NCASI METHOD MD-99

POLAR VOLATILE ORGANIC COMPOUNDS IN PULP INDUSTRY WASTEWATERS BY MICRODISTILLATION AND GC-FID

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Disclaimer:

The mention of trade names or commercial products does not constitute endorsement or recommendation for use. The microdistillation step has been included in the Third Update of SW-846 as Method 5031.

This method is included in the NCASI Methods Manual as a PROPOSED method. The purpose of including proposed methods in the NCASI Methods Manual is to make it known that a method is under development and to solicit comment regarding the technical merit and applicability of the method. This method should not be construed as having been rigorously validated on any matrix; therefore, those electing to apply the method are strongly encouraged to conduct rigorous QA/QC or validation such that the quality of the data generated can be evaluated. Please note that PROPOSED methods are not suitable for use as regulatory monitoring or compliance methods.

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POLAR VOLATILE ORGANIC COMPOUNDS IN PULP INDUSTRY WASTEWATERS BY MICRODISTILLATION AND GC-FID

1.0 Scope and Application

1.1 This method describes a procedure for separating nonpurgable, water-soluble, and volatile organic compounds from pulp mill treatment plant influent and effluent wastewaters using azeotropic distillation. The azeotropic microdistillation technique was first described by Bruce, Lee, and Stephens (1) and has been included as Method 5031 in the Third Update of SW-846. This method optimizes the microdistillation technique for pulp mill matrices and integrates it into a complete analytical method. Prepared samples are analyzed by gas chromatography (GC) with flame ionization detection (FID). The method has been evaluated and found to work successfully for the compounds listed in Table 1.

1.2 The estimated method detection limits (MDL) determined for an effluent sample and the calibration range of the method are also listed in Table 1. The MDLs for a sample may differ from those listed, depending on the nature of interferences in the sample matrix. The method has been single-laboratory validated for waste treatment influents and effluents from kraft and sulfite mills with and without bleach plants.

1.3 Additional compounds may be separated successfully using this method, and the method may be applicable to other matrices in a pulp mill. However, this method may be used to detect and measure additional analytes and for different matrices only after establishing acceptable accuracy and precision data for each additional analyte or matrix.

2.0 Summary of Method

2.1 Water-soluble nonpurgable organic compounds are selectively removed from a complex aqueous matrix by azeotropic distillation. A 40-mL sample is distilled and compounds which either distill at lower boiling points than water (e.g., methanol) or that form azeotropes with water are concentrated into the first 300 µL of condensate collected. Most of the semi- and non-volatile compounds which could cause interferences remain in the boiling flask. As the distillate condenses, most water-soluble organics remain in the condensate while the hydrophobic volatile organics escape into the atmosphere. Concentration factors for the target compounds have been found to range from 70 to 230.

2.2 An internal standard is spiked before distillation to correct for distillation/condensation variables as well as for instrument drift. A recovery spike is added to the condensate before analysis to determine the recovery of the internal standard. The concentrated condensate is analyzed by direct aqueous injection GC-FID. Because the FID analysis is nonspecific, confirmation that no native compounds

interfere with the internal standard or the recovery standard is required for each new sample matrix encountered. Column resolution is critical to ensure separation of the target analytes and a daily resolution check is required.

2.3 If analyte concentrations are high (>1000 µg/L) and the matrix is clean (no salts or corrosives), the distillation step may be omitted and samples can be analyzed by direct aqueous injection. Calibration and validation of accuracy and precision will be required if the distillation step is omitted. To improve the selectivity of the method, GC/mass spectrometry (MS) can be used with a loss in sensitivity and precision due to the disruptive effects water has on the MS. Independent validation is required if GC/MS is used.

3.0 Definitions

The definitions and purposes below are specific to this method, but have been conformed to common usage as much as possible**.**

3.1 Units of weight and measure

3.1.1 L—liter

3.1.2 mg—milligram

3.1.3 mL—milliliter

3.1.4 µg—microgram

3.1.5 µL—microliter

3.2 Definition of terms, acronyms, and abbreviations

3.2.1 Azeotrope—Liquid mixture of two or more substances which behaves like a single substance, in that it boils at a constant temperature and the vapors released have a constant composition

3.2.2 Internal standard—Compound not present in a sample spiked at a known amount into the sample before distillation and used to calculate the concentration of the target analytes

3.2.3 May—This action, activity, or procedural step is neither required nor prohibited.

3.2.4 Must not—This action, activity, or procedural step is prohibited.

3.2.5 Must—This action, activity, or procedural step is required.

3.2.6 Recovery standard—Compound not present in a sample spiked at a known amount after the condensate is collected and used to determine the internal standard recovery

3.2.7 Should—This action, activity, or procedural step is suggested but not required.

4.0 Interferences

4.1 Method interferences

Contaminants in solvent, reagents, glassware, and other sample processing hardware can lead to discrete artifacts and/or elevated baselines in the chromatograms. All of the following materials must be demonstrated to be free from interferences under the conditions of the analysis by running laboratory method blanks daily.

4.1.1 Glassware must be cleaned as soon as possible after use by rinsing several times with hot tap water followed by several rinses with volatile organic-free water. Prior to use, glassware should be drained and heated in a circulating laboratory oven above 110°C until completely dry.

4.1.2 All glassware must be kept and stored away from areas where volatile solvents such as acetone and methanol are being used. Ovens used to dry glassware should not contain glassware that has been rinsed with these solvents.

