NCASI METHOD SPME/MEOH-02

METHANOL IN WEAK BLACK LIQUOR BY HS-SPME/GC/FID

NCASI
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Organic Analytical Program
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NCASI METHOD SPME/MEOH-02

METHANOL IN WEAK BLACK LIQUOR BY HS-SPME/GC/FID

1.0 Scope and Application

1.1 This method is used for the determination of methanol (CAS # 67-56-1) in weak black liquor samples from pulp and paper mills by headspace solid phase microextraction/gas chromatography/flame ionization detection (HS-SPME/GC/FID).

1.2 The method has been applied only to weak black liquor.

1.3 This method has been validated, to a limited extent, for a single laboratory.

1.4 This method is applicable for detecting methanol in weak black liquor.

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 weak black liquor 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 a 10 mL sealed vial. An aliquot of an internal standard solution is added to each of the vials. The headspace above the aqueous samples is exposed to the SPME fiber, where the methanol is adsorbed. The methanol is desorbed from the fiber in the injection port of 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 an FID.

2.3 Identification of methanol is determined by comparison of its relative retention time with the relative retention time of a known standard. If the results are questionable, confirmation may be performed by using a mass spectrometer or a second column confirmation.

2.4 Because both the fraction of methanol and internal standard partitioning into the headspace is highly dependent on the black liquor matrix, quantification is accomplished by the standard addition method. The difference in calibration between DI water and black liquor varied from a factor of 2.0 to a factor of 8.5, with an average of 5.9. In all cases the actual black liquor concentration was less than predicted by the DI water calibration.

2.5 The sensitivity of the method has not been determined and the detection limit has not been established for this method. Of the eleven black liquors tested, the methanol concentration fell within the operating range (i.e., calibration range) of the method.

2.6 Data quality is assured with standard addition calibration for each sample, duplicate analysis, multilevel standard additions, and blank analyses. Methanol standards are checked by comparing the results with an independently prepared standard. Method quality is controlled with daily calibration checks and internal standard checks

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 mg/L – milligrams per liter

3.1.2 May – This action, activity, or procedural step is neither required nor prohibited.

3.1.3 Must not – This action, activity, or procedural step is prohibited.

3.1.4 Must – This action, activity, or procedural step is required.

3.1.5 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.

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 until completely dry.

4.3 Headspace sampling must be made with a clean SPME fiber. Carryover of analytes from previously sampled standards or samples can have a large influence on the measured values of subsequent samples or standards. New fibers must be conditioned as described by the manufacturer. The specified desorption time and temperature minimizes the potential of carryover. Blanks should be run after unusually high sample loadings.

4.4 Some compounds can interfere with the chromatography if the separation is not efficient. Specific interference includes methyl mercaptan with methanol. When performed properly, this method does sufficiently separate these compounds at concentrations found in weak black liquor.

4.5 Compounds may interfere with the internal standard. When initially analyzing samples of unknown composition, a desorbtion without internal standard can be performed to

determine if an interference exists. If there is an interference, either chromatographic conditions should be changed to separate the interferent or a new internal standard should be used. Cyclohexanol, a common internal standard for methanol analysis, was found to have a common interferent in softwood weak black liquor.

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 is a flammable liquids which may be harmful if inhaled or ingested. Use it in a laboratory fume hood and wear appropriate gloves, eye protection, and other protective clothing.

6.0 Equipment and Supplies

***Note**: 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.*

6.1 Sampling equipment

6.1.1 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.

6.1.2 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).

