality assurance for the Douglas-fir charge (NCASI 98.01).

				Spike				
Methanol	Massin	Impinger	Corrected	Mass	Spike	Spike	M ass	Recovery
Run	impinger	flow	mass	difference	mass	Concentration	in Spike	·
	þд	m∪min	μg	þд	g	ppmw	µg	%
2	138.9	440.7	132-2			13.1.27		or of the
102	4367.3	419.3	4367:3	4235.2	4.13	1000	4130	102.5

				Spike				
Formaldehyde	Massin	Impinger	Corrected	Mass	Spike	Spike	M ass	Recovery
Run	impinger	flow	mass	difference	mass	Concentration	in Spike	·
	μд	mUmin	μg	ha	g	ppmw	Пd	%
2	5.0	440.7	4.8			æ	14 1/	
102	0.0	419.3	0.0	-4.8	4.13	15	61.95	-7.7

	Duplicate										
Methanol	Massin	Impinger	Corrected	Mass							
Run	impinger	flow	mass	difference							
	μд	m∐min	µg	%							
12	2381.3	452,3	2345.3	1. 3.							
112	2252.0	445.4	2252.0	4.1							

	Field blank							
0.0	Concentrations							
	M ethanol	Formald.						
-	ppm	ppm						
	0.0	0.0						

	Duplicate									
Formaldehyde	Corrected	Mass								
Run	impinger	flow	mass	difference						
	μα	mL∕min	μq	%						
12	33.2	452.3	32.7	75 ***						
112	27:0	445.4	27.0	20.9						

	Spike								
Methanol	Massin	Impinger	Corrected	Mass	Spike	Spike	M ass	Recovery	
Run	impinger	flow	mass	difference	mass	Concentration	in Spike		
	þф	mUmin	μq	μq	q	ppmw	рц	%	
9	2126.7	476,6	1964 0				也世界學多語	<b>建</b>	
109	4792.0	440.1	47920	2828.0	4.13	1000	4130	68.5	

				Spike				
Formaldehyde	Massin	Impinger	Corrected	Mass	Spike	Spike	M ass	Recovery
Run	impinger	flow	mass	difference	mass	Concentration	in Spike	
	μg	m∪min	μg	μд	g	ppmw	μg	%
9	18.8	476.6	17.4	a dan			20	+ + +
109	80.0	440.1	80.0	62.7	4.13	15	61.95	1.01.2

**Appendix 1. Detailed Sampling Procedures** 

#### INSTRUCTIONS FOR CHECKS OF EMISSIONS KILN

Purpose: Ensure kiln is operating correctly

Clock time: Record from computer

Run time: Record from computer. Check the box if the computer screen being

refreshed and time is advancing.

**Box temperature:** Read from metal electrical box under desk, left controller. The top and bottom numbers should be similar on the box should be similar, about 126 C..

Valve temperature: Read from metal electrical box under desk, right controller. The top and bottom numbers should be similar on the box should be similar, about 154 C..

**Dry-bulb temperature:** Read from computer screen. Compare to graph to be sure it's correct. If it's not within a degree or two of the chart, check again in a few minutes. During startup (the first 3 or so hours), it may not be able to track. If it's too high, the heat valve should be closed, too low and the heat valve should be open. If it does not appear to be working correctly, call Mike or Mark.

Wet-bulb temperature: Read from computer screen. Compare to graph to be sure it's correct.

If it is too low, it means that the kiln atmosphere is too dry. Check the flow meters. If Flow1 is about 10 L/min (its lower limit), make sure that Flow2 and Flow3 are turned off

If it's too high, then either the kiln atmosphere is too humid or the sock is not being wetted. If Flow 1 is near 200 L/min (its upper limit) add venting by opening Flow2 and/or Flow 3. The maximum for Flow2 is 50 L/min, if it reads over this value for several readings, reduce it to about 45 L/min. Don't change Flow3 often, rather set it and leave it for several hours if possible. Keep the Flow 3 reading constant by small adjustments. As Flow1 decreases or Flow2 turned down, there is more pressure behind Flow3 and the flow increased. Check for water in the wet-bulb reservoir (push the float down and make sure it's getting water).