4.1.3 Volatile organic-free water can be obtained by distilling deionized water until the first 15 to 20% of the water has been removed. Store the remaining portion in an organic-free environment (e.g., under an N_2 atmosphere).

4.1.4 After distillation of a sample containing high concentrations of volatile organic compounds, one or more blanks should be analyzed to check for cross contamination.

4.2 Matrix interferences

Contaminants in the sample can interfere with the analysis by coeluting with an internal standard, recovery standard, or analyte. Sample contaminants can also interfere with the distillation step, chromatographic separation, or the FID determination. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the matrix being sampled.

4.2.1 Internal standard interference in influent samples have been observed from the results of the method evaluation. Multiple internal standards have been used to correct this problem.

4.2.2 To ensure that an internal standard interference is not present in the sample matrix, a trial microdistillation should be performed without addition of internal standard or recovery standard whenever a sample of unknown

composition is first encountered. Any signal identified as the internal standard or recovery standard would suggest an interference exists and an alternate internal standard should be used. Recovery of greater than 100% for the internal standard during a routine analysis is a good indicator that a matrix compound is interfering.

5.0 Safety

5.1 Good laboratory safety practices should ensure safe operation of this method. Adequate eye protection, a lab coat, and gloves should be worn at all times and a portable exhaust vent should be used if the apparatus is used outside of a fume hood.

5.2 Acrylonitrile has an IARC 2A classification (probable carcinogen) and is an OSHA select carcinogen. Special precautions will be required to handle this compound.

5.3 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 file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

6.0 Equipment and Supplies

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

6.1 Sampling equipment

Glass storage containers of at least 40 mL volume with Teflon™-coated silicone lined screw caps are required.

6.2 Microdistillation system equipment

6.2.1 Wadsworth VOC^3 System, Shamrock Glass (302-629-5500), or equivalent (Figure 1)

6.2.1.1 Round-bottom flask, 100-mL, 14/20 ground glass joint

6.2.1.2 Fractionation column, 14/20 ground glass joint, 1.6-cm OD, 1.3-cm ID, 60-cm length

6.2.1.3 Glass reducing union, 14/20 ground glass joint to 6-mm OD tubing

6.2.2 Column packing, spherical glass beads, 5-mm diameter

6.2.3 Pipe insulation, polyurethane foam, 4-cm OD, 1.5-cm ID, 55-cm length

6.2.4 Keck clamps for 14/20 joints

6.2.5 Stainless steel reducing union, 1/4 in. to 1/16 in. with PTFF ferrules

6.2.6 Air condenser, 40 cm 1/16 in. OD PTFE tubing

6.2.7 Heating mantle, 100-mL round-bottom flask, 230 watts

6.2.8 Heating mantle temperature controller

6.2.9 Porous boiling stones (not Teflon chips)

6.2.10 Autosampler vials, 2-mL, with Teflon-lined caps

6.3 Analytical equipment

6.3.1 Gas chromatograph—Must have a splitless injection port for capillary column, sub-ambient temperature program capabilities, and a FID

6.3.2 GC column—30- x 0.53-mm ID with 1.0-µm film of bonded Carbowax (J&W DB-Wax or equivalent)

6.3.3 Data system to record chromatogram, retention times, and measure areas of peaks

6.4 Other equipment

6.4.1 Oven large enough to dry the fractionation column (60 cm)

6.4.2 Analytical balance capable of weighing ±0.0001 g

7.0 Reagents and Standards

7.1 Volatile organic-free water

Water should be deionized or distilled and purged with nitrogen until free from interfering compounds. If blank problems persist, distill off 15 to 20% and keep what remains. Store the water under a nitrogen purge until ready to use.

7.2 Standards

7.2.1 Internal standard—Weigh (to nearest 0.1 mg) 50 mg of 2,2,2-trifluoroethanol and dilute to volume in a 25-mL volumetric flask with volatile organic-free water. Transfer the solution into a bottle with a Teflon-lined screw cap, and

store under refrigeration in an atmosphere free of solvent vapors. 2-Chloroacetonitrile can be prepared in the same manner for use as an alternative internal standard or recovery standard

7.2.2 Recovery standard—Weigh (to nearest 0.1 mg) 50 mg of 2,2,2-trichloroethanol and dilute to volume in a 25-mL volumetric flask with volatile organic-free water. Transfer solution into a bottle with a Teflon-lined screw cap and store under refrigeration in an atmosphere free of solvent vapors.

7.2.3 Primary standard stock solutions—Prepare individual primary stock solutions of the compounds listed in Table 1 by weighing (to the nearest 0.1 mg) 250 mg of each compound, except 4-methyl-2-propanone (MIBK) and acetophenone, into a 10-mL volumetric flask and dilute to volume with volatile organic-free water. MIBK is prepared by weighing 125 mg into 10 mL and acetophenone is prepared by weighing 50 mg into 10 mL. Lower concentrations are required for MIBK and acetophenone because of the solubility limitations. The primary stocks are transferred into bottles with Teflon-lined caps and stored in a refrigerator free of solvent vapors. The primary standards have been found to be stable for up to six months.

Note: *Acetaldehyde is a gas at room temperature (boiling point 21°C) and all glassware that comes in contact with the neat standard needs to be chilled to 4°C (prior to use).*

7.2.4 Working standard solutions—Using a 1-mL syringe add 0.8 mL of MIBK primary solution, 2.0 mL of acetophenone and methanol primary solutions, and 0.4 mL of the remaining primary solutions to a 100-mL volumetric flask and dilute with organic free water. Transfer the working solution into bottles with Teflon-lined screw caps and store in a refrigerator free of solvent vapors. The working standards have been found to be stable for up to six months if kept isolated from potential contaminating solvents.

