NCASI METHOD DI/HAPS-99.01

SELECTED HAPS IN CONDENSATES BY GC/FID

NCASI
Southern Regional Center
February 2000

Acknowledgements

This method was prepared by Dr. MaryAnn Gunshefski, Senior Research Scientist at the NCASI Southern Regional Center. Other assistance was provided by Alex Gholson, Senior Research Scientist, Dean Hoy, Research Associate, and Larry LaFleur, NCASI Fellow, at the NCASI West Coast Regional Center.

NCASI would like to acknowledge the following laboratories and individuals for their voluntary participation in the interlaboratory validation of this method:

- Columbia Analytical Services, Jacksonville FL, Ward Dickens and Josh Apple
- Columbia Analytical Services, Kelso WA, Ed Wallace and Loren Portwood
- Data Analysis Technologies, Inc. Dublin OH, Ron Mitchum
- Performance Analytical Inc. (a division of Columbia Analytical Services), Simi Valley CA, Michael Tuday and John Yokoyama
- STL-Savannah Labs, Savannah GA, Craig Ratkey and Myron Young
- Weyerhaeuser Co., Federal Way WA, Rick Bogar and Mike Grove

For more information about this method, contact:

MaryAnn Gunshefski, Ph.D.
Senior Research Scientist
NCASI Southern Regional Center
P.O. Box 141020
Gainesville FL 32614
(352) 377-4708, ext. 244
mgunshefski@ncasi.org

For more information about NCASI publications, contact:

Publications Coordinator
NCASI
P.O. Box 13318
Research Triangle Park NC 27709-3318
(919) 558-1999
publications@ncasi.org

National Council for Air and Stream Improvement, Inc. (NCASI). 2000. *Methods Manual - Selected HAPS in Condensates by GC/FID*. Research Triangle Park, NC: National Council for Air and Stream Improvement, Inc.

Disclaimer

The mention of trade names or commercial products does not constitute endorsement or recommendation for use.

NCASI METHOD DI/HAPS-99.01

SELECTED HAPS IN CONDENSATES BY GC/FID

1.0 Scope and Application

1.1 This method is used for the analysis of methanol (CAS # 67-56-1), acetaldehyde (CAS # 75-07-7), methyl ethyl ketone (CAS # 78-93-3), and propionaldehyde (CAS # 123-38-6) in condensate samples from pulp and paper mills by gas chromatography/flame ionization detection (GC/FID). A version of this method was published as Appendix I of NCASI Technical Bulletin No. 684, *Method for Analysis of Methanol, Acetone, Acetaldehyde and Methyl Ethyl Ketone in Liquid Samples*, and has been rewritten to conform with the contents and format established by the EMMC for EPA wastewater methods.

1.2 Types of condensates for which this method can be used include condensate to be piped to a biological treatment system and condensate entering the stripper system.

1.3 The method has been validated in two laboratories using United States Environmental Protection Agency (EPA) Method 301, *Field Validation of Emission Concentrations from Stationary Sources* (Appendix A to CFR 63), and is a validated method.

1.4 This method is applicable for detecting methanol, acetaldehyde, MEK, and propionaldehyde in condensates at the parts per million (ppm) level. A correction factor may be needed. All correction factors are given in Section 17.0.

1.5 This method is restricted to use by, or under the supervision of, analysts experienced in the use of gas chromatographs and skilled in the interpretation of chromatograms. Each analyst must demonstrate an ability to generate acceptable results with this method.

2.0 Summary of the Method

2.1 Samples are collected directly from the condensate stream using an appropriate collection vessel. For sample streams which are extremely hot, a cooling coil is used to lower the temperature of the sample to below 160°F. The samples are kept refrigerated until analysis.

2.2 In the laboratory, an aliquot of the sample is transferred to an autosampler vial. An aliquot of an internal standard solution is added to each of the autosampler vials. The internal standard is also used as a time reference peak. An aliquot of a surrogate solution can also be added. The aqueous samples are then introduced directly into the gas chromatograph equipped with a capillary column. The GC column is temperature programmed to separate the analytes from other compounds which may be present in

the sample. The analytes are detected with a flame ionization detector which is interfaced to the gas chromatograph.

2.3 Identification of the analytes is determined by comparison of their relative retention times with the relative retention times of a known standard. If the results are questionable, confirmation may be performed by using a mass spectrometer as the detector.

2.4 The sensitivity of the method is defined as the minimum measurement level (MML) and for undiluted samples is set at 1 mg/L for this method.

2.5 Quality is assured through frequent testing of the analytical systems. This is accomplished by using a second source reference material, a resolution test mixture, calibration check samples and spike recovery samples. Method blanks , duplicates, and matrix spikes must also be analyzed with each analytical batch to ensure data quality.

3.0 Definitions

3.1 The definitions below are specific to this method, but conform to common usage as much as possible.

3.1.1 Batch - grouping of samples, not more than 20

3.1.2 mg/L - milligrams per liter

3.1.3 May - This action, activity, or procedural step is neither required nor prohibited.

3.1.4 Must not - This action, activity, or procedural step is prohibited.

3.1.5 Must - This action, activity, or procedural step is required.

3.1.6 Should - This action, activity, or procedural step is suggested, but not required.

4.0 Interferences

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analyses by running laboratory blanks as described in Section 9.2.6.

4.2 Glassware must be scrupulously cleaned. Clean all glassware by detergent washing with hot water and rinsing with tap water. The glassware should then be drained dry and baked at over 100°C for several hours.

4.3 Injections into the GC must be made with a clean syringe. Carryover of analytes from previously injected high level standards or samples can have a large influence on the measured values of subsequent samples or standards. After injection of the sample, the syringe should be cleaned immediately by rinsing the syringe ten times with VOC-free DI water.

4.4 Several compounds which are not HAPs can interfere with the chromatography if the separation is not efficient. These compounds include methyl mercaptan, ethanol, acetone, and dimethyl sulfide. When performed properly, this method does sufficiently separate these compounds from the analytes of interest at concentrations found in condensates.

4.5 Compounds may interfere with the internal standard. Two internal standards are specified by the method so that one free of interference can be selected. When initially analyzing samples of unknown composition, an injection without internal standard can be performed to determine if an interference exists.

5.0 Safety

5.1 All chemicals should be treated as potential health hazards. It is recommended that prudent practices for handling chemicals in the laboratory (EPA Good Laboratory Practice) be employed.

5.2 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness of OSHA regulations regarding safe handling of chemicals used in this method. Material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

5.3 Methanol, MEK, propionaldehyde, and acetaldehyde are flammable liquids which may be harmful if inhaled or ingested. Use in a laboratory fume hood and wear appropriate gloves, eye protection, and other protective clothing.

6.0 Equipment and Supplies

6.1 Brand names and suppliers are cited for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and material other than those specified here, but demonstration of equivalent performance that meets the requirements of this method is the responsibility of the laboratory.

6.2 Sampling equipment

6.2.1 Samples are to be collected in glass bottles to zero headspace. It is recommended that 40 mL glass vials with Teflon™ faced silicone backed lids (VOA vials) be used.

6.2.2 Figure 1 gives a schematic showing the configuration of a VOA sample cooling train. Valve sizes should be small enough to yield controllable low flow rates (i.e., <1000 mL per minute). The diameter of the tubing should be small (i.e., around 0.25 inch inside diameter).

6.3 Laboratory glassware and supplies

6.3.1 Autosampler vials capable of holding 2 mL[1]

6.3.2 Volumetric flasks

6.3.3 Volumetric pipets

6.3.4 Syringes (including gas-tight syringes)

6.4 Analytical equipment

6.4.1 Gas chromatography system - gas chromatography analytical system complete with a cryogenically cooled temperature-programmable gas chromatograph with either a purge-packed or split/splitless injection port

6.4.2 Guard column - 10 m x 0.53 mm deactivated fused silica capillary column

6.4.3 Column - 75 m x 0.53 mm x 3 µm, 6% cyanopropylphenyl 94% dimethylpolysiloxane bonded phase (624 phase) fused silica capillary column (for example: J&W Scientific DB-624, Hewlett Packard HP-624)

6.4.4 GC detector - flame ionization with appropriate data system; a large-bore jet tip is recommended, capillary jet tips were found to result in frequent flame-outs

7.0 Reagents and Standards

7.1 **Deionized water** - Deionized water should be tested immediately before use to verify the absence of any target analytes. If it is found to be contaminated, it may be necessary to prepare fresh deionized water, purge the water with nitrogen or helium, or boil the water to remove the contaminant(s).

7.2 **Analytical standards** - Reagent grade or the highest purity methanol, acetaldehyde, propionaldehyde, methyl ethyl ketone, cyclohexanol, and 2,2,2-trifluoroethanol must be used. Each neat material should be analyzed for purity and to verify the absence of other target analytes or contaminants prior to being used for the preparation of

[1] It was found that a small bubble in the vial allowed rapid mixing of the sample to disperse the internal standard.

standards. The minimum acceptable purity is 95%. Some suppliers of propionaldehyde report 97% purity and upon inquiry indicate there may be from 1 to 2% water.

7.3 Internal standard primary spiking solution - Cyclohexanol or 2,2,2-trifluoroethanol can be used as the internal standard.

7.3.1 Prepare primary stock solution by adding 1.56 mL cyclohexanol to a tared 50 mL ground glass stoppered volumetric flask. Weigh the flask after the addition of the internal standard and record the weight to the nearest 0.1 mg. Fill the flask to 50 mL with DI water. This will result in a nominal 30,000 mg/L primary stock solution. Compute the exact concentration (mg/L) using the weight gain. The solution can be stored at room temperature for over 6 months.

7.3.2 Prepare primary stock solution by adding 1.36 mL of 2,2,2-trifluoroethanol to a tared 50 mL ground glass stoppered volumetric flask partially filled with DI water. Weight the flask after the addition of the standard and record the weight to the nearest 0.1 mg. This should result in a nominal 40,000 mg/L primary stock solution. Compute the exact concentration (mg/L) using the weight gain. This solution must be stored in a refrigerator.

7.4 Calibration primary stock solution - Fill a 50 mL ground glass stoppered volumetric flask with approximately 45 mL DI water. Tare the flask after the addition of the water. After each addition of analyte, weigh and record the weight gain to the nearest 0.1 mg. Using a syringe, add 3.15 mL of methanol, taking care to drop the methanol directly into the water without wetting the sides of the flask. In a like manner, add 64 µL of acetaldehyde, 62 µL of propionaldehyde, and 62 µL of methyl ethyl ketone. Once all the analytes have been added, fill the flask to the mark. This will result in a nominal 50,000 mg/L methanol, 1000 mg/L acetaldehyde, 1,000 mg/L propionaldehyde, and 1000 mg/L methyl ethyl ketone primary stock solution. Use this weight gain to compute the exact analyte concentrations. Note that acetaldehyde and propionaldehyde are extremely volatile and degrade in the neat solutions over time. A chilled gas-tight syringe must be used to deliver the neat compounds to the volumetric flask. New neat standards for acetaldehyde and propionaldehyde should be obtained when the second source standard requirement is not met using freshly prepared standards. An alternative would be to purchase a primary stock solution from a chemical reference supply company. The primary stock must be stored in the refrigerator and must be re-prepared monthly. The storage time of sealed or nitrogen blanketed standard solutions has not been evaluated at this time. Longer storage time may be allowed in cases where data are provided that supports it.

7.5 Calibration and matrix spike solutions - Prepare standard solutions by dilutions of the stock solution using gas-tight syringes to measure the required aliquots of primary standard. The required dilutions are shown below. Prepare matrix spike solutions by

calculating the concentration of analytes desired and diluting the primary stock solution.

µL of stock solution to add to 10 mL volumetric flask	Resulting acetaldehyde, MEK, and propionaldehyde concentration (mg/L)	Resulting methanol concentration (mg/L)
2,000	200	10,000
500	50	2,500
200	20	1,000
50	5	250
10	1	50

7.6 **Second source standard or certified reference standard** - A second source standard or certified reference standard containing the analytes in an aqueous solution must be prepared or obtained and analyzed after every recalibration of the instrument. The standard must be stored in a refrigerator and must be re-prepared monthly. The storage time of sealed or nitrogen blanketed standard solutions has not been evaluated at this time. Longer storage time may be allowed in cases where data are provided that supports it.

7.7 **Resolution test mixture** - Prepare a resolution test mixture containing the analytes of interest along with the possible interferences described in Section 4.3. This mixture can be prepared by first preparing a resolution stock solution by adding 2.5 mL of dimethyl sulfide, 1.0 mL of acetone, and 0.5 mL of ethanol to a 25 mL volumetric flask and diluting with methanol. Then add 10µL of the primary stock solution and 50 µL of resolution stock solution to 10 mL of DI water. Analyze 2.0 mL of this mixture as if it were a sample.

8.0 Sample Collection, Preservation, and Storage

8.1 **Collection** - Grab samples are collected directly from the process liquid stream using an appropriate collection vessel, typically a 40 mL VOA vial. For sample streams which are greater than 160°C, a cooling coil is used to lower the temperature of the sample to below 160°F. The cooling coil tubing should be flushed for two to three minutes with the condensate to be sampled prior to collecting a sample. This is done by opening both valves and allowing the sample to run through the tubing. After the line is flushed, valves are throttled back to slow the flow rate. The temperature of the liquid to be sampled should be checked to be sure it is cool prior to collecting the sample. Use caution when sampling even moderately hot streams into glass vials, since the heat may cause the glass to break. Fill the vial to zero headspace with the sample.

8.2 **Preservation** - No preservation is necessary for condensate samples.

8.3 **Storage** - All samples must be stored in a refrigerator (4°C) until analysis. Samples may be stored for 14 days, at which time the recovery of acetaldehyde may fall to less than 80%.

9.0 Quality Control

9.1 Each field sampling program or laboratory that uses this method is required to operate a formal quality assurance program. Laboratory or field performance is compared to established criteria to determine if the results of the analyses meet the performance criteria of the method.

9.2 GC Maintenance

9.2.1 Injector maintenance - The septum and injection liner should be replaced when necessary. If this is not done, retention time shifts and peak broadening can occur.

9.2.2 Bakeouts - Water can build up in the GC, causing peak broadening and FID flame out. Frequent bakeouts of the system help to purge the system of excess water. Keeping the injection port purge flowing throughout the chromatographic run will help to remove water from the system (e.g., disable "gas saver" on HP 6890 systems).

9.3 Initial GC/FID performance

9.3.1 Second source or certified reference material - A second source or certified reference material must be evaluated after each recalibration of the instrument. Recoveries between 85 and 115% are required for methanol, and between 80 and 120% for the other three analytes.

