NCASI METHOD DI/MEOH-94.03

METHANOL IN PROCESS LIQUIDS AND WASTEWATERS BY GC/FID

NCASI
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NCASI METHOD DI/MEOH-94.03

METHANOL IN PROCESS LIQUIDS AND WASTEWATERS BY GC/FID

1.0 Scope and Application

1.1 This method is used for the analysis of methanol (CAS # 67-56-1) in process liquid samples from pulp and paper mills by gas chromatography/flame ionization detection (GC/FID). This is an update of the NCASI Method DI/MEOH-94.02. An older version of this method was published in Appendix I of NCASI Technical Bulletin 684 as *Method for 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. This version includes only methanol, since methanol is the only compound for which the method has been validated at this time.

1.2 Types of process liquids for which this method can be used include samples from both kraft pulping mills and sulfite pulping mills. Liquid types include condensate, dirty hot water plant liquid, evaporator condensate, foul condensate, influent to sludge ponds, stripped condensate, treated effluent, untreated effluent and weak wash.

1.3 The method has been single laboratory validated using the 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 in process liquids at the part per million (ppm) level.

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 the ability to generate acceptable results with this method.

2.0 Summary of the Method

2.1 Samples are collected directly from the process liquid 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. Effluent samples must be preserved with acid to pH 2-3 upon collection. The samples are kept refrigerated until analysis.

2.2 In the laboratory, an aliquot of the sample is transferred to an autosampler vial. To each of the autosampler vials, an aliquot of an appropriate internal standard solution must be added. The internal standard is also used as a time reference peak. The aqueous samples are then directly introduced into the gas chromatograph equipped

with a capillary column. The GC column is temperature programmed to separate the methanol from other compounds which may be present in the sample. The methanol is detected with a flame ionization detector which is interfaced to the gas chromatograph.

2.3 Identification of methanol is determined by comparison of its retention time with the retention time of a known standard. If the results are questionable, confirmation can be performed by using a different GC column.

2.4 The sensitivity of the method is defined as the minimum measurement level (MML) and for undiluted samples is set at 0.5 mg/L for this method.

2.5 Quality is assured through testing of the analytical systems. This is accomplished by using a second source reference material, calibration check samples and spike recovery samples. Method blanks, duplicates and matrix spikes should 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 9.4.1.

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 can interfere with the chromatography if the separation is not efficient. These compounds include methyl mercaptan, ethanol, acetone, and dimethyl sulfide. When the cryogenic GC method is performed properly, this method does sufficiently separate these compounds from methanol at concentrations found in condensates. When the non-cryogenic GC method is performed properly, the method used dilution to remove these interferences. This can be achieved because the methanol concentration in these types of samples is much larger than the concentration of these other compounds.

4.5 Compounds may interfere with the internal standard. 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 a potential health hazard. It is recommended that prudent practices for handling chemicals in the laboratory 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 is a flammable liquid 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 or plastic 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 shows 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

6.3.2 Volumetric flasks

6.3.3 Volumetric pipets

6.3.4 Syringes

6.4 Analytical equipment

6.4.1 Gas chromatography system - gas chromatography analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories including syringes, analytical columns and gases.

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

6.4.3 Column - 30 m x 0.53 mm x 3 μm bonded phase DB-624 fused silica capillary column (J&W Scientific or equivalent), 30 m x 0.32 mm x 025 μm bonded phase DB-WAX fused silica capillary column (J&W Scientific or equivalent), 75 m x 0.53 mm x 3 μm bonded phase DB-624 fused silica capillary column (J&W Scientific or equivalent) [non-cryogenic method], or other column shown to be capable of separating methanol from typical components found in process liquids.

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 and cyclohexanol must be used.

7.3 **Internal standard primary spiking solution**- Prepare primary stock solution by adding 0.312 mL cyclohexanol to a tared 100 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 100 mL with DI water. This will result in a nominal 3,000 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. A higher concentration of internal standard should be prepared and used if the upper limit of the calibration curve being used is above 100 mg/L. Additionally, another internal standard material could be used if it is demonstrated that it does not interfere with any other peaks in the chromatogram.