Check both Wet-bulb1 and Wet-bulb2 and make sure they are reading about the same. If they differ by more than 2 C, call Mike or Mark.

If both wet-bulbs are reading the same as the dry-bulb, check the wet-bulb water.

If these procedures do not correct the wet-bulb temperature within 30 minutes, call Mike or Mark.

**Line temperature**: Read from gray box on wall above analyzer. It should read about 275°F.

Chiller temperature: Read the chiller temperature. It should be about -1°C.

Flow 1: Read from computer. The value of Flow1 changes depending on the wetbulb. If Flow 1 is 10 L/min and the wet-bulb is too low, there's probably nothing we can do. If it's 200 L/min and the wet-bulb is too high, Flow2 and/or Flow3 can be opened. Flow2 and Flow3 should be adjusted so that Flow1 stays below 175 to 200 L/min.

Flow 2: Read from computer. The value of Flow2 is set by you. It will vary a little - as flow 1 goes down, flow 2 will go up. Do not set it to < 40 L/min if you think Flow1 is going to decrease or it will go off scale and not be read by the computer

Flow 3: Read from meter. The value of Flow3 is set by you. It will vary a little - as flow 1 goes down, flow 2 will go up. Be sure to clearly record this value and when you change it

**Dilution flow:** Read dilution flow meter. It should read the same setting as the red flag. Do not adjust. If significantly different, investigate.

F/M Flow: Read from rotometer. This should be about 400 to 500 cc/min.

Line vacuum: Read from the vacuum gauge. This should be about 20"Hg.

## INSTRUCTIONS - FIELD DATA SHEET FOR TOTAL HYDROCARBON ANALYZER PRE-SAMPLE PROCEDURE

#### **BACKGROUND INFORMATION**

Get the dry- and wet-bulb temperatures from the kiln schedule or off the computer. Use the highest expected values for the run.

Read absolute humidity off the psychrometric chart or table.

Calculate or read from tables -

Percent moisture = 100 / [1 + 1 / 1.61\*AbHum]
Target Dilution Ratio (TDR) = 15 / Percent Moisture

Event = the name of the drying cycle.

Run = the number of the 3-hour interval.

Operator, that's you.

Date and time are now, as you start the data collection process.

#### **AMBIENT DATA**

Call 9-754-0081 and get altimeter setting.

Read the laboratory temperature from the thermometer.

#### ANALYZER CALIBRATION

Set valves so that 1, 2 = off; 3 = on; 4 = vent. This allows gas to flow out of the vents from the calibration tanks and shuts off all other sources. Only calibration gas should go through the detector.

Open the zero gas tank valve

zero toggle switch up (on), others down (off) set flow to 3.5 L/min using regulator on tank wait for a stable reading (about 30 to 60 seconds) use the zero dial (pot) on THA to get a zero reading read the analyzer read computer note pot setting close valve on zero gas tank

Open span gas tank valve

span toggle switch up (on), others down (off) set flow to 3.5 L/min using regulator on tank set analyzer to range 3 wait for a stable reading (about 30 to 60 seconds) use the span dial (pot) on THA to get a reading of 905 ppm

read the analyzer, record, for example, 9.05 or 900 read computer (should read about 905) note pot setting

#### Open mid gas tank valve

mid toggle switch up (on), others down (off) set flow to 3.5 L/min using regulator on tank wait for a stable reading (about 30 to 60 seconds) read analyzer (do not adjust pot settings), record, for example, 4.12 or 412 read computer (should about 412) check for within tolerance turn off mid gas all toggle switches off

#### SET DILUTION FLOW BEFORE RUN

Set valves so that 1, 2, 3 = off; 4=meter. This allows gas to flow only from the meter to the detector.

Use the Gilibrator to take 4 readings of the total flow rate (TFR). This is the total flow drawn by the analyzer and should be about 2.6 L/min

Make sure the average does not include any "bad" readings Record the average, L/min = cc/min / 1000 Write the Event, Run, and "Pre-TFR" on the Gilibrator printout.

#### Calculate the next two values -

Target dilution flow rate (TDFR) is the TFR x (1 - DR) Target sample flow rate (TSFR) is the TFR x DR Check that the sum of these is the Total Flow Rate

#### Set dilution flow

Set red pointer to desired dilution flow (on meter with valve 1)
Slowly open lower valve on dilution flow meter (1=on; 2, 3=off; 4=meter)
Use upper valve on dilution flow meter to adjust flow
Do not adjust this meter after this point
Read the meter that you just set and record the value

Use the Gilibrator to take 4 readings of the sample flow rate (SFR). This is the flow through the analyzer after dilution is set. It will vary, depending on the dilution setting.

Make sure the average does not include any "bad" readings Record the average, L/min = cc/min / 1000 Write "Pre-SFR" on the Gilibrator printout.

#### CHECK DILUTION FLOW BEFORE RUN

Set valves so that 1, 3 = on; 2=off; 4=vent. This allows gas to flow out of the vent from the calibration tank and shuts off all other sources. Calibration gas and dilution air will go through the detector.

Open span gas tank valve

span toggle switch up (on), others down (off)
set flow to 3.5 L/min using regulator on tank
set analyzer to range 3
wait for a stable reading (about 30 to 60 seconds)
record
turn off all calibration gas tank valves
all toggle switches off

Calculate the dilution ratio based on gas flow by dividing the Sample Flow Rate by the Total Flow Rate.

Calculate the dilution ratio based on span gas by dividing the Diluted span by the undiluted span.

If the Dilution ratios do not agree within 5% - DO NOT PROCEED\*\*\*\*. Use  $100*(DR_{Span}$  -  $DR_{Flow}$ )/DR  $_{Flow}$  to calculate the % difference.

\*\*\*\* check calculations, check that values for ppm and flows make sense, remeasure everything. If it still does not agree, call Mike or Mark

#### START RUN

Set valve so that 1, 2, 5 = on; 3, 4=off; all calibration tank valves off

Record the start time. Use the computer clock for all times or set your watch to the computer time.

Make sure analyzer is on appropriate range, usually range 3, to keep THC reading on computer between 60 and 750.

Monitor system, as needed. Record system condition at least hourly.

End time should be no more than 3 hours from start time.

#### POST-SAMPLE PROCEDURE

#### AT END OF RUN

Record your name as the operator.

Event = the drying cycle. Run = the 3-hour interval.

Operator, that's you. Date and time are now, as you start the data collection process.

#### AMBIENT DATA

Call 9-754-0081 and get temperature and altimeter

Local pressure = (Altimeter - 0.23) x 3.3867

Read the laboratory temperature from the thermometer.

Fill out appropriate information on Pre-sample side of data sheet for next run. This will save time in between runs.

#### **END TIME**

Record computer time.

DO NOT adjust dilution gas yet.

#### **CHECK DILUTION FLOW AFTER RUN**

Set valves so that 1, 3 = on; 2=off; 4=vent. This allows gas to flow out of the vent from the calibration tank and shuts off all other sources. Calibration gas and dilution air will go through the detector.

Open span gas tank valve

span toggle switch up (on), others down (off) set flow to 3.5 L/min using regulator on tank wait for a stable reading (about 30 -60 seconds) record all toggle switches off

Sample flow rate. Set valves so that 1=on; 2, 3 = off; 4=meter. This allows gas to flow only from the meter and the dilution to the detector.

Use the Gilibrator to take 5 readings of the sample flow rate (SFR). This is the flow through the analyzer with dilution on.

Make sure the average does not include any "bad" readings

Record the average, L/min = cc/min / 1000

Write "Post-SFR" on the Gilibrator printout.

Read dilution flow meter
To calculate the L/min, divide scfh by 2.12
Turn off dilution flow meter using valve 1

**Total flow rate**. Set valves so that 1, 2, 3 = off; 4=meter. This allows gas to flow only from the meter to the detector.

Use the Gilibrator to take 5 readings of the total flow rate (TFR). This is the total flow drawn by the analyzer and should be about 2.6 L/min Make sure the average does not include any "bad" readings Record the average, L/min = cc/min / 1000 Write "Post-TFR" on the Gilibrator printout.

#### **CHECK CALIBRATION OF ANALYZER**

Set valves so that 1, 2 = off; 3 = on; 4 = vent. This allows gas to flow out of the vents from the calibration tanks and shuts off all other sources. Only calibration gas should go through the detector.