6.2 Laboratory glassware and supplies

6.2.1 Headspace sampler vials capable of holding 10 mL with a gas tight seal; crimp top vials with thin PFTE faced silicone septa work best for easy penetration with the SPME needle

6.2.2 Volumetric flasks

6.2.3 Syringes (including gas-tight syringes)

6.3 Analytical equipment

6.3.1 Gas chromatography system – gas chromatography analytical system complete with a cryogenically cooled temperature-programmable gas chromatograph with a split/splitless injection port

6.3.2 Column – 30 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)

6.3.3 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

6.3.4 Supelco 65 μm Carbowax™/divinylbenzene 24 gauge SPME fiber either for use by automated sampler (Leap or Varian) or for manual use

6.3.5 Supelco SPME inlet guide and fiber holder (for manual injection); Leap or Varian SPME autosampler for automated analysis

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 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 standards. The minimum acceptable purity is 95%.

7.3 Internal standard primary spiking solution

7.3.1 Either 2,2,2-trifluoroethanol or a similar compound which is shown to be free of interference should be used as the internal standard.

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. The net weight of 2,2,2-trifluoroethanol should be approximately 2000 mg. This should result in a nominal 40,000 mg/L primary stock solution. Compute the exact concentration (mg/L) using the measured weight. 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. 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, weight to the nearest 0.1 mg, and fill the flask to the mark. The net weight of methanol added should be approximately 2500 mg. This will result in a nominal 50,000 mg/L methanol primary stock solution. Use this weight gain to compute the exact analyte concentrations. An alternative is to purchase a primary stock solution from a chemical reference supply company. The primary stock must be stored in the refrigerator and should be 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 support it.

7.5 Calibration, standard addition, and matrix spike solutions

Calibration standards of headspace above methanol in water are used to establish the linear operating range of the method. Prepare the standard solutions by diluting the stock solution using gas-tight syringes to measure the required aliquots of primary standard. The required dilutions are shown below. Prepare standard addition and matrix spikes by calculating the concentration of analyte desired and determining the volume of the primary stock solution to add to a 2.0 mL sample.

μL of stock solution to add to 2.0 mL in sample vial	Resulting methanol concentration (mg/L)
800	20,000
200	5,000
20	500
5	125

7.6 Second source standard or certified reference standard

A second source standard or certified reference standard containing methanol in an aqueous solution should be prepared or obtained and analyzed periodically. The standard must be stored in a refrigerator and must be 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 support it.

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 have temperatures exceeding 160°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 weak black liquor 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 with the sample, leaving a minimum headspace.

8.2 Preservation

No preservation other than refrigeration is necessary for weak black liquor samples.

8.3 Storage

All samples must be stored in a refrigerator (4°C) until analysis. No storage stability studies have been conducted.

9.0 Quality Control

To control the quality of the data generated using this method, an initial calibration, independent standard check, daily blank check, daily fiber/internal standard check, periodic duplicates, and periodic multiple level standard additions should be performed.

9.1 Initial calibration check

Although the method uses standard addition to determine concentration, it is necessary to establish the linear operating range of the method by analyzing a series of standards prepared in deionized water. The suggested range to calibrate is from 125 to 20,000 mg/L, but a wider or narrower range is acceptable if all sample and spiked responses (not concentrations) fall within this range. The criterion for acceptable linearity is a relative standard deviation of the average relative response factor of less than or equal to 15%.

9.2 Independent standard check

When a primary methanol standard is prepared for calibration and standard additions, it should be compared with an independent standard either prepared from another source of methanol or obtained from a certified standard vendor. The independent standard should match the primary standard used for calibration and standard additions within 15%. This check will minimize bias due to errors in the methanol spike concentrations.

9.3 Daily blank checks

A daily blank check should be performed before running samples. A blank check should be performed if carryover is suspected (e.g., after running a sample outside the calibration range). A blank check consists of analyzing 2.0 mL of deionized water with internal standard as described in Section 11.1. The methanol level in the blank should not exceed 20% of the lowest calibration point. During the method validation, no concentration

above 3.0 mg/L was detected. The blank methanol response after an 11,000 mg/L spike response was 1.1 mg/L. A high blank level of methanol is most likely a result of incomplete desorption (check desorption temperature and time) or contaminated laboratory air (remove sources of methanol such as rinse solvents from the vicinity of the SPME fiber).