7.3 pH adjustment solutions

7.3.1 Sulfuric acid—Concentrated sulfuric acid (H_2SO_4, 95 to 98% ACS reagent grade) diluted 1:1 with volatile organic-free water by carefully adding the acid to the water.

7.3.2 Sodium hydroxide—Five grams of sodium hydroxide (NaOH, 97+% ACS reagent grade) was dissolved into 100 mL of volatile organic-free water.

7.3.3 Potassium hydrogentartrate ($KO_2CCH(OH)CH(OH)CO_2H$, 99%) baked in an oven at 110°C to remove residual ethanol.

8.0 Sample Collection, Preservation, and Storage

8.1 Sample collection

All equipment which comes in contact with the sample should be constructed of glass, Teflon, or stainless steel. Grab samples must be collected in glass containers having a Teflon-lined silicone-septum-lined screw cap. Composite samples should be refrigerated during the sampling process. Samples should be collected with a minimum of headspace present, but do not have to be headspace-free.

8.2 Sample preservation

Biologically active samples should be preserved by one of the following methods.

8.2.1 Adjust to pH 2 using 1:1 sulfuric acid immediately after sample collection.

8.2.2 Add potassium hydrogentartrate at a rate of 6 g/L to the sample container prior to sample collection.

8.3 Sample storage

Store the sample in the dark at 4°C for up to 24 days. Distillates should be analyzed within 14 days. Samples and distillates should be stored in areas free of volatile organic solvents.

9.0 Quality Control

9.1 Quality assurance program

Each laboratory that uses this method should operate a formal quality assurance program. The minimum requirements of this program consist of an initial demonstration of laboratory capability, and ongoing analyses of standards and blanks as a test of continued performance. Laboratory performance is compared to established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

9.2 Background checks

9.2.1 Method blank—A method blank analysis must be performed after the daily calibration check is performed and should be performed after a high-level sample (>1000 µg/L) has been distilled and before low-level samples will be analyzed. A method blank consists of distilling a 40-mL aliquot of the volatile organic-free water with the internal and recovery standards added. The level of each compound in the method blank should be below the method detection limit (MDL), and must be five times lower than the concentration found in a sample before the concentration can be reported without a flag. If high blank levels are encountered, clean the glassware and recheck the blank, check the

source of volatile organic-free water for contamination, and replace if necessary. Check the standards to determine if they have become contaminated and prepare fresh solutions if necessary.

9.2.2 Field blank—A field blank should be performed with each set of samples collected. A field blank is a sample of volatile organic-free water that is sent with the sample container to the site, transferred in the field to a sample container, transported back to the laboratory, stored, and analyzed with the other samples from the set. The level of each compound in the field blank should be below the MDL and must be five times lower than the concentration found in a sample before the concentration can be reported without a flag.

9.3 Calibration verification

9.3.1 Initial calibration check—The linearity of the GC-FID analyses must be checked by microdistillation of a minimum of five different standards at levels ranging from 10 to 10,000 µg/L for all compounds except methanol, which is calibrated from 50 to 50,000 µg/L (range can be smaller if project data objectives warrant). Relative response factors are calculated for each compound at each level. Table 2 lists the ranges of average response factors and relative standard deviations found using the internal standard, 2,2,2-trifluoroethanol. The relative standard deviation of the mean must be less than 25%. If a standard deviation of less than 25% cannot be achieved the following corrective action should be taken.

9.3.1.1 If the relative response factors are high at lower concentrations, check the method blank to determine if the system is contaminated and eliminate the contamination.

9.3.1.2 If the relative response factors are low at the lower concentration levels, the injection port and column may be dirty and should be serviced (replace liner and clip the column).

9.3.1.3 If compounds can not be detected at the lower calibration range, the calibration range will have to be adjusted.

9.3.1.4 If relative response factors are lower at the high concentration levels, the detector may be saturated and the calibration range will need to be lowered.

9.3.1.5 If relative response factors are both high and low at high concentrations, the chromatographic resolution may be lost due to column overloading and the calibration range may need to be lowered.

9.3.1.6 If relative response factors show variation at one level, carefully repeat that level. If relative response factors vary randomly, repeat the calibration being careful to spike the correct volume and insure that both the fractionation columns are completely dry and the glassware is clean.

9.3.1.7 If the calibration range is changed, the operating range of the method must be changed accordingly and at least four standards must be analyzed within that range.

9.3.2 Daily calibration check

Every day before samples are analyzed the calibration must be verified by distilling a mid-level calibration standard. The recovery for the compounds must be between 75 and 125%. If the check fails to meet this criterion, the check is to be repeated. If it continues to fail, the cause for the failure must be identified and corrected or the initial multipoint calibration must be repeated.

9.4 GC resolution check

The resolution of the critical separation between 2-butanone and methanol must be checked on the daily calibration run using Equation 1.

Equation 1

$$R = \frac{\left(W_{MeOH} + W_{MEK}\right)}{2} * \left(RT_{MeOH} - RT_{MEK}\right)$$

where:
R = *resolution*
W_{MeOH} = *width of the methanol peak*
W_{MEK} = *width of the 2-butanone peak*
RT_{MeOH} = *retention time of the methanol peak*
RT_{MEK} = *retention time of the 2-butanone peak*

If the resolution falls below 1.5, then the column needs to be replaced. Carbowax columns are susceptible to oxidation and damage from water and need to be checked frequently. A typical column will last approximately three months with regular use.