Span gas tank valve should be open

span toggle switch up (on), others down (off) set flow to 3.5 L/min using regulator on tank set analyzer to range 4 wait for a stable reading (about 30 -60 seconds) read analyzer (do not adjust pot settings), record, for example, 1.50 as 1500 read computer (should read about 152 due to range 4 setting) note pot setting check for within tolerance - between 1483 and 1573

#### Open mid gas tank valve

mid toggle switch up (on), others down (off) set flow to 3.5 L/min using regulator on tank set analyzer to range 3 wait for a stable reading (about 30 -60 seconds) read analyzer (do not adjust pot settings), record, for example, 8.50 as 850 read computer (should read same as analyzer) check for within tolerance

#### Open the zero gas tank valve

zero toggle switch up (on), others down (off) set flow to 3.5 L/min using regulator on tank wait for a stable reading (about 30 -60 seconds)

read analyzer (do not adjust pot settings) read computer note pot setting

Calculate the dilution ratio based on gas flow by dividing the Sample Flow Rate by the Total Flow Rate.

Calculate the dilution ratio based on gas flow by dividing the Sample Flow Rate by the Total Flow Rate.

Calculate % difference as 100 \* {Absolute Value (DR<sub>Span</sub>-DR<sub>Flow</sub>)} / DR<sub>Flow</sub>

Record the time now as the end time for check.

Tear off the four sets of Gilibrator readings (Pre-TFR, Pre-SFR, Post-SFR, Post-TFR) and staple to paper with other records.

Start Pre-Sample procedure for next run.

## INSTRUCTIONS FOR FORMALDEHYDE / METHANOL COLLECTION AND HAPS SAMPLING

#### **BACKGROUND DATA**

Operator, that's you.

Date and time are now, as you start the data collection process.

Event = Kiln Charge

Run = sequence of HAP measurement

#### PRE RUN DATA

Call 9-754-0081 and get altimeter setting.

Read the laboratory temperature from the thermometer.

#### **IMPINGER WEIGHTS**

Lab wash impingers, Dry the outside. Weigh the impingers.

Put 15 mL BHA solution in impinger #1. (10 mL distilled water for 98.01 and 99.02)
Put 15 mL BHA solution impinger #2 (20 mL distilled water for 98.01 and 99.02)
Put 15 mL BHA solution in impingeer (Empty for 98.01 and 99.02)

Reweigh the impingers.

Install impingers and lower into chiller

#### LEAK CHECK

Close valve to sample probe.

Turn on pump

Evacuate to 15 to 18 " Hg

Close valve that is near pump

Turn off pump

Note pressure and start timer

Allowable pressure change is 1" Hg in 2 minutes, if it is much more than this, find the source of the leak.

Slowly open valve near probe tip. When bubbles are no longer seen, open completely Open valve near pump

#### SAMPLE FLOW RATE

Attach probe tip to Gilibrator
Take 4 readings
Make sure all readings in average are "good" readings
Record the average

#### START TIME

Put probe into kiln Open port on Summa canister (99.02 only) Record time.

#### FLOW READINGS DURING TEST

Note flow meter reading at least every hour Run test for 3 to 6 hours, less if impingers fill (98.01). 99.02 is limited by Summa canister time limit. Run < 3 hours for 98.01.

#### **POST RUN DATA**

Call 9-754-0081 and get altimeter setting.
Read the laboratory temperature from the thermometer
Label a clean vial with the Event and Run numbers

#### **END TIME**

Remove probe from kiln Close Summa cannister Record time

#### SAMPLE FLOW RATE

Rinse probe with 5 mL of DI water (weighed)
Attach probe tip to Gilibrator
Take 4 readings
Make sure all readings in average are "good" readings
Record the average
Lift impingers from chiller
Remove impingers

#### **IMPINGER WEIGHTS**

Pre weigh and label sample bottle and lid

Dry the outside of the impingers

Weigh the impingers with the water (no tops) and record

Combine the water from the two (or three) impingers into the labeled bottle

Weight the bottle with its lid (105 only)

Rinse the impingers with 10 mL distilled water - #3 then #2 then #1 (105 only)

Put the rinse into the vial and weigh the vial with its lid (105 only)

Rinse the impingers with 5 mL hexane - #3 then #2 then #1 (105 only)

Put the rinse into the vial and weigh the vial with its lid (105 only)

Place sealed vial into refrigerator

Note any liquid lost during this procedure

Appendix 3. Samples of field data sheets.