9.4 Daily fiber/internal standard check

The coating on the SPME fiber is delicate and can be damaged with extended use. By comparing the area counts of the internal standard from the daily blank check with the mean value, the capacity of the SPME fiber and/or the stability of the internal standard solution can be monitored. Any change in area count of greater than 30% from the mean value would indicate that either the SPME fiber has been damaged or the internal standard solution has degraded. Visual inspection of the fiber can often detect when the fiber coating has been damaged.

9.5 Duplicate analyses

A duplicate sample should be analyzed with each set of samples (batch of samples no greater than 20). Duplicate analysis requires the analyses of separate aliquots of the native and standard addition samples. The relative percent difference between the two samples should be calculated and charted to estimate the method's precision.

9.6 Multilevel standard addition check

A multilevel standard addition analysis should be performed with each set of samples (batch of samples no greater than 20). In addition to the single standard addition point, additional spike levels different from the original are added and the concentration is calculated using the same native response. The difference between the single level spike and the multiple level spike (D) is calculated as described in Section 12.3. The calculated D values should be charted to estimate the bias due to using a single calibration level. During the method validation, a mean D of 2.6% with a standard deviation of 2.8% was found for eleven single point determinations compared with multiple point determinations. Using three times the standard deviation above the mean as a criterion, the calculated D should be less than 11%.

10.0 Calibration and Standardization

10.1 FID operating conditions

Assemble the GC/FID and establish the operating conditions outlined in Table 1. Once the GC/FID system is optimized for analytical separation and sensitivity, the same operating conditions must be used to analyze all samples, blanks, standard additions, and quality assurance samples.

10.2 HS-SPME/GC/FID analysis of aqueous calibration standards

The HS-SPME response is dependent on the sample concentration, sample volume, temperature, headspace volume, fiber exposure time, and sample matrix. The sample concentration must be determined by calibrating for each sample using the standard addition technique. To ensure the linearity of the instrumentation and provide a quality control measure, aqueous calibration standards are analyzed.

10.2.1 Determine the retention times of the analytes by preparing 2.0 mL of the 500 mg/L calibration solution and adding 10 µL of the internal standard solution. This will result in concentrations of 500 mg/L and 100 mg/L of methanol and 2,2,2-trifluoroethanol, respectively, in the extraction vial. Analyze the headspace as described in Section 11.0. Identify the two peaks and determine the relative retention time for methanol using Equation 1.

Equation 1

$$RRT_M = \frac{RT_M}{RT_{IS}}$$

where: RRT_M *is the relative retention time for methanol*
RT_M *is the retention time for methanol*
RT_{IS} *is the retention time for the internal standard*

10.2.2 Prepare a four point calibration curve to determine instrument linearity and operating range for methanol by taking 2.0 mL of each calibration solution and adding the internal standard solution as described in Section 7.5. Use of an internal standard for calibration is required.

10.2.3 Calculate the relative response factor for methanol (RRF_M) using Equation 2 for each calibration level.

Equation 2

$$RRF_M = \left(\frac{A_M \times C_{IS}}{A_{IS} \times C_S} \right)$$

where: RRF_M *is the relative response factor for methanol in water*
A_M *is the area of the methanol peak*
A_{IS} *is the area of the internal standard peak*
C_S *is the concentration of methanol in the standard (mg/L)*
C_{IS} *is the concentration of internal standard injected (mg/L)*

Calculate the mean and relative standard deviation (RSD) of the four levels. If the relative standard deviation (RSD) of the average RRF_M is less than 15% for methanol the calibration is acceptable. If the calibration does not pass this

criterion, the calibration solutions must be reanalyzed. It may be necessary to perform instrument maintenance prior to reanalysis. If reanalysis also fails to produce a linear calibration, new calibration standards may need to be prepared and analyzed. If the calibration deviates from linearity at either end of the calibration range, the concentration range of the method may need to be shortened.