9.5 Recovery and precision checks

9.5.1 Matrix spikes—To estimate the method recovery, a matrix spike should be run with each sample set (at least one in ten) and when a new sample matrix is encountered. The matrix spike concentration should be at least two times the native concentration. Table 3 shows the recoveries found during the initial validation of this method. Recoveries of between 65 and 125% should be

obtained for all compounds except methyl acetate which should have a recovery of between 40 and 120%.

9.5.2 Duplicate analyses—To estimate the method's precision, duplicates should be run with each sample set (at least one in ten samples) and when a new sample matrix is encountered. The relative percent differences between duplicates should be within 20%. The precision found during the initial method validation can be found in Table 4.

9.5.3 Depending upon specific program requirements, field replicates and field spikes of the analytes of interest into samples may be required to assess the precision and accuracy of the sampling and sample transporting techniques.

10.0 Calibration and Standardization

10.1 Calibration conditions

Calibration for this method includes the microdistillation step as well as the instrumental analysis. The calibration standards are distilled as described in Section 11.0. The collected condensate is analyzed by GC-FID using the conditions below.

Parameter	Setting
Injector	1-µL splitless with 0.35-min split vent time at 110°C
Syringe rinse	water
Carrier gas	Helium at 4-mL/min
Column	30-m x 0.53-mm ID with 1.0-µm film of DB-Wax (J&W)
Oven Program	
Initial Temperature	10°C and hold for 1 min
Rate 1	20°C/min to 20°C
Rate 2	6°C/min to 120°C
Rate 3	12°C/min to 200°C hold for 3 min
Detector	FID
Temperature	250°C
Fuel	30 mL/min hydrogen
Oxidant	300 mL/min air
Make-up	25 mL/min nitrogen

10.2 Method calibration procedure

10.2.1 A calibration is performed by spiking a volume of the working stock solution and 10 µL of the internal standard solution (500 µg/L 2,2,2-trifluoroethanol) into 40 mL of volatile organic-free water. No pH adjustment is made for

calibration standards. The sample is distilled according to Section 11.0. After the collection of the distillate add 10 µL of the recovery check standard (500 µg/L 2,2,2-trichloroethanol).

10.2.2 For a five-point calibration covering a range of 10 to 10,000 µg/L for all compounds (except methanol, range 50 to 50,000 µg/L), step 10.2.1 is repeated with working stock volumes of 4, 20, 100, 800, and 4000 µL. A blank with no working stock solution spiked should also be included with the initial calibration.

10.2.3 Instrument linearity is established by generating relative response factors (RRF) for each compound at each level of the calibration using Equation 2.

Equation 2

$$RRF_i = \left(\frac{A_i}{A_{IS}}\right) * \left(\frac{C_{IS}}{C_i}\right)$$

where:
RRF_i = *relative response factor for compound i*
A_i = *area of the peak for compound i*
A_{IS} = *area of the peak for the internal standard*
C_{IS} = *concentration of internal standard in the sample (µg/L)*
C_i = *concentration of compound i in the sample (µg/L)*

The mean RRF is calculated for each compound using Equation 3.

Equation 3

$$RRF_{iM} = \frac{\sum RRF_i}{n}$$

where:
RRF_{iM} = *mean relative response factor for compound i*
n = number of levels in the calibration range

The relative standard deviation is calculated for each mean RRF using Equation 4.

Equation 4

$$RSD_i = \sqrt{\frac{\sum \left(RRF_i - RRF_{iM}\right)^2}{(n-1)}} \; / \; RRF_{iM} \; x\; 100$$

where:
RSD_i = *percent relative standard deviation of the mean relative response factor for compound i*

The mean relative response factor is used to calibrate for the compound and calculate the compound concentration in a sample. The RSD is used to check the linearity of the calibration as described in Section 9.3.1.

10.2.4 The recovery of the internal standard is determined by calibrating the internal standard response relative to the recovery standard response using Equation 5.

Equation 5

$$RRF_{IS} = \left(\frac{A_{IS}}{A_{RS}}\right) * \left(\frac{C_{RS}}{C_{IS}}\right)$$

where:
RRF_{IS} = *relative response factor for the internal standard*
A_{is} = *area of the peak for the internal standard*
A_{RS} = *area of the peak for the recovery standard*
C_{IS} = *concentration of internal standard in the sample (µg/L)*
C_{RS} = *concentration of the recovery standard in the sample (µg/L)*

A mean RRF_{IS} is calculated for the initial calibration using Equation 6.

Equation 6

$$RRF_{ISM} = \frac{\sum RRF_{IS}}{n}$$

where:
RRF_{ISM} = *mean relative response factor for the internal standard*
n = *number of determinations from the initial calibration*

11.0 Procedure

11.1 Assemble apparatus

11.1.1 The microdistillation apparatus is pictured in Figure 1. To assemble the apparatus first fill the fractionation column with glass beads to within 5 cm of the top. Rinse the column with hot tap water followed by volatile organic-free water and dry in an oven at 110°C. Follow this same procedure for all glassware, metal fitting, and PTFE tubing used for the microdistillation.