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		^		Line	ပံ့	<u>\\$</u> .\\$.)	135	135	135	135	N N	35	F				1				
Time	Q :57	7:2	Temperatures	Wet- bulb	ပံ	44.0	9.5%	65.0	3,50	629	65,8	65,6	270								
Date	70-19-5	3-2(-07	Tempe	Dry- bulb	ပံ	H-28		82,1		27.16	~ ~	É	87.6 646								
۵	1	2.2		Valve	ပံ	1451	1515	14.5	75	747	SHI	54	911								
	Start	End		Box	ပ္	125	12	155	17.6	133	33	18	32								
	, c		Run		#	9	의	٥	=	_	ū	1	5								
J		2	Run	time	hrs	30:05	37:02	37:52	39:32	125.57	43.48	45:24	150.03								
Charge:		0 0 0	Clock	time	. 2	10:72	_	05.75.72	$\sim 1$	4			<b>₹</b> 000		, (*)					÷.	

82-146

### FIELD DATA SHEET, 105 HAPS MEASUREMENT - BEFORE SAMPLING

BACKGROUND INFO	ORMATION	Han	upton Heut						
Operator: P. M.	osher	TRAIN #1 - BE							
Date: 3-19-		Event (kiln charge):							
Time now :		Run (sample):							
PRE RUN DATA									
Altimeter setting: 2	9,87 inHg	Laboratory temper	rature: 21.2 °C						
Isopropanol rinse or la	ab wash:								
MPINGER WEIGHTS	, –								
	Dry Weight, g	Wet Weight, g	Water added, g						
Impinger #1	42.85	66,90	(~10 mL)						
Impinger #2	42.23	66.27	(~15-20 mL)						
Impinger #3	39.63	65.88							
		Total added:							
LEAK CHECK	/-	Hg after 2 minutes							
SAMPLE FLOW RATE	E: 494,3 m	L/min [ Average	e of 4. Label printout]						
START CLOCK	TIME: 13:49								
EVENT	EVENT TIME: 3.52 (elapsed time)								
FLOW READINGS DU	JRING TEST (hourly)								
Clock time	·	£1							
Flow rate, mL/min			W						
Vent flow, L/min	s) ()								

### FIELD DATA SHEET, 105 HAPS MEASUREMENT - AFTER SAMPLING

BACKGROUND INFORMATION										
Operator: P-Mosher Time now: 16:50		TRAIN #1 - AFTER Event (kiln charge):								
		Run (sample): 2-Q								
POST RUN DATA										
Altimeter setting: 29.86		Laboratory temperature: 20,20°C								
END CLOCK TIME: $16-50$										
EVENT TIME: 6:53 (elapsed time)										
EMPTY BOTTLE WEIGHT:										
SAMPLE LINE RINSE : 22.			(~5 mL)							
SAMPLE FLOW RATE : _	496,4 mL/mi	n [Average	of 4. Label printout]							
IMPINGER WEIGHTS		=								
	Wet Weight, g	Dry Weight, g	Water removed, g							
Impinger #1	75.74	*42+BS	32.89							
Impinger #2	73.40	ul 23	31.17							
Impinger #3	71.21	3463	31.58							
BOTTLE WEIGHT WITHOUT	RINSE: 221.	<u>56 g</u>								
BOTTLE WEIGHT WITH RIN	SE: 226.23	<u>,</u> ≥ g	·							
HEXANE RINSE:										
FILLED BOTTLE WEIGHT: 231,47 g										
Water lost during handling:	Water lost during handling: mL [ estimate ]									
Comments:	Comments:									