10.2.4 Analyze and calculate the concentration of the 500 mg/L calibration standard daily, prior to each sample set, using Equation 3. Calculate the percent recovery of the standard using Equation 4 to verify the calibration. In-house percent recovery control limits should be determined, and should not exceed ±15%.

Equation 3

$$C_E = \left(\frac{A_M \times C_{IS}}{A_{IS} \times RRF_M} \right)$$

where: C_E *is the estimated methanol concentration based on aqueous calibration (mg/L)*

Equation 4

$$R = \left(\frac{C_{EC}}{C_S} \right) \times 100$$

where: R is the recovery in percent
C_{EC} *is the estimated methanol concentration for the calibration standard (mg/L)*

11.0 Procedure

11.1 Native sample analysis

Transfer an aliquot (2.0 mL) of the sample to a 10 mL vial by gas-tight syringe. Add 10 µL of the internal standard primary spike solution (40,000 mg/L 2,2,2-trifluoroethanol) to the vial. Be sure that the spike goes into the sample liquid and that it is well mixed. After the sample has come to room temperature (20 to 25°C), sample the headspace by exposing the SPME fiber to the sample headspace for 2 minutes. The temperature can be controlled by placing the vial in a water bath or aluminum block. It is important that the native and standard addition samples are analyzed at the same temperature (±2°C) The whole fiber should be exposed to the headspace and no part of the fiber should contact the liquid. See the manufacturer's instructions describing how to manipulate the SPME fiber. Desorb the sample by exposing the fiber in the middle of the GC injection port liner for 1 minute at 200°C. Calculate an estimated native methanol concentration using Equation 3.

11.2 Standard Addition Analysis

Prepare a second sample of weak black liquor, adding the internal standard plus a volume of either the methanol primary solution or neat methanol required to increase the native concentration by a factor of at least two. The volume of standard added should not exceed 5% of the sample volume (i.e., 100 µL). Either prior knowledge of the sample or the estimated native methanol can be used to help determine the level of methanol needed. Note that the actual concentration can be less than one-eighth of the estimated concentration, depending on the matrix. Analyze the headspace of the spiked sample and calculate an estimated native methanol concentration using Equation 3. If the estimated concentration of methanol in the spiked solution is more that 10% above the established calibrated range, the native sample and the spiked sample should be diluted with water by the same factor and reanalyzed. The spiked estimated concentration should be at least twice but no more than ten time that of the native to obtain the best results. More than one standard addition level can be analyzed to improve the accuracy of the measurement.

11.3 Dilution

If dilution is necessary, inject some fractional volume less than 2.0 mL using a gas-tight syringe into the vial, then bring it to 2 mL with DI water and analyze it as described in Sections 11.1 and 11.2. The dilution factor is the ratio of the volume of sample used divided by 2.0 mL. If standard addition samples require dilution the native samples must be diluted by the same factor and reanalyzed.

12.0 Data Analysis and Calculations

12.1 Calculation of sample concentration from single addition

After calculating the estimated methanol concentrations using the internal standard method shown in Equation 3 for both the native and the spiked samples, Equation 5 is used to calculate the actual concentration of methanol in the sample. Derivation of this equation is provided in Appendix B.

Equation 5

$$C_M = \left(\frac{C_{SA}}{C_{ES} - C_{EN}} \right) \times C_{EN}$$

where: C_M *is the concentration of methanol in the sample (mg/L)*
C_{SA} *is the concentration of standard addition into the sample (mg/L)*
C_{ES} *is the estimated concentration of methanol in the spiked sample (mg/L)*
C_{EN} *is the estimated concentration of methanol in the native sample (mg/L)*

The concentration of the standard addition into the sample (C_{SA}) is calculated with Equation 6.