11.1.2 Place the round-bottom flask in the heating mantle. Insert the fractionation column into the flask and insert the glass adapter into the top of the fractionation column. Attach the metal reducing union to the 6-cm glass tube on the glass adapter using a PTFE ferrule (finger tight). Attach the PTFE tube to the 1/16-in. fitting of the metal reducing union (be careful not to crimp the tubing when tightening the fitting). Position the other end of the PTFE tube into a 2-mL autosampler vial with a 300-µL volume mark on the outside. Secure the total apparatus.

11.2 Microdistillation

11.2.1 Add 40 mL of a well mixed sample to the 100-mL round-bottom flask. A smaller volume of sample can be used, but the volume has to be brought to 40 mL using volatile organic-free water.

11.2.2 If the sample pH is less than 4 or higher than 9, adjust the pH to between 6 and 7 using sodium hydroxide or sulfuric acid solution (Section 7.3).

11.2.3 Add 10 µL of the internal standard solution (Section 7.2.1) into the flask and the appropriate volume of working standard solution for calibration or matrix spike samples (Section 7.2.4). Add a boiling stone and return the flask to the apparatus.

11.2.4 Add heat to the sample to bring it to a boil in two to four minutes. Use of pipe insulation (Section 6.2.3) to insulate the fractionation column will shorten the time required for the distillation to occur. Collect the first 300 µL of distillate in the autosample vial.

Note*: Once steam starts to collect in the condenser section, it normally takes less than 20 seconds for 300 µL of distillate to collect. After 30 seconds, the condenser quits working and steam blows the collected distillate out of the vial invalidating the analysis.*

11.2.5 As the distillate collects in the insert, slowly back the condenser line out of the vial as it fills. This allows the bubbles that form to escape without dislodging or stripping the distillate from the vial. Remove the free end when the 300-µL volume is achieved. Turn off the heating mantel and back it away from the flask.

11.2.6 At this time add 10 µL of the recovery solution (Section 7.2.2). Seal the vial and store at 4°C until the distillate is analyzed.

11.3 GC-FID analysis

11.3.1 The instrumental conditions described in Section 10.1 are used.

11.3.2 Daily calibration checks and resolution checks must be performed (Sections 9.3.2 and 9.4).

11.3.3 A method blank must be analyzed (Section 9.3.2).

11.3.4 The sample distillates are analyzed.

12.0 Data Analysis

12.1 Qualitative identification

12.1.1 Compound identification is made by the comparison of relative retention time (RRT) of a sample peak to that found for a compound in the calibration standard. The RRT for a compound in a sample should be within ±0.006 RRT units of the mean relative retention time for the compound in the initial calibration. When a peak's RRT falls within the window of more than one compound, the compound whose RRT matches most closely is assigned to the peak. Table 5 shows the mean retention times and standard deviations of the mean RRT found during the method validation study for spiked effluent and influent samples. The relative retention time is calculated using Equation 7.

Equation 7

$$RRT_i = \frac{RT_i}{RT_{IS}}$$

where:

RRT_i = *relative retention time of compound i*
RT_i = *retention time of compound i*
RT_{IS} = *retention time of the reference standard*

12.1.2 Confirmation of identifications—Because the FID is nonspecific, when samples of unknown compositions are encountered, confirmation of any identified compound should be performed. Full scan GC/MS is an ideal method to use for confirmation, but it is not as sensitive as GC-FID and is prone to interferences due to water. Analysis of the sample on a second GC column with different separation characteristics can be used to confirm identifications. A megabore DB-624 column has been used successfully for confirmations.

12.2 Sample quantification

When a compound has been identified, use Equation 8 to determine the concentration of the compound.

Equation 8

$$C_i = \left(\frac{A_i}{A_{IS}} \right) * RRF_{iM} * C_{IS}$$

where:
C_i = *concentration of compound i (µg/L)*

12.3 Internal standard recovery

The recovery of the internal standard relative to the recovery standard is calculated with Equation 9.

Equation 9

$$R_{IS} = \left(\frac{A_{IS}}{A_{RS}} \right) * \left(\frac{C_{RS}}{C_{IS}} \right) * RRF_{ISM} * 100$$

where:

R_{IS} = *recovery of internal standard in percent*

12.4 Matrix spike recovery

Matrix spike recovery is calculated using Equation 10.

Equation 10

$$R_{MS} = \frac{\left(C_{iMS} - C_i\right)}{C_{MS}} * 100$$

where:
R_{MS} = *matrix spike recovery in percent*
C_{iMS} = *concentration of compound i in the matrix spike sample (µg/L)*
C_{MS} = *concentration of compound i spiked in the sample (µg/L)*

The spiked concentration should be at least twice the native concentration for the recoveries to be valid.

12.5 Duplicate analysis

Precision is estimated by calculating the relative percent difference between duplicate analysis using Equation 11.

Equation 11

$$RPD = \frac{\left|C_1 - C_2\right|}{C_m} * 100$$

where:
RPD = relative percent difference
C_1 = *concentration in the first of duplicate analyses*
C_2 = *concentration in the second of duplicate analyses*
C_M = *mean of the two duplicate analyses*

12.6 Sample dilution

If the concentration found for any of the compounds is above the calibration range, then the samples have to be diluted in one of two ways.

12.6.1 Distillate dilution—The collected distillate can be diluted up to a factor of ten by adding volatile organic-free water. No correction in the calculation is required if this method is used because the internal standard is diluted as well as is the sample.