### FIELD DATA SHEET, 98.01 HAPS MEASUREMENT - BEFORE SAMPLING

	•							
<i></i>	TRAIN # - BEFORE							
	Event (kiln charge):							
	Run (sample): Bg							
PRE RUN DATA								
inHg	Laboratory temper	ature: 22.8°C						
Dry Weight, g	Wet Weight, a	Water added, g						
42.94		9.7 (-10 mL)						
42.39	59.09	16.7 (-15-20 mL)						
39.71								
,	Total added:	26.4						
inl	Hg after 2 minutes							
0.4985 ml	L/min [ Average	e of 4. Label printout]						
ME: 14: 29								
	elapsed time)							
NG TEST (hourly)								
	Dry Weight, g 42.94 47.39 39.71 inl c.4985 m	Event (kiln charge Run (sample):						

FIELD DATA SHEET, 98.01 HAPS MEASUREMENT - AFTER SAMPLING							
BACKGROUND INFORMATION  Operator: P. Mosher  Time now: 17:00	TRAIN #2 - AFTER Event (kiln charge):						
	Run (sample): 8 q						
Altimeter setting: 30.16 inHg	Laboratory temperature 23.0 °C						
EVENT TIME: 31:21 (e	elapsed time)						
SAMPLE LINE RINSE SAMPLE FLOW RATE: 50 \ mL/n	(~5 mL) nin [Average of 4. Label printout]						
IMPINGER WEIGHTS							
Impinger #1 72.54 Impinger #2 59.28 Impinger #3 39.96	Dry Weight, g Water removed, g						
Water lost during handling: mL Comments:	[ estimate ]						
3							

PRESENTE CONTROL OF THE PARTY NAMED OF

	LD DATA SHEET		ROCARBON ANAL	YZER - BEFORE
Event (kil	n charge): <u>Hampto</u>	on	Time now :	6:37
Run (sam	nple):		Dry-bulb temperatu	
Operator:	P. Mosha	w	Wet-bulb temperat	
Run (sample):/ Operator:			•	io (TDR): 0.63
AMBIENI	DATA			
Laborator	y temperature: <u>2</u>	2.4°c		
ΑΝΑΙ ΥΖΕ	R CALIBRATION	1	[1.5	? = off; 3=on; 4=vent ]
	Analyzer, ppm	Computer	Within range	Pot settings
zero	(0)	0	does not apply	470
span	611 (611)	6(1	does not apply	468
mid	305 (412)	305	.382 to 442	none
			New 300 pf	)h~
	ITION FLOW BEF	•	7	
	rate (TFR):	1,67,	L/min [1	, 2, 3 = off; 4=meter]
Target dilu	tion flow rate (TDI	<sup>-</sup> R)	_ L/min <sup>-</sup>	[TFR x (1 - DR)]
san	nple flow rate (TSI	FR)	_ L/min	[TFR x DR]
Set and re	ad dilution meter:		_scfh [	scfh = L/min * 2.12 ]
Sample flo	ow rate (SFR):	0.958	$\int L/\min$ [1 = on;	2, 3 = off; 4=meter]
CHECK D	ILUTION FLOW	· · · · · · · · · · · · · · · · · · ·	[1.	3=on; 2=off; 4=vent ]
	Analyzer	DR <sub>Span</sub> [Span <sub>Diluted</sub> /Span]	DR Flow [SFR/TFR] 100*(	Difference, % (DR <sub>Span</sub> - DR <sub>Flow</sub> )/DR <sub>Flow</sub>
Span	1ted 348	0.5696	0.573	0.3
START TI		2 [1	, 2, 5 = on; 3, 4 = c	off; tank valves off ]
ANALYZE	R RANGE:		[ 60 < compa	iter reading < 750 }

\* High his state of the second of the second

Operator: J. Keiber				Hampton 4
Time now: 19:57			Run (sample	,
AMBIENT DATA				1
Laboratory temperature: 2	74 00			
Laboratory temperature	<u>C. 1</u> C			
END TIME: 19:57	_			
CHECK DILUTION FLOW	AFTER RUN		[1,	3=on; 2=off; 4=vent
<u> </u>	Analyzer	-		Computer
Span <sub>Diluted</sub>	1 549			350
Sample flow rate (SFR) :	0.9514	_ L/min	[1= or	, 2, 3 = off, 4=meter
Read dilution meter:	scfh	_ L/min		[ L/min = scfh*0.472
Total flow rate (TFR): (attach print out with all four	sets of data)	_L/min	[ 1	, 2, 3 = off; 4=meter
Dilution ratio (DR <sub>Flow</sub> ):	0.5704	-		[SFR/TFR
CHECK OF ANALYZER CA	LIBRATION		[1,	2=off; 3=on, 4=vent
Analyzer	Computer	Withi	n range	Pot settings
span (13	613	593	to 629	468
mid 305	305	394 to 430		none
zero 🂢	Ø	-18	to +18	470
Dilution ratio (DR <sub>Span</sub> ):	0.5693			[ Span <sub>Diluted</sub> / Span
Dilution ratio difference:	0.1874	% [100	)*(Abs(DR <sub>s</sub>	<sub>Span</sub> - DR <sub>Flow</sub> ))/DR <sub>Flow</sub>
End time for check:	8	ZO:0	2	
Comments:				

Appendix 4. Calibration Data

# Airgas

## **CERTIFICATE OF ANALYSIS Grade of Product: EPA Protocol**

Airgas Speciality Gases 12722 S. Wenbyorth Avenue

Chicago, IL 60628

Part Number:

E02Al99E15A0453

Reference Number: 54-124086894-1 FAX: 1-773-785-1928

1-773-785-3000

Cylinder Number: XC031356B

Cylinder Volume:

http://www.airgas.com

Laboratory:

ASG - Chicago - IL

Cylinder Pressure:

146 Cu.Ft. 2015 PSIG

Analysis Date:

Feb 09, 2007

Valve Outlet:

590

Expiration Date: Feb 09, 2010

Certification performed in accordance with "EPA Traceability Protocol (Sept. 1997)" using the assay procedures listed. Analytical Methodology does not require correction for analytical interferences. This cylinder has a total analytical uncertainty as stated below with a confidence level of 95%. There are no significant impurities which affect the use of this calibration mixture. All concentrations are on a volume/volume basis unless otherwise noted. Do Not Use This Cylinder below 150 psig.i.e. 1 Mega Pascal

ANALYTICAL RESULTS								
Component	Requested Concentration	Actual Concentration	- Protocol - Method	Total Relative Uncertainity				
PROPANE	300.000 PPM	299.9 PPM	G1	+/- 1% NIST Traceable				
Air	Balance:	ALL VANCES TO SERVICE						

			CALIBRATION STANDARD	S ·
Туре	Lot ID	Cylinder No	Concentration	<b>Expiration Date</b>
NTRM	51919	SG9101963ALB	483.6PPM PROPANE/	Jul 01, 2009
			ANALYTICAL EQUIPMENT	r
Instrum	ent/Make/Mo	odel	Analytical Principle	Last Multipoint Calibration
VARIAN (	CP3800		FID	Feb 02, 2007

Triad Data Available Upon Request

Notes:

QA Approval

# **Airgas**

### Certificate of Analysis: EPA Protocol Gas Mixture

Airgas Specialty Gases 12722 S. Wentworth Avenue

Chicago, IL 60628

1-733-785-3000 Fax: 1-733-785-1928

Cylinder Number: Cylinder Pressure: 2000.6 PSIG Expiration Date:

CC44350

Reference Number: 54-124076439-1

10/4/2009

Certification Date: 10/4/2006 Laboratory:

ASG - Chicago - IL

**Certified Concentrations** 

Component	Concentration	Accuracy	Analytical Principle	Procedure
PROPANE	611.3 PPM	+/- 1%	FID	G1
Air	Balance			

Certification performed in accordance with "EPA Traceability Protocol (Sept.-1997)" using the assay procedures listed. Analytical Methodology does not require correction for analytical interferences.

Notes:

Do not use cylinder below 150 psig.

Approval Signature

Reference Standard Information

<u>Type</u>

Balance Gas

Component Cyl.Number

Concentration

NTRM 51919

PROPANE\_ SG9101953ACB

423.6 PPM

**Analytical Results** 

1st Component **PROPANE** 

1st Analysis Date:

10/04/2006

R 310807

S 391575 Z 0 R 310893

S 392797

Conc 609.7 PPM Conc 612.6 PPM

S 393458 Z 0

R 316077

Conc 611.6 PPM

AVG: 611:3 PPM