7.4 **Calibration primary stock solution** - Fill a 100 mL ground glass stoppered volumetric flask with approximately 90 mL DI water. Tare the flask after the addition of the water. Using a syringe, add 0.126 mL of methanol, taking care to inject the methanol directly into the water. This will result in a nominal 1,000 mg/L methanol primary stock solution. Use this weight gain to compute the exact methanol concentration.

7.5 **Calibration solutions** - Prepare five standard solutions by serial dilutions of the stock solution. For the cryogenic GC methods, the calibration range is 0.5 to 1000 mg/L. It has been found that the linear range can be extended up to 10,000 mg/L, but the accuracy at the lower concentrations is compromised, and the possibility for interferences increases. For the non-cryogenic GC method, the required calibration range is 0.5 to 100 mg/L.

7.6 **Second source standard or certified reference material** - A second source standard or certified reference standard containing methanol in an aqueous solution must be prepared or obtained and analyzed after every calibration of the instrument. A second source standard is a standard that is made from methanol purchased from a different vendor than that which was used to prepare the calibration primary stock solution.

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^{o}F, 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 wastewater 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 restricted 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** - Effluent samples must be preserved with acid upon collection. This can be accomplished by adding several drops of dilute (1N) acid (i.e., HCl, H_2SO_4) to

the sample vial before sample collection to bring the pH down to 2-3, then fill to zero headspace as described above. Do not acidify to below pH 2. No preservation is necessary for other types of process liquids.

8.3 **Storage** - All samples must be stored in the refrigerator (4°C) until analysis. Samples may be stored for at least 30 days.

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, peak broadening and low continuing calibration verification recoveries 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.

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.

9.3.2 Reproducibility check - When the instrument is set up to perform this method a reproducibility/sensitivity check must be performed. Seven aliquots of the 0.5 mg/L calibration standard must be analyzed. The %RSD of the seven analyses for methanol must be less that 15%.

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 methanol 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 concentration of methanol must be within ±10% of the expected concentration. 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 or matrix spike solution 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, 2, or 3. Other chromatographic columns and conditions may be used if it has been established that methanol is separated from compounds which may cause interference, and quality control parameters are met. Once the GC/FID system is optimized for analytical separation and sensitivity, the sample 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 after approximately 50 injections a bakeout of the system be performed. This should consist of heating the injector to 250°C, the oven to over 200°C and the detector to 350°C for at least several hours.

10.2 GC/ FID analysis of calibration standards

10.2.1 Determine the retention time of methanol by taking 2.0 mL of the mid-range calibration solution and adding 10 µL of the internal standard solution. If a 3,000 mg/L internal standard primary stock solution was prepared, this will result in a concentration of 15 mg/L of cyclohexanol in the autosampler vial. If a different concentration was used, calculate the correct concentration resulting in the autosampler vial. Inject 1 µL of this solution and determine the relative retention time of methanol to the internal standard using Equation 2.

10.2.2 Prepare a five-point calibration curve for methanol 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 7.5. Use of an internal standard for calibration is required.

10.2.3 Calculate the relative response factor (RRF_M) for methanol using Equation 3. If the relative standard deviation (RSD) of the average RRF_M is less than 10% for methanol, 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.

10.2.4 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. If the limits are exceeded, either prepare a new standard or perform instrument maintenance. If necessary, recalibrate the instrument.

Equation 2

$$RRT_M = \left[\frac{Rt_M}{Rt_{IS}} \right]$$

Where:

RRT_M = relative retention time of methanol
Rt_A = retention time of methanol
Rt_{IS} = retention time of internal standard (cyclohexanol)

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

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

Where:

C_M = concentration of methanol in sample (mg/L)
A_M = area of methanol 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 methanol (Section 10.2.3)

Equation 5

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

Where:

C_M = concentration of methanol measured
C_E = concentration of methanol expected

10.3 Analytical range and minimum calibration level

10.3.1 Demonstrate that the calibration curve is linear (relative response factors exhibit a RSD less than 10% for methanol) throughout the range of the calibration curve described in Section 7.5.