12.6.2 Sample dilution—A smaller volume of sample can be distilled by adding the adjusted volume of sample to a volume of volatile organic-free water whose

sum equals 40 mL. The same amount of internal standard is added to the diluted sample. The sample concentration is calculated by multiplying the concentration calculated by Equation 8 by the dilution factor which is calculated using Equation 12.

Equation 12

$$DF = \frac{40}{V_S}$$

where:
DF = dilution factor
V_S = volume of sample added (mL)

13.0 Method Performance

13.1 This method has been single-laboratory validated for the analysis of kraft and sulfite pulp and paper mill influent and effluent from treatment systems. The results of the method evaluation have been presented previously and contain information leading to the selection of the procedure described here (2). A summary of matrix spike recoveries for both effluents and influents have been combined in Table 3. Estimates of method precision based on pooling of duplicate results for influents and effluents are shown in Table 4.

13.2 Method precision was found to be a function of concentration. A series of spiked effluent samples were analyzed to determine the relationship between relative standard deviation and concentration (3). The relationship was found to be described by the exponential function obtained with Equation 13.

This relationship allows determination of the concentration at which a specified precision can be obtained. The procedure also allows a more reliable detection limit to be determined. Table 6 lists the regression determined detection limits for each compound and the experimentally determined constants A and B for Equation 13.

Equation 13

$$RSD = \frac{\left(Ae^{BC}\right)}{C} * 100$$

where:
RSD = relative standard deviation
A and B are constants
C = concentration in (µg/L)

13.3 Matrix spike recovery can also be determined as a function of concentration using the same data set described in Section 13.2. The recovery for most of the compounds was found to fall within the 70 to 130% acceptance window over the total range of concentrations spiked. The four compounds whose recoveries fell outside that range for one or more spike levels are shown in Figure 2. Although the range of recoveries was greater for these compounds, the recoveries were scattered and did not show a trend with concentration. These results indicate that the bias for the method is consistent throughout the calibrated range of the method.

14.0 Pollution Prevention

Pollution prevention approaches were not evaluated for this method.

15.0 Waste Management

15.1 It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly hazardous waste identification rules and land disposal restrictions. In addition it is the laboratory's responsibility to protect air, water, and land resources by minimizing and controlling all releases from fume hoods and bench operations. Compliance with any sewage discharge permits and regulations is required.

15.2 Samples containing acids at a pH of less than 2 are hazardous and must be neutralized before being poured down a drain or must be handled as hazardous waste.

15.3 For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel*, available from the American Chemical Society, Department of Government Relations and Science Policy, 115 Sixteenth Street NW, Washington, DC 20036.

16.0 References

1. Bruce, M.L., Lee, R.P., and Stephens, M.W. Concentration of water-soluble volatile organic compounds from aqueous samples by azeotropic microdistillation. *Environmental Science and Technology* 26(1992): 160-63.

2. Gholson, A., Cook, D., and Hoy, D. *Evaluation of the microdistillation method (Method 5031) for measuring volatile water-soluble compounds in pulp mill treatment influents and Effluents.* Presented at US EPA/ACS 12th Annual Waste Testing and Quality Assurance Symposium, Washington, DC, July, 1996.

3. Gholson, A., Cook, D., and LaFleur, L. *Application of a regression based detection limit determination for volatile water soluble compounds in pulp mill effluent using microdistillation (SW-846 Method 5031*). Presented at US EPA 19th Annual Conference on Analysis of Pollutants in the Environment, Norfolk, VA, May, 1996.

17.0 Tables and Figures

Table 1. Microdistillation Analytes and Method Operation Range

Analyte	CAS Number	MDL[a] (µg/L)	Calibration range (µg/L)
Acetaldehyde	75-07-0	45.4	10-10,000
Acetone	67-64-1	26.6	10-10,000
Methyl acetate	79-20-9	35.7	10-10,000
Ethyl acetate	141-78-6	24.8	10-10,000
2-Butanone (MEK)	78-93-3	6.9	10-10,000
Methanol	67-56-1	26.6	50-50,000
2-Propanol (isopropanol)	67-63-0	5.9	10-10,000
Ethanol	64-17-5	7.8	10-10,000
Acrylonitrile	107-13-1	7.6	10-10,000
4-Methyl-2-pentanone (MIBK)	108-10-1	7.5	10-10,000
Propionitrile	107-12-0	6.1	10-10,000
1-Propanol	71-23-8	5.1	10-10,000
1,4-Dioxane	123-91-1	12.8	10-10,000
2-Methyl-1-propanol (isobutanol)	78-83-1	5.8	10-10,000
1-Butanol	71-36-3	6.2	10-10,000
Cyclohexanone	108-94-1	6.2	10-10,000
Acetophenone	98-86-2	8.6	10-10,000

[a] MDL = method detection limit determined for effluent using EPA procedure 40CFR Part 136 Appendix B

Table 2. Results of Initial Multipoint Calibration for the Microdistillation Method