Equation 6

$$C_{SA} = \frac{V_{Std} \times C_{Std}}{V_{Sam}}$$

where: V_{Std} *is the volume of methanol primary stock solution added (mL)*
C_{Std} *is the concentration of the methanol primary stock solution (mg/mL)*
V_{Sam} *is the volume of sample (L)*

12.2 Calculation of sample concentration from multiple additions

If more than one standard addition level is analyzed, the native concentration can be calculated by using a linear least squares regression of the estimated concentration versus the spiked concentration. Plot the estimated concentration as calculated using Equation 3 on the y-axis and the spike level on the x-axis with the native value at x equals zero. Using Equations 7 and 8, determine the slope and intercept, respectively, for the regression line.

Equation 7

$$m = \frac{n\left(\sum C_{SA}C_E\right)\left(\sum C_{SA}\right)\left(\sum C_E\right)}{n\left(\sum \left(C_{SA}{}^2\right)\right) - \left(\sum C_{SD}\right)^2}$$

where: m is the slope of the line
n is the number of standard additions and native samples analyzed
C_E *is the estimated concentration (mg/L) of the native and the standard additions*

Equation 8

$$b = \frac{\left(\sum C_E\right)\left(\sum (C_{SA})^2\right) - \left(\sum C_{SA}\right)\left(\sum C_{SA}C_E\right)}{n\left(\sum \left(C_{SA}{}^2\right)\right) - \left(\sum C_{SA}\right)^2}$$

where: b is the y-intercept (mg/L)

The native concentration of methanol is calculated from Equation 9.

Equation 9

$$C_M = \frac{b}{m}$$

The linear regression should have a correlation coefficient of greater than 0.995 to be used to calculate the concentration of methanol. If the correlation coefficient is less than 0.995, addition points should be reanalyzed or the range of the spike levels should be condensed.

12.3 Second spike confirmation

As part of the quality assurance for the method, a sample concentration should be checked periodically using multiple standard addition spikes. This checks the assumption that the standard addition response is linear and that a single addition can provide a result equivalent to a multiple addition. Calculate the native methanol concentration using a single standard addition with Equation 5 and with multiple additions using Equation 9. Compare the difference between the two approaches using Equation 10.

Equation 10

$$D = \frac{2 \times \left| C_M - C_{MP} \right|}{\left(C_M + C_{MP} \right)} \times 100$$

where: D is the relative percent difference in the two determinations
C_M is the methanol concentration calculated with a single standard addition (mg/L)
C_{MP} is the methanol concentration calculated with multiple standard additions (mg/L)

13.0 Method Performance

This method was evaluated by comparison with an independent method and by comparing a single standard addition calculation with multilevel standard addition results.

13.1 Eleven different weak black liquor samples were compared. Samples included softwood, hardwood, and combined kraft liquors and a combined softwood/hardwood sulfite liquor. The independent method used a precipitation in acid sample preparation step described in Appendix A, followed by NCASI Method DIMEOH 94.03 (NCASI 2000). Table 2 lists the results of the comparison, where a mean percent difference between the SPME method and the precipitation method was found to be 5.9%. A paired sample t-test showed that the difference in the two methods was not significant at P=0.05 for a two-tailed distribution.

13.2 For the analysis of the eleven black liquor samples, a three point standard addition was performed for each sample. The results of each of the single point determinations were compared to the results using all three points. Considering only the points that met the criterion (spike is equal or greater than the native level), the mean percent difference was found to be –0.96% with a standard deviation of 4.1% for 21 values. This supports the use of a single-point standard addition.

13.3 Interlaboratory and intralaboratory precision estimates have not been determined for this method.

14.0 Pollution Prevention

14.1 The laboratory should check state and local requirements to determine if pollution prevention equipment is 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 for Air and Stream Improvement, Inc. (NCASI). 2000. NCASI Method DI/MEOH-94.03 Methanol in Process Liquids by GC/FID. *NCASI Methods Manual*. Research Triangle Park, NC: National Council for Air and Stream Improvement, Inc.