10.3.2 Demonstrate that methanol is detectable at 0.5 mg/L with an RSD of less than 15% for methanol as described in Section 9.3.2.

11.0 Procedure

11.1 Transfer an aliquot (2.0 mL) of the sample to an autosampler vial. Add 10 µL of the internal standard primary spike solution 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, volumetric flasks can be utilized to achieve the desired concentrations. An aliquot of the diluted sample is then analyzed as described in Section 11.1. Calculate the dilution factor using Equation 6.

Equation 6

$$DF = \frac{V_T}{V_S}$$

Where:

DF = dilution factor
V_S = volume of sample (mL) used
V_T = total volume of dilution (mL)

12.0 Data Analysis and Calculations

12.1 GC/FID data analysis

12.1.1 The analytes are identified by comparison of the relative retention times established in the calibration to the 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 10.2.3, according to Equation 7.

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

12.2 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 of analytical results.

12.2.2 All chromatograms must be manually reviewed to confirm internal standard and analyte identification and area integrations. 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 if the level of interferences and baseline noise can be corrected with dilution of the samples. 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.

12.2.4 Any inconsistencies between replicate analyses are resolved (i.e., if methanol is detected in one replicate and not the other), and attempts are made to determine the reason.

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

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

12.2.7 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 appropriate number of significant figures for individual situations.

12.3.2 Report all corresponding blanks, replicates and matrix spikes 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). The method performance data are presented in Section 17, Table 4.

14.0 Pollution Prevention

14.1 The laboratory should check with state and local requirements to determine if pollution prevention equipment, such as solvent recovery devices, are required or recommended in their area. Use of these devices to reclaim solvents can be part of a pollution prevention program to reduce air emissions.

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 in treated effluent, untreated effluent, stripped condensate, foul condensate and weak wash from kraft mill sources; and condensate, evaporator condensate, influent to sludge and dirty hot water plants from sulfite mill sources. A summary of these validation data are presented in Table 4.

Table 1. GC/FID Operating Conditions for Methanol Analysis
DB-624 Column with Cryogenics

Injection:	Direct (Splitless)
Injector Temperature:	110°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, 30 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:	0°C for 3 min
Ramp 1:	5°C/min to 50°C for 0 minutes
Ramp 2:	70°C/min to 105°C for 17 minutes
Ramp 3:	70°C/min to 220°C for 3 minutes
Retention Time Order:	Acetaldehyde, Methyl Mercaptan, Methanol, Ethanol, Propionaldehyde, Methyl Ethyl Ketone, Cyclohexanol
Relative Retention Time:	Methanol - 0.260

Table 2. GC/FID Operating Conditions for Methanol Analysis
DB-WAX Column with Cryogenics

Injection:	Direct (Splitless)
Injector Temperature:	110°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-WAX, 30 m x 0.32 mm id x 025 micron fused silica capillary column with 10 m deactivated fused silica guard column
Cryogenics:	On
Temperature Program °C:	
Initial:	0°C for 3 min
Ramp 1:	5°C/min to 50°C for 4 minutes
Ramp 2:	70°C/min to 100°C for 10 minutes
Ramp 3:	70°C/min to 200°C for 4 minutes
Retention Time Order:	Acetaldehyde, Acetone, Methyl Ethyl Ketone, Methanol, Cyclohexanol
Relative Retention Time:	Methanol - 0.235

Table 3. GC/FID Operating Conditions for Methanol Analysis
DB-624 Column without Cryogenics

Injection:	Direct (Splitless)
Injector Temperature:	110°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:	Off
Temperature Program °C:	
Initial:	35°C for 1 min
Ramp 1:	6°C/min to 90°C for 0 minutes
Ramp 2:	70°C/min to 150°C for 10 minutes
Ramp 3:	70°C/min to 220°C for 3 minutes
Retention Time Order:	Acetaldehyde, Methyl Mercaptan, Methanol, Ethanol, Propionaldehyde, Methyl Ethyl Ketone, Cyclohexanol
Relative Retention Time:	Methanol - 0.260