Compound	Range of Average RRFs[a]	Range of RSD[b] (%)	n[c]
Acetaldehyde	1.079 - 1.587	12.1 - 26.6	5
Acetone	2.942 - 3.720	12.2 - 14.4	5
Methyl acetate	1.020 - 1.368	7.4 - 19.5	5
Ethyl acetate	1.248 - 1.883	9.0 - 21.0	5
2-Butanone (MEK)	3.122 - 3.415	3.0 - 19.8	5
Methanol	1.391 - 2.234	8.5 - 18.2	5
2-Propanol (isopropanol)	3.454 - 4.859	4.9 - 13.5	5
Ethanol	2.924 - 4.437	5.3 - 13.5	5
Acrylonitrile	2.426 - 3.407	6.3 - 19.9	5
4-Methyl-2-pentanone (MIBK)	2.537 - 3.291	12.9 - 25.5	5
Propionitrile	3.676 - 5.074	6.5 - 20.3	5
1-Propanol	4.472 - 5.962	10.4 - 14.0	2
1,4-Dioxane	1.403 - 2.583	11.2 - 18.1	5
2-Methyl-1-propanol (isobutanol)	5.393 - 6.963	4.8 - 12.2	5
1-Butanol	4.948 - 7.545	7.2 - 20.7	5
Cyclohexanone	4.962 - 7.493	7.9 - 19.8	5
Acetophenone	5.641 - 8.127	9.6 - 17.7	5

[a] Average of multipoint calibrations using 2,2,2-trichloroethanol as the internal standard

[b] Range of percent relative standard deviation for multipoint calibrations

[c] Number of multipoint calibrations included in range

Table 3. Microdistillation Matrix Spike Recovery for Influents and Effluents

Compound	Recovery (%)	St. dev.[a] (%)	n[b]
Acetaldehyde	93.2	18.5	20
Acetone	95.6	9.5	19
Methyl acetate	76.3	26.0	20
Ethyl acetate	92.3	23.0	19
2-Butanone (MEK)	91.9	14.2	20
Methanol	102	27.4	18
2-Propanol (isopropanol)	99.2	17.7	18
Ethanol	97.1	19.1	18
Acrylonitrile	86.0	16.8	17
4-Methyl-2-pentanone (MIBK)	114	30.5	20
Propionitrile	95.8	8.8	20
1-Propanol	na[c]	na[c]	na[c]
1,4-Dioxane	95.2	15.7	20
2-Methyl-1-propanol (isobutanol)	96.3	12.5	20
1-Butanol	101	13.1	20
Cyclohexanone	98.7	16.3	20
Acetophenone	106	7.5	9

[a] Standard deviation of the mean matrix spike recovery

[b] Number of matrix spike recovery values averaged

[c] na = no data available for this compound

Table 4. Microdistillation Precision Estimate from Pooled Duplicate Results

	Effluent Precision		Influent Precision	
Compound	RSD[a] (%)	n[b]	RSD[a] (%)	n[b]
Acetaldehyde	21.5	7	4.6	11
Acetone	11.4	8	4.1	11
Methyl acetate	13.0	4	8.4	7
Ethyl acetate	11.6	4	9.1	5
2-Butanone (MEK)	5.3	4	4.5	11
Methanol	21.7	9	9.1	11
2-Propanol (isopropanol)	2.3	4	10.9	10
Ethanol	4.4	4	12.0	11
Acrylonitrile	5.7	4	5.2	5
4-Methyl-2-pentanone (MIBK)	9.1	4	14.3	5
Propionitrile	3.5	6	2.3	9
1-Propanol	na[c]	na[c]	na[c]	na[c]
1,4-Dioxane	10.0	4	11.9	9
2-Methyl-1-propanol (isobutanol)	2.4	4	1.7	11
1-Butanol	3.9	4	11.0	11
Cyclohexanone	6.5	4	14.5	11
Acetophenone	8.0	5	16.0	6

[a] Relative standard deviation of pooled duplicates

[b] Number of duplicate data points with both values above the MDL

[c] na = no data available for this compound

Table 5. Microdistillation Mean Relative Retention Times and Standard Deviations for Effluents and Influents

	Effluent		Influent	
Compound	Mean RRT[a]	s[b]	Mean RRT[a]	s[b]
Acetaldehyde	0.1916	0.0016	0.1930	0.0033
Acetone	0.3049	0.0021	0.3071	0.0045
Methyl acetate	0.3257	0.0022	0.3274	0.0041
Ethyl acetate	0.4156	0.0021	0.4170	0.0039
2-Butanone (MEK)	0.4339	0.0021	0.4357	0.0037
Methanol	0.4455	0.0016	0.4477	0.0027
2-Propanol (isopropanol)	0.5025	0.0016	0.5039	0.0026
Ethanol	0.5136	0.0016	0.5151	0.0024
Acrylonitrile	0.6021	0.0015	0.6034	0.0024
4-Methyl-2-pentanone (MIBK)	0.6275	0.0016	0.6289	0.0025
Propionitrile	0.6672	0.0014	0.6684	0.0022
1-Propanol	0.6992	0.0019	0.7003	0.0030
1,4-Dioxane	0.7389	0.0013	0.7400	0.0019
2-Methyl-1-propanol (isobutanol)	0.8097	0.0011	0.8108	0.0016
1-Butanol	0.9285	0.0012	0.9293	0.0012
Cyclohexanone	1.1789	0.0013	1.1795	0.0013
Acetophenone	1.6133	0.0030	1.6140	0.0019
2,2,2-Trichloroethanol (recovery std)	1.6468	0.0032	1.6472	0.0019
Internal Standard	Retention Time (min)	s[b] (min)	Retention Time (min)	s[b] (min)
2,2,2-Trifluoroethanol	14.99	0.045	14.99	0.028

[a] RRT = retention time relative to the internal standard 2,2,2-trifluoroethanol

[b] s = standard deviation of the mean RRT

Table 6. Regression Based Detection Limit and Precision Estimate Coefficients for Effluents

Compound	RBDL[a] (µg/L)	A[b]	B[b]
Acetaldehyde	45.4	19.3	0.005
Acetone	26.6	8.79	0.002
Methyl acetate	35.7	5.62	0.009
Ethyl acetate	24.8	6.40	0.005
2-Butanone (MEK)	6.9	1.85	0.010
Methanol	na[c]	na[c]	na[c]
2-Propanol (isopropanol)	5.9	1.52	0.008
Ethanol	7.8	2.64	0.011
Acrylonitrile	7.6	1.94	0.013
4-Methyl-2-pentanone (MIBK)	7.8	2.32	0.014
Propionitrile	6.1	1.53	0.010
1-Propanol	na[c]	na[c]	na[c]
1,4-Dioxane	12.8	3.04	0.010
2-Methyl-1-propanol (isobutanol)	5.8	1.81	0.007
1-Butanol	6.2	2.08	0.008
Cyclohexanone	6.2	2.14	0.009
Acetophenone	8.6	2.86	0.011

[a] RBDL = regression based detection limit described in Reference 3

[b] Regression variables for the exponential regression of standard deviation versus concentration as described in Equation 14

[c] na = no data available for this compound

Figure 1. Azeotropic Microdistillation System

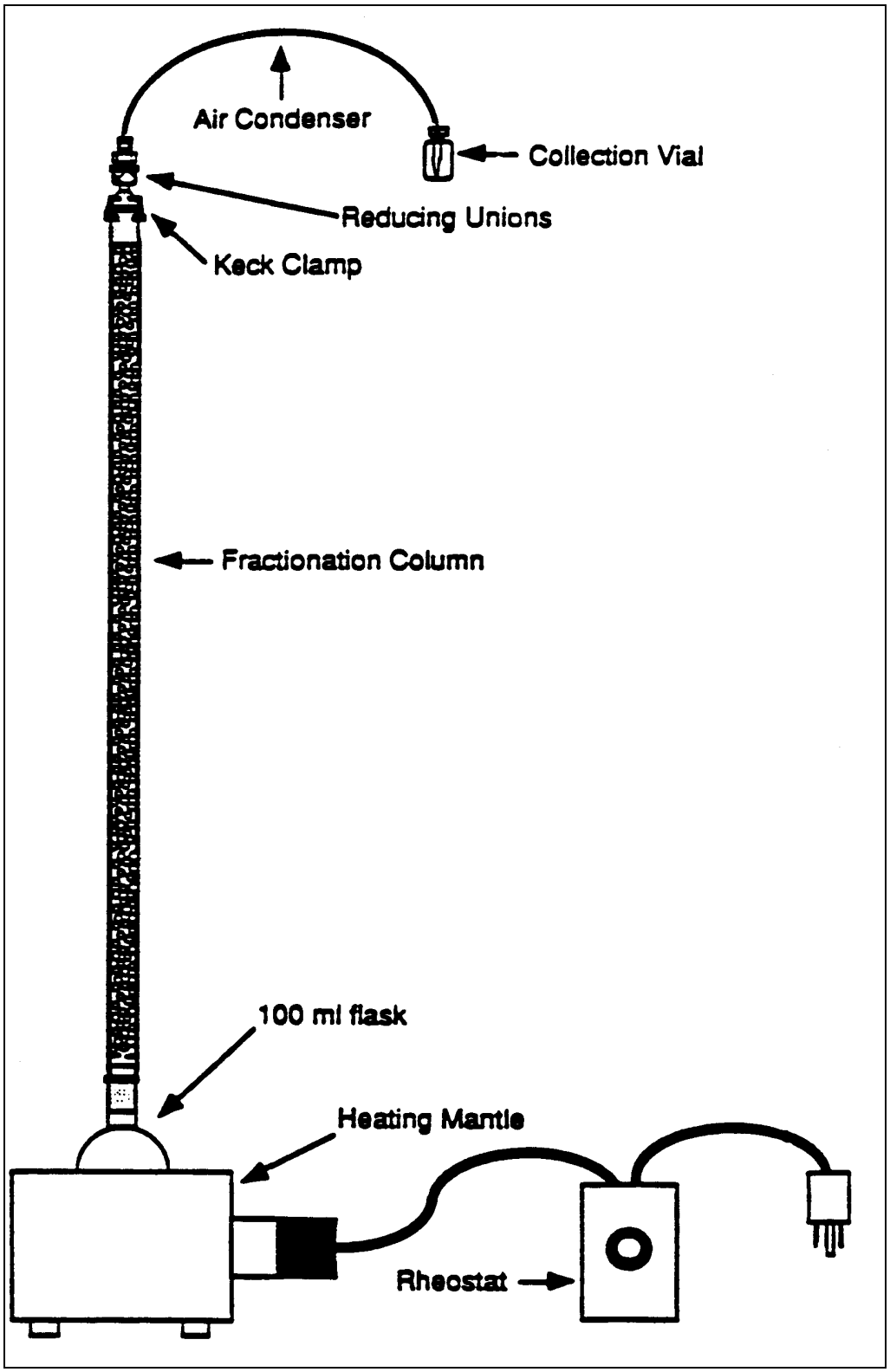

Figure 2. Percent Recovery Versus Concentration of Compounds Which Have Values Outside 70 to 130 Percent for the Microdistillation of Pulp Mill Effluent