17.0 Tables and Diagrams

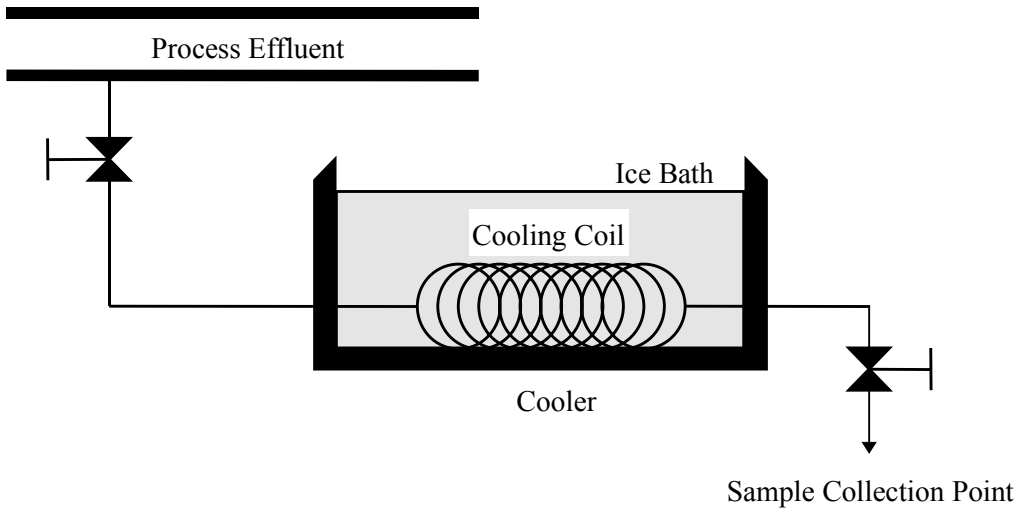
Table 1. GC/FID Operating Conditions for Selected HAPs Analysis Split/Splitless Injector

Injection port:	Direct (Splitless)
Purge flow rate:	approx. 40 mL/min
Purge vent Time	1.0 min
Desorbtion time:	1.0 min
Injector temperature:	200°C
Injection liner:	1 mm id deactivated
FID temperature:	275°C
H_2 flow rate:	approx. 40 mL/min
Air flow rate:	approx. 400 mL/min
Makeup gas:	Nitrogen or helium
Makeup gas flow rate:	approx. 30 mL/min
Carrier gas:	Helium
Carrier gas flow rate:	Constant pressure mode to give 6 mL/min at room temperature, or constant flow mode at 6 mL/min
Column:	J&W DB-624, 75 m x 0.53 mm id with 3 micron film fused silica capillary column
Oven temperature program:	
Initial:	5°C for 1 min
Ramp 1:	6°C/min to 170°C for 0 minutes
Ramp 2:	40°C/min to 250°C for 4 minutes
Retention time order:	Methanol, 2,2,2-Trifluoroethanol, Cyclohexanol

Table 2. Comparison of Methanol Weak Black Liquor Results using the SPME Headspace Method with the Precipitation Direct Injection Method

Mill description	Methanol Concentration (mg/L)		Percent difference
	Direct method	SPME	
Western softwood kraft	247	286	15.6
Western softwood kraft	231	244	5.4
Western soft and hardwood kraft	374	371	-0.8
Southern hardwood kraft	418	460	10.0
Southern softwood kraft	348	373	7.2
Southern softwood kraft	889	972	9.4
Southern hardwood kraft	822	805	-2.1
Southern softwood kraft	654	610	-6.7
Southern hardwood kraft	480	538	12.1
Southern softwood kraft	677	765	13.0
Northeast soft and hardwood sulfite	440	448	1.8

Figure 1. VOA Sample Cooling Train



APPENDIX A

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NATIONAL COUNCIL OF THE PAPER INDUSTRY FOR AIR AND STREAM IMPROVEMENT, INC.