Table 4. Method 301 Validation Results for Methanol

Source	Statistical Parameters			Interpretation Information		
	RSD (S) %	RSD (U/L) %	CF	High Spiked Sample Conc. (mg/L)	Low/Unspiked Sample Conc. (mg/L)	Average Sample Conc. (mg/L)
Condensate [a]	10	9	NA	957	567	578
Dirty Hot Water Plant [a]	18	36	NA	5891	2688	2450
Evaporator Condensate [a]	14	17	NA	1467	782	757
Foul Condensate	21	9	NA	6735	3006	3382
Influent to Sludge [a]	16	36	NA	585	274	246
Stripped Condensate	7	2	NA	447	70	63
Untreated Effluent	2	16	NA	12	53	51
Weak Wash	34	8	NA	3690	24	-98 [c]
Treated Effluent [b]	15	13	NA	133	30	10

[a] from a sulfite mill
[b] used double spiking procedure, and treated with nitric acid for preservation
[c] This value is negative due to less than 100% recovery of the spike, and the small concentration of methanol present as compared to the spike concentration
RSD(S) - Relative standard deviation of spiked samples
RSD(U/L) - Relative standard deviation of unspiked or low level spiked samples
CF - Correction factor as calculated in the Method 301 validation procedure. A correction factor is calculated only if there is a high bias present
NA - Not applicable

Figure 1. VOA Sample Cooling Train

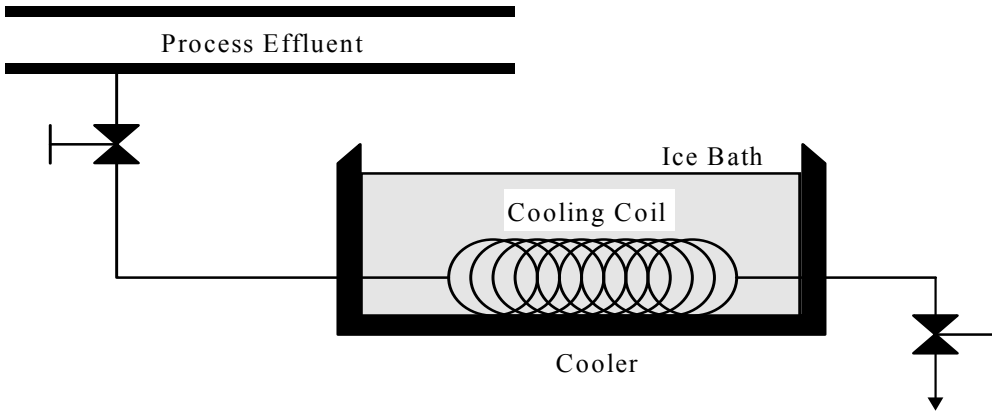

Figure 2: Approval Letter from EPA - Page 1

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

FEB 24 1998

OFFICE OF
AIR QUALITY PLANNING
AND STANDARDS

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

Dear Ms. Gunshefski:

We have reviewed your report entitled, "Method 301 Validation of the NCASI Method 'Methanol in Process liquids by GC/FID'." We agree with your conclusion that this method met Method 301 criteria for measuring methanol in process liquids from the sources that are summarized in the enclosed table. The NCASI Method may be used for measuring the methanol content of wastewater samples as required in 40 CFR Part 63, Subpart S.

To complete the approval process, 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,

for William F. Hunt, Jr.
Director
Emissions, Monitoring and
Analysis Division

cc: Penny E. Lassiter (MD-13)
Stephen A. Shedd (MD-13)
Jeffrey A. Telander (MD-13)

Enclosure

Figure 3: Approval Letter form EPA - Page 2

Source	Validated	Correction Factor
Kraft Pulp Mills	Yes	None
Treated Effluent	Yes	None
Untreated Effluent	Yes	None
Stripped Condensate	Yes	None
Foul Condensate	Yes	None
Weak Wash	Yes	None
Sulfite Mills		
Condensate	Yes	None
Evaporator Condensate	Yes	None
Influent to Sludge	Yes	None
Dirty Hot water Plants	Yes	None