9.3.2 Resolution test mixture - The resolution test mixture described in Section 7.6 must be analyzed after each recalibration, and weekly thereafter. This is to assure that the chromatography system is working appropriately. Baseline resolution between acetaldehyde/methanol and ethanol/propionaldehyde/ acetone is required. The dimethyl sulfide and acetone need not be baseline resolved. Figures 2 and 3 contain sample chromatograms.

9.3.3 Reproducibility check - When the instrument is set up to perform this method a reproducibility/sensitivity check must be performed. Seven aliquots of the resolution test mix must be analyzed. The %RSD of the seven analyses must be less that 14% for acetaldehyde and less than 10% for propionaldehyde and MEK.

9.4 Continuing GC/FID performance

9.4.1 Blanks - One method blank must be prepared per analytical batch to demonstrate that all materials are interference free. The concentration of the analytes in the blank must be below 0.5 mg/L.

9.4.2 Calibration verification - Before each set of samples is analyzed, a calibration check is done to determine that the GC/FID system is operating within acceptable parameters. The calibration check must involve the analysis of a calibration standard in the mid-range of the calibration curve. The concentrations of the analytes must be within ±15% of the expected concentration for acetaldehyde, propionaldehyde, and MEK, and ±10% for methanol. If the calibration fails to meet these expected criteria, the GC/FID system may require maintenance. If routine maintenance does not correct the problem, a new standard prepared from a fresh calibration stock solution should be run. If this still fails, the instrument will need to be recalibrated.

9.4.3 Replicates - Replicates consist of running two or more separate aliquots of the sample through the entire analytical procedure. A duplicate must be performed for each batch of samples. The relative percent difference and the mean should be tabulated in a method precision log.

9.4.4 Matrix spike recovery - A matrix spike may be prepared for each batch of samples. Using the mean concentration determined by the replicate analyses or the level determined from a single measurement, determine the spiking level which will give at least three times the sample concentration. If the sample does not have detectable levels of analytes, spike the sample at approximately five times the lowest calibration level of the instrument. Spike the sample with the determined amount of the calibration standard/matrix spike solution (Section 7.4) and analyze the sample in the normal manner. Calculate the percent recovery using Equation 1.

Equation 1

$$R = \left(\frac{C_S - C_N}{C_T} \right) \times 100$$

Where:

R = percent recovery of matrix spike
C_S = measured concentration of spiked sample
C_N = measured concentration of native sample
C_T = theoretical concentration of spike

10.0 Calibration and Standardization

10.1 FID operating conditions

Assemble the GC/FID and establish the operating conditions outlined in Table 1 or 2. Once the GC/FID system is optimized for analytical separation and sensitivity, the same operating conditions must be used to analyze all samples, blanks, calibration standards, and quality assurance samples. Note that constant injections of aqueous samples can cause water to build up in the system. This will cause the retention times to shift and the peaks to broaden. It is recommended that a bakeout of the system be performed after approximately 50 injections. This should consist of heating the injector to 250°C, the oven to over 200°C but less than 260°C, and the detector to 350°C for several hours.

10.3 GC/FID analysis of calibration standards

10.3.1 Determine the retention times of the analytes by taking 2.0 mL of the mid-range calibration solution and adding 10 µL of the internal standard solution. This will result in concentrations of 150 mg/L or 200 mg/L of cyclohexanol or 2,2,2-trifluoroethanol, respectively, in the autosampler vial. Inject 1 µL of this solution and determine the relative retention times of the analytes to the internal standard using Equation 2.

10.3.2 Prepare a five-point calibration curve for the four analytes by taking 2.0 mL of each calibration solution and adding the internal standard solution as described above. The calibration range is defined in Section 7.4. Use of an internal standard for calibration is required.

10.3.3 Calculate the relative response factor (RRF_M) for each analyte using Equation 3. If the relative standard deviation (RSD) of the average RRF_M is less than 10% for methanol and 15% for acetaldehyde, propionaldehyde, and MEK, the calibration is acceptable. The average RRF_M can be used in all subsequent calculations. If the calibration does not pass the criteria the calibration curve solutions must be reanalyzed and reevaluated. It may be necessary to perform instrument maintenance prior to reanalysis. If reanalysis also fails to produce a linear curve, new calibration standards must be prepared and analyzed.

10.3.4 Analyze and calculate the concentration of the mid-range calibration standard daily, prior to each sample set, using Equation 4. Calculate the percent recovery of the standard using Equation 5 to verify the calibration. In-house percent recovery control limits must be determined, and are not to exceed ±10% for methanol and ±15% for the other three analytes. If the limits are exceeded, either prepare a new standard or perform instrument maintenance. If necessary, recalibrate the instrument.

Equation 2

$$RRT_A = \left[\frac{Rt_A}{Rt_{IS}} \right]$$

Where:

RRT_A = relative retention time of compound A
Rt_A = retention time of compound A
Rt_{IS} = retention time of internal standard (cyclohexanol or 2,2,2-triflouroethanol)

Equation 3

$$RRF_M = \left[\frac{A_M}{A_{IS}} \times \frac{C_{IS}}{C_M} \right]$$

Where:

A_M = area of methanol peak
A_{IS} = area of internal standard peak
C_M = concentration of methanol injected
C_{IS} = concentration of internal standard injected

Equation 4

$$C_A = \left[\frac{A_A \times C_{IS}}{A_{IS} \times RRF_A} \right]$$

Where:

C_A = concentration of compound A in sample (mg/L)
A_A = area of the compound A peak in the sample
C_{IS} = concentration of the internal standard (mg/L)
A_{IS} = area of the internal standard peak
RRF_M = relative response factor of compound A (Section 10.3)

Equation 5

$$\text{Percent Recovery} = \left[\frac{C_M}{C_E} \times 100 \right]$$

Where:

C_M = concentration of analyte measured
C_E = concentration of analyte expected

10.4 Analytical range and minimum calibration level

10.4.1 Demonstrate that the calibration curve is linear (relative response factors exhibit a RSD less than 10% for methanol or 15% for the other three analytes) throughout the range of the calibration curve described in Section 7.4.

10.4.2 Demonstrate that acetaldehyde, propionaldehyde and MEK are detectable at 1.0 mg/L with an RSD of less than 14% for acetaldehyde and less than 10% for the other two analytes as described in Section 9.3.3.

11.0 Procedure

11.1 Transfer an aliquot (2.0 mL) of the sample to an autosampler vial by gas-tight syringe. Add 10 µL of the internal standard primary spike solution (30,000 mg/L cyclohexanol or 40,000 mg/L 2,2,2-trifluoroethanol) to each of the autosampler vials. Perform the analysis by direct aqueous injection into the GC/FID. If the concentration of an analyte is more that 10% above the calibrated range, the sample should be diluted and reanalyzed to measure the analyte concentration.

11.2 If dilution is necessary, inject some fractional volume less than 2.0 mL using a gas-tight syringe into an autosample vial which is then brought to 2 mL with DI water and analyzed as described in Section 11.1. Calculate the dilution factor using Equation 6.

Equation 6

$$DF = \frac{2}{V}$$

Where:

DF = the dilution factor
V = the volume of sample (mL) injected into the autosample vial

12.0 Data Analysis and Calculations

12.1 GC/FID data analysis

12.1.1 The analytes are identified by comparison of the retention times relative to the internal standard established in the calibration to the relative retention times in the samples. The sample component relative retention time (RRT) should fall within ±0.01 RRT units of the RRT of the standard component.

12.1.2 Calculate the sample concentration, using the internal standard response factors established in Section 10.3.3, according to Equation 7. Use a dilution factor of 1 if no dilution is made and choose the proper correction factor based on the internal standard and hardware configuration used. Use a correction factor of 1 if no significant correction factor is found.

Equation 7

$$C_A = \left[\frac{A_A \times C_{IS} \times CF \times DF}{A_{IS} \times RRF_A} \right]$$

Where:

C_A = concentration of compound A in sample (mg/L)
A_A = area of the compound A peak in the sample
C_{IS} = concentration of the internal standard (mg/L)
A_{IS} = area of the internal standard peak
RRF_M = relative response factor of compound A (Section 10.3)
CF = correction factor from Method 301 validation (Table 3)
DF = dilution factor

12.1.3 If samples cannot be analyzed without dilution, the MML must be adjusted to reflect the lowest dilution factor used by multiplying the MML (1 mg/L) by the dilution factor calculated in Equation 6.

12.2 Data review requirements

12.2.1 The data are reviewed for accuracy of the identification, GC problems, interferences, and bias. Any problems should be corrected prior to reporting analytical results.

12.2.2 All the chromatograms are manually reviewed to confirm internal standard and analyte identification as well as the integration areas. As part of this

review, the analyst assesses whether or not the concentration is within the calibration range of the instrument. The analyst should determine whether dilution of the samples is required. Another tool that can be utilized to identify the analyte peaks is to overlay the sample chromatogram with the standard chromatogram.

12.2.3 The internal standard area counts must be reviewed and added to a control chart. The in-house determined control limits must not exceed ±20% of the mean.

12.2.3 Any inconsistencies between replicate analyses must be resolved (i.e., if an analyte is detected in one replicate and not the other), and attempts made to determine the reason for the inconsistencies.

12.2.4 Generate a report that includes the retention time, the area, and the calculated concentrations of the analytes, internal standard recovery (based on area counts), and surrogate recovery in percent.

12.2.5 Report the results for the least dilute sample where the concentration measured was within the acceptable calibration range.

12.2.6 Where analytes are not detected or are detected below the lowest calibration standard, report the Minimum Measurement Level. Report a revised Minimum Measurement Level in accordance with Section 12.1.3 for any dilute analyses where less dilute samples were not run and for any analyte that was not detected.

12.3 Data reporting requirements

12.3.1 Report results in mg/L to three significant figures.

12.3.2 Report all corresponding blanks, replicates, and matrix spike recoveries for each analytical batch of samples.

13.0 Method Performance

13.1 Single laboratory method validation studies were performed during the development of the method, and included evaluation based on the United States Environmental Protection Agency (EPA) Method 301, *Field Validation of Emission Concentrations from Stationary Sources* (Appendix A to CFR 63). A summary of the method performance data is presented in Section 17, Table 3.

14.0 Pollution Prevention

14.1 The laboratory should check state and local requirements to determine if pollution prevention equipmentis required or recommended in its area.

15.0 Waste Management

15.1 It is the responsibility of the laboratory to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and lands by minimizing releases into the environment. Compliance with all sewage discharge permits and regulations is also required.

16.0 References

16.1 National Council of the Paper Industry for Air and Stream Improvement, Inc. (NCASI). 1994. *Volatile organic emissions from pulp and paper mill sources, Part X - Test methods, quality assurance/quality control procedures, and data analysis protocols*. Technical Bulletin No. 684. Research Triangle Park, NC: National Council of the Paper Industry for Air and Stream Improvement, Inc.

16.2 United States Environmental Protection Agency (EPA). Method 301, *Field Validation of Emission Concentrations from Stationary Sources* (Appendix A to CFR 63).

17.0 Tables, Diagrams, Flowcharts, and Validation Data

17.1 Through the use of the EPA Method 301 validation procedure, this method has been shown to be a valid method for measurement of methanol, acetaldehyde, methyl ethyl ketone, and propionaldehyde in condensates from kraft mill sources. A summary of these validation data is presented in Table 3.

Table 1. GC/FID Operating Conditions for Selected HAPs Analysis
Purged-Packed Injector

Injection:	Direct (Splitless)
Injector Temperature:	170°C
Injection Volume:	1 µL
Injection Liner Size:	2 mm id (no packing)
Syringe Rinse	10 rinses with VOC free DI water
FID Detector Temperature:	275°C
H_2 Flow Rate:	approx. 50 mL/min
Air Flow Rate:	approx. 500 mL/min
Makeup Gas:	Nitrogen or Helium
Makeup Gas Flow Rate:	approx. 25 mL/min
Carrier Gas:	Helium
Carrier Gas Flow Rate:	constant pressure mode to give 6 mL/min at room temperature, or use constant flow mode at 6 mL/min
Column:	J&W DB-624, 75 m x 0.53 mm id x 3 micron fused silica capillary column with 10 m deactivated fused silica guard column
Cryogenics:	On
Temperature Program °C:	
Initial:	5°C for 1 min
Ramp 1:	6°C/min to 90°C for 0 minutes
Ramp 2:	40°C/min to 150°C for 7 minutes
Ramp 3:	70°C/min to 250°C for 4 minutes
Retention Time Order:	Acetaldehyde, Methanol, Propionaldehyde, 2,2,2-Trifluoroethanol, Methyl Ethyl Ketone, Cyclohexanol
Cyclohexanol Retention Time:	22.081 min
Relative Retention Time:	Acetaldehyde - 0.336 Methyl Mercaptan - 0.356 Methanol - 0.367 Ethanol - 0.458 Propionaldehyde - 0.487 Acetone - 0.499 Dimethyl sulfide - 0.503 2,2,2-Trifluoroethanol - 0.608 MEK - 0.672

Table 2. GC/FID Operating Conditions for Selected HAPs Analysis
Split/Splitless Injector

Injection:	Direct (Splitless)
Purge Flow Rate:	approx. 40 mL/min
Purge Time:	0.25 min
Injector Temperature:	110°C
Injection Volume:	1 µL
Injection Liner Size:	2 mm id with fused silica packing in the bottom (Restex #20713-200.5)
Syringe Rinse	10 rinses with VOC free DI water
FID Detector Temperature:	275°C
H_2 Flow Rate:	approx. 50 mL/min
Air Flow Rate:	approx. 500 mL/min
Makeup Gas:	Nitrogen or Helium
Makeup Gas Flow Rate:	approx. 25 mL/min
Carrier Gas:	Helium
Carrier Gas Flow Rate:	constant pressure mode to give 6 mL/min at room temperature, or use constant flow mode at 6 mL/min
Column:	J&W DB-624, 75 m x 0.53 mm id x 3 micron fused silica capillary column with 10 m deactivated fused silica guard column
Cryogenics:	On
Temperature Program °C:	
Initial:	5°C for 1 min
Ramp 1:	6°C/min to 90°C for 0 minutes
Ramp 2:	40°C/min to 150°C for 7 minutes
Ramp 3:	70°C/min to 250°C for 4 minutes
Retention Time Order:	Acetaldehyde, Methanol, Propionaldehyde, 2,2,2-Trifluoroethanol, Methyl Ethyl Ketone, Cyclohexanol
Cyclohexanol Retention Time:	22.081 min
Relative Retention Time:	Acetaldehyde - 0.336 Methyl Mercaptan - 0.356 Methanol - 0.367 Ethanol - 0.458 Propionaldehyde - 0.487 Acetone - 0.499 Dimethyl sulfide - 0.503 2,2,2-Trifluoroethanol - 0.608 MEK - 0.672

Table 3. Method 301 Validation Results

	Correction Factor (CF)			
Internal standard Injector	Acetaldehyde	Methanol	Propionaldehyde	Methyl ethyl ketone
Cyclohexanol Packed purge	1.12	NA[a]	1.12	0.97
Cyclohexanol Split/splitless	1.09	1.04	1.09	1.03
2,2,2-Trifluoroethanol Packed purge	1.14	NA[a]	1.14	1.07
2,2,2-Trifluoroethanol Split/splitless	1.06	NA[a]	1.06	NA[a]

[a] not applicable due to insignificant bias

Figure 1. VOA Sample Cooling Train

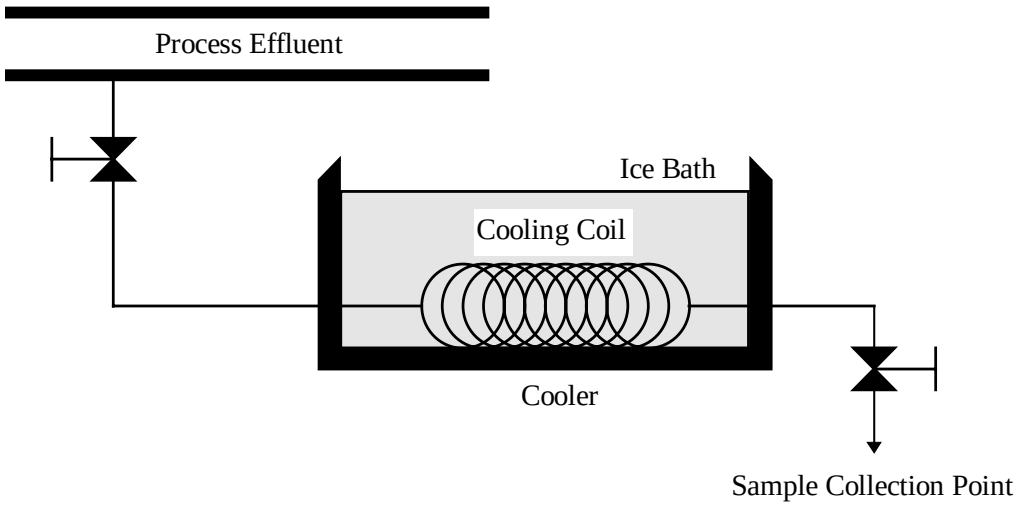

Figure 2: Entire Sample Chromatogram of Resolution Test Mixture

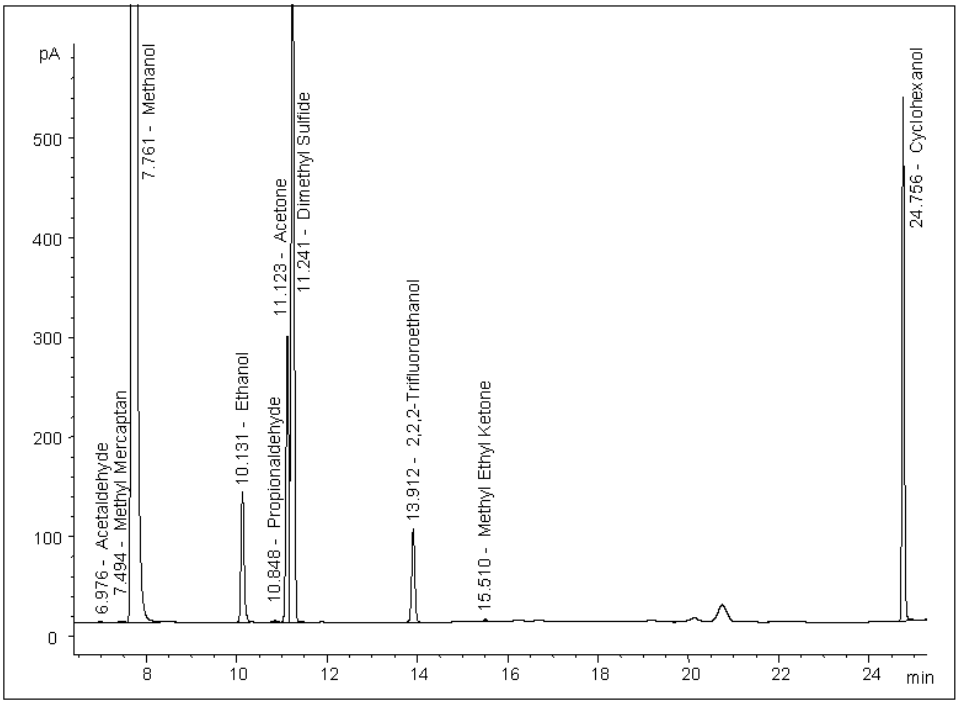

Figure 3: Partial Sample Chromatogram of Resolution Test Mixture

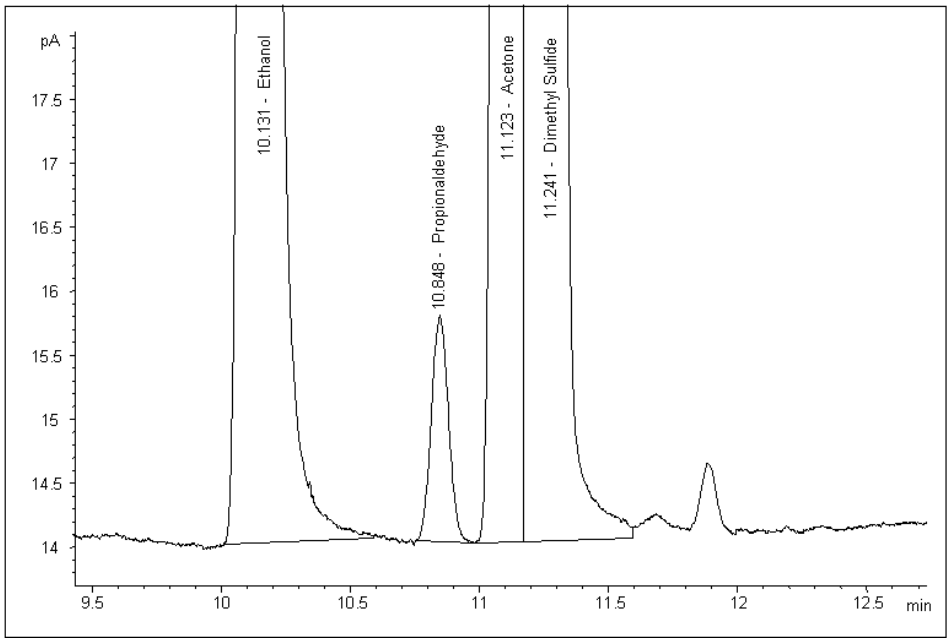

Figure 4. EPA Method 301 Validation Approval Letter – page 1

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

SEP 22 2000

Dr. Mary Ann Gunshefski
NCASI
Southern Regional Center
P.O. Box 141020
Gainesville, Florida 32614-1020

OFFICE OF
AIR QUALITY PLANNING
AND STANDARDS

Dear Dr. Gunshefski:

We have reviewed your report entitled, "EPA Method 301 Validation Report of the NCASI Method 'Selected HAPS in Condensates By GC/FID.' " We agree with your conclusion that this method, in all of its variations, met Method 301 criteria for measuring acetaldehyde, methanol, propionaldehyde, and methyl ethyl ketone in samples from the pulp and paper mill condensate streams regulated under 40 CFR Part 63, Subpart S, Paragraph 446(b). I have summarized in the enclosed Tables 1-4 the correction factors for the individual HAP's for each of the four variations in the test method. During any future testing, the tester must document and use the appropriate correction factor to correct the data from the test method.

As we discussed, each specific source must make its own alternative test method request. However, we can and will consider the validation data that you submitted in evaluating an alternative method request from any source similar to the ones at which you collected your validation data.

For our records we would like to have an electronic file copy of the test method and the supporting report in Wordperfect 6.x format.

If you have any questions about our comments or you would like to meet to discuss them, please contact Gary McAlister of my staff at (919) 541-1062.

Sincerely,

J. David Mobley, Acting Director
Emissions, Monitoring and Analysis Division

cc: K. C. Hustvedt (MD-13)
Stephen A. Shedd (MD-13)
Jeffrey A. Telander (MD-13)

Enclosure

Figure 4. (cont.) EPA Method 301 Validation Approval Letter – page 2

2

Table 1. NCASI Method DI/HAPS-99.01 - Purged-Packed Injector and Cyclohexanol as the Internal Standard

Compound	Validated	Correction Factor
Acetaldehyde	Yes	1.12
Methanol	Yes	None
Propionaldehyde	Yes	1.12
Methyl Ethyl Ketone	Yes	0.97

Table 2. NCASI Method DI/HAPS-99.01 - Split/Splitless Injector and Cyclohexanol as the Internal Standard

Compound	Validated	Correction Factor
Acetaldehyde	Yes	1.09
Methanol	Yes	1.04
Propionaldehyde	Yes	1.09
Methyl Ethyl Ketone	Yes	1.03

Table 3. NCASI Method DI/HAPS-99.01 - Purged-Packed Injector and 2,2,2-Trifluoroethanol as the Internal Standard

Compound	Validated	Correction Factor
Acetaldehyde	Yes	1.14
Methanol	Yes	None
Propionaldehyde	Yes	1.14
Methyl Ethyl Ketone	Yes	1.07

Table 4. NCASI Method DI/HAPS-99.01 - Split/Splitless Injector and 2,2,2-Trifluoroethanol as the Internal Standard

Compound	Validated	Correction Factor
Acetaldehyde	Yes	1.06
Methanol	Yes	1.01
Propionaldehyde	Yes	1.06
Methyl Ethyl Ketone	Yes	None