Date: January 22, 1999
Prepared by: MaryAnn Gunshefski and Steve Cloutier

NCASI Procedure for Collection of Black Liquor Samples

This document is to discuss the procedure to be used when collecting black liquor samples which are less than 60 percent solids. This new procedure is being used because NCASI has encountered two problems when analyzing black liquor samples for methanol by gas chromatography with flame ionization detection (GC/FID). First, the black liquor tends to degrade the GC column. Second, we have seen an increase in the methanol content of black liquor samples when diluted with water for GC analysis. We have developed a procedure to minimize, or eliminate, these problems. This procedure involves diluting the black liquor sample in a buffer to decrease the pH of the sample until the black liquor solids precipitate out of the solution. The supernatant is then analyzed by GC to determine the concentration of methanol in the black liquor. Initial work has utilized a buffer solution of pH 7 with a dilution ratio in the range of 20:1 to 30:1 (buffer to sample). Black liquor samples above 60 percent solids can be shipped directly to the lab, where they are reheated and diluted 30:1 with buffer for analysis.

Sampling Procedure:

(1) Determine the amount of buffer and sample that is needed to achieve the proper ratio. For example: 300 g buffer to 10 g sample.

(2) The buffer solution is prepared by dissolving 68 g of H_2KPO_4 and 20 g of KOH in one liter of distilled water.

(3) Weigh the empty sample container. Add buffer solution to the container and reweigh. The difference of the two measurements will give the exact amount of buffer solution added.

(4) At the sampling point, add the approximate amount of black liquor to the buffer in the sample container. Make sure that the liquor sample temperature is below 160ºF. This will minimize vaporization of the methanol from the liquor. This can be achieved by attaching an extra piece of stainless steel or Teflon tubing to the sampling port and running the tubing through a cooler filled with ice. This type of setup should be sufficient to cool the liquor to below 160ºF. Note that the black liquor will get viscous

and hard to pour. Agitate the sample to mix the black liquor and the buffer. This is the only mixing necessary, since ultimately you want the solids to settle out of the solution.

(5) Upon returning to the lab from the sampling point, reweigh the sample container again. From this measurement, the exact amount of liquor collected can be calculated. At this point the pH should be checked to assure that the solution is still buffered around pH 7. If the pH gets much above 7.2 you may want to use a buffer with increased buffering capacity.

(6) The sample container should be refrigerated immediately after collection and kept cold until day of shipment.

(7) For analysis, an aliquot of the supernatant is needed. For shipment of samples to a different location for analysis, 40 mL VOC vials can be used. Before shipment, take an aliquot of each sample and fill two 40 mL vials (with no headspace). A duplicate sample is needed due to possible breakage during shipment. Ship samples in a cooler with ice packs. Ship overnight delivery, but do not ship on a Friday, unless there are arrangements for someone to receive them on Saturday. Also include two vials with buffer solution only, to serve as blanks. Each sample should be labeled with the mill name, sample time, date, and sample location.

(8) It is best to keep the remaining portions of the samples (refrigerated) until completion of the analysis and the results are satisfactory.

(9) If a measurement of the solids content of the black liquor is to be performed, a 250 mL sample of the black liquor must also be collected at the time of sampling. The method which is used to measure the solids content of black liquor is TAPPI test method T650 pm-84.

APPENDIX B

DERIVATION OF STANDARD ADDITION EQUATION AND SAMPLE CALCULATIONS

B.1 Single Addition Equation

Due to the different Henry's law constants for methanol in black liquor and DI water, the HS-SPME response for a concentration of methanol in black liquor is much higher than that of the same concentration in water. Standard addition can correct for this by first determining the difference in response of a known addition of methanol to the matrix.

Standard addition is not commonly used for calibrating chromatographic data and is not available as an option of most data systems. The classical textbook application of standard addition compares the signals (usually spectroscopic) of spiked and unspiked samples. For chromatographic data, signal is related to peak area that is often normalized to the area of an internal standard. For the HS-SPME analysis of black liquor, we have found it convenient to relate the signal to the FID response calibrated for the response of methanol in DI water using the internal standard method. This approach is simplified by the calculations provided with all chromatographic data systems. The internal standard corrects for small variations in temperature, exposure time, sample dilution due to spike additions, and fiber dimensions. This approach provides a means to establish the linearity of the instrumentation and to check that a sample response is within this range of linearity. The instrument's signal can be equated to the concentration based on aqueous calibration. For this discussion, that signal is expressed in Equation B1.

Equation B1

$$S = C_{ES} - C_{EN}$$

where: S is the signal increase due to the standard addition
C_{ES} is the response of the spiked sample calibrated for water
C_{EN} is the response of the native sample calibrated for water

A response factor for the matrix can be obtained by dividing the concentration of the standard addition by the response increase due to that addition as shown in Equation B2. Remember that for the reasons given above, concentrations calibrated for DI water are used in place of signal.

Equation B2

$$RF_M = \frac{C_{SA}}{S}$$

where: RF_M is the response factor for the sample matrix
C_{SA} is the concentration of the standard addition

The concentration of the standard addition is calculated from the volume of standard added, the concentration of the standard, and the volume of sample as shown in Equation 6.

The response factor is applied to the response of the native sample calibrated for water as shown in Equation B3 to obtain the concentration corrected for the matrix.

Equation B3

$$C_M = RF \times C_{EN}$$

where: C_M is the concentration of methanol in the native sample

When Equations B1 and B2 are combined, the result is Equation B4, which is also Equation 5.

Equation B4

$$C_M = \left(\frac{C_{SA}}{C_{ES} - C_{EN}} \right) \times C_{EN}$$

B.2 Example Calculation Using Single Standard Addition

For this example, the mean relative response factor for methanol in DI water was calculated from the RRFs using Equation 2. Table B1 lists the calibration data and the calculated RRFs.

Table B1. Calibration of Methanol in DI Water

Calibration level (mg/L)	Methanol Response (area)	Trifluoroethanol[a] Response (area)	RRF
125	7826	37672	0.3086
250	15670	38616	0.3014
500	31037	38235	0.3015
1000	62636	37949	0.3065
2000	119963	36472	0.3054
		Mean RRF	0.3047
		RSD (%)	1.04

[a] The concentration of trifluoroethanol was 185.7 in all levels.

A softwood weak black liquor was analyzed using the HS-SPME technique, and area counts of 26529 for methanol and 8389 for the internal standard (trifluoroethanol) were found. Using Equation 3, the concentration estimated using the DI water calibration was calculated as shown below.

$$C_E = \frac{26529 \times 185.7 \, {}^{mg}/_{L}}{8389 \times 0.3047} = 1927 \, {}^{mg}/_{L}$$

A 400 mg/L spike of methanol was added to 2 mL of the sample by injecting 16 µL of the 50 mg/mL methanol stock solution as calculated by Equation 6.

$$C_{SA} = \frac{0.016mL \times 50\,{}^{mg}/_{mL}}{0.002L} = 400\,{}^{mg}/_{L}$$

The response found for the spiked sample was 70284 for methanol and 8383 for the internal standard, which results in a concentration of 5110 mg/L based on the DI water calibration using Equation 3. This passes the criterion of the spiked response (5110 mg/L) being twice the native response (1927 mg/L).

$$C_{ES} = \frac{70284 \times 185.7\,{}^{mg}/_{L}}{8383 \times 0.3047} = 5110\,{}^{mg}/_{L}$$

The methanol concentration by standard addition is then calculated using Equation 5(B4).

$$C_{M} = \left(\frac{400\,{}^{mg}/_{L}}{5110\,{}^{mg}/_{L} - 1927\,{}^{mg}/_{L}} \right) \times 1927\,{}^{mg}/_{L} = 242\,{}^{mg}/_{L}$$