# NCASI METHOD CI/SG/PULP-94.03

# CHILLED IMPINGER TEST METHOD FOR USE ON PULP MILL SOURCES TO QUANTIFY METHANOL EMISSIONS

NCASI Southern Regional Center

February 2005

**Acknowledgements**

The original method (CI/SG/PULP-94.02) was prepared by Dr. MaryAnn Gunshefski, Senior Research Scientist, and Ward Dickens, Research Associate, with the NCASI Southern Regional Center. The method has been modified for use on pulp mill sources when sampling and analyzing only for methanol. This method (CI/SG/PULP-94.03) was prepared by Dr. Vipin K. Varma, Project Leader, at the NCASI Southern Regional Center. Other assistance was provided by Terry Bousquet, Project Leader, at the NCASI West Coast Regional Center. The authors also thank Dr. Bruce Ferguson for his help and comments on writing this method.

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National Council for Air and Stream Improvement, Inc. (NCASI). 2005.
Methods Manual, *Chilled Impinger Test Method for use on Pulp Mill Sources to Quantify Methanol Emissions*, Research Triangle Park, N.C.: National Council for Air and Stream Improvement, Inc.

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## 1.0 Introduction

**1.1** NCASI Method CI/SG/PULP-94.03 has been approved as an alternative method for use on pulp and paper mill sources, regulated under 40 CFR Part 63, Paragraph 446, when the analyte of interest is only methanol (CAS # 67-56-1). The methanol is captured in midget impingers and analyzed using gas chromatography/flame ionization detection (GC/FID).

This method was originally published in Appendix B of NCASI Technical Bulletin 684 as "NCASI Chilled Impinger Train Method for Methanol, Acetone, Acetaldehyde, Methyl Ethyl Ketone and Formaldehyde." As originally designed, the method required the analysis of both the chilled impinger catch and the silica gel sorbent tubes. Analysis of the silica gel sorbent tubes is critical in order to accurately determine acetaldehyde, acetone, and methyl ethyl ketone emissions, as these compounds are not sufficiently captured in the impinger. Methanol, on the other hand, is very soluble in water and is effectively captured in the chilled impinger. Results obtained during the field validation study confirm that the silica gel sorbent tube is not necessary while sampling stationary sources only for methanol. They indicate that breakthrough of methanol from the chilled impingers is statistically insignificant.

Subsequently, the original method has been rewritten for use when sampling for methanol only and has been named NCASI Method CI/SG/PULP-94.03. This method conforms to the content and format of EPA Air Methods.

## 2.0 Method Description

### 2.1 Principle, applicability, interferences and stability

**2.1.1** Principle - This method involves the collection of an air sample by drawing it through midget impingers. The impingers are placed in an ice water bath during sampling to enhance collection efficiency. The impinger catch is analyzed for methanol by direct injection into a gas chromatograph equipped with a flame ionization detector (GC/FID).

EPA Methods 1 through 4, or other equivalent methods, must be performed in order to calculate mass emissions rates. These methods are not described in this document.

**2.1.2** Applicability - The method has been validated in a single laboratory study according to the requirements specified in the United States Environmental Protection Agency (US EPA) Method 301, *Field Validation of Emission Concentrations from Stationary Sources* (Appendix A to CFR 63). This method has been found to be applicable for the measurement of methanol in emissions from recovery furnaces, bleach plant scrubbers, smelt dissolving tank vents, and brownstock washer vents. Correction factors calculated from the accuracy section of the Method 301 validation studies are provided in Section 2.9, Table 1. Studies on method precision, carried out according to Method 301 requirements, indicate that at least three samples must be taken at each location in order to obtain a representative stack concentration.

**2.1.3** Interferences - Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing hardware. All glassware should be cleaned using suitable detergent and hot water, followed by rinsing with tap water. The glassware should subsequently be drained dry and baked at greater than 100$^{o}$C for over 2 hours.

**2.1.4** Stability - With refrigeration at approximately 4$^{o}$C, methanol in the chilled impinger catch was found to be stable over 30 days.

## 2.2 Apparatus

**2.2.1** Sampling apparatus - A diagram of the sampling train is shown in Figure 1.

**2.2.1.1** Probe/sampling line - The probe is made from Teflon tubing or stainless steel, which is then attached to the first impinger.

**2.2.1.2** Impinger train - Two 30 mL capacity midget impingers are connected in series to the sampling probe. The first impinger is empty and serves as the dropout impinger. The impingers should have regular tapered stems. All impinger train connectors should either be made of glass and/or Teflon.

**2.2.1.3** Unheated Particulate Filter – If the tester relies on a calibrated critical orifice for flow measurement or control, a suitable unheated filter (Balston AQ or equivalent) should be used in order to protect the rotameter and critical orifice from entrained particulate matter.

**2.2.1.4** Rotameter - A 1000 mL/min capacity rotameter should be placed in line after the chilled impingers for a visual flow check during sampling and leak checking. The rotameter is not used to determine the actual flow rate through the impingers.

**2.2.1.5** Critical orifice - A 400 ± 50 mL/min critical orifice should be used for flow control.

**2.2.1.6** Vacuum pump - The critical orifice is followed by a pump capable of providing a vacuum of about 18 inches of Hg. (Pump capacity should be sufficient to obtain and maintain critical conditions at the orifice.)

**2.2.1.7** Pressure gauges - One pressure gauge is placed before the critical orifice, and one pressure gauge is placed before the pump, and both are used when leak checking the sample train. The pressure gauge downstream of the critical orifice provides a check for critical flow conditions at the orifice.

**2.2.1.8** On/off valve - An on/off valve, placed between the critical orifice and the second pressure gauge, is used when leak checking the sample train.

**2.2.1.9** Flow measurement - A bubble tube flowmeter was used in the NCASI study to measure flow rates at the sampling line tip prior to and after sampling. Alternatively, a calibrated critical orifice may be used along with the filter arrangement described in Section 2.2.1.3. Thirdly, as promulgated in EPA Method 308, a dry gas meter capable of measuring sample volume to within 2 percent may also be used.

**2.2.1.10** Thermometer – A calibrated thermometer is used to measure ambient temperature.

**2.2.1.11** Barometer - A barometer is used to measure barometric pressure.

**2.2.1.12** Sample storage bottles - Glass (i.e., 40 mL VOA vials) or polyethylene bottles can be used to store the impinger catch sample after stack sampling is complete.

**2.2.2** Laboratory glassware and supplies – Volumetric pipets, volumetric flasks, autosampler vials, and syringes necessary for preparation of standards and analysis.

**2.2.3** GC/FID analysis apparatus – Details about the analytical equipment are provided in Section 6.4 of NCASI Water Method DI/MEOH-94.03[1].

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[1] NCASI Method DI/MEOH-94.03 titled "Methanol in Process Liquids by GF/FID" specifically addresses the analytical procedure for quantifying methanol concentration in pulp mill condensates, weak wash, and untreated/treated effluents. The procedures outlined in DI/MEOH-94.03 are applicable when analyzing the impinger catch for methanol.

## 2.3 Reagents

**2.3.1** Water - Deionized water is to be used, both as the impinger collection liquid and in the preparation of all standard and spike solutions.

**2.3.2** Pure compounds - Reagent grade methanol for the preparation of standard and spike solutions.

**2.3.3** GC/FID calibration primary stock solution – A 1000 mg/L primary stock solution of methanol was used. This can be prepared, for example, by diluting 0.126 mL of pure methanol in a 100 mL volumetric flask with DI water (1000 mg/L). Other appropriate mixing recipes/ratios may also be used.

**2.3.4** GC/FID calibration and matrix spike solutions - Prepare standard solutions by serial dilutions of the stock solution. The recommended 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. Prepare matrix spike solutions by calculating the concentration of analytes desired and diluting the primary stock solution.

**2.3.5** GC/FID internal standard primary spiking solution (if used) - Prepare primary stock solution by adding 0.312 mL cyclohexanol and diluting to 100 mL with DI water in a 100 mL volumetric flask (3 mg/mL cyclohexanol). Another internal standard material could be used if it is demonstrated that it does not interfere with the analyte peaks in the chromatogram.

## 2.4 Sampling Procedures

**2.4.1** Sample bottle preparation - Determine the number of sample bottles required for the sampling trip. If the volume of impinger catch is to be determined gravimetrically, weigh each bottle and record the pre-sampling weight on the bottle.

**2.4.2** Sampling - A sample field data sheet is shown in Figure 2.

**2.4.2.1** Measure and record ambient temperature and barometric pressure.

**2.4.2.2** Preparation of collection train – As discussed in Section 2.2.1.2, the first midget impinger in this train is empty. Measure approximately 20 mL of DI water into the second impinger and connect the probe, impingers, rotameter, critical orifice, and pump as shown in Figure 1.

An unheated filter is included upstream of the rotameter if the calibrated critical orifice is used for quantifying flow rates. An impinger filled with silica gel may also be placed in the ice bath and used to remove any residual moisture upstream of the unheated filter. When the silica gel impinger is used, the term '$PW_{4c}$' in Equation 2 (Section 2.6) would be zero.

**2.4.2.3** Leak check procedure - Make sure that the on/off valve is in the on position. Plug the sampling line inlet tip and turn on pump to draw a vacuum. When the vacuum reading is approximately 25 inches of Hg, turn the on/off valve to the off position and record the time and vacuum reading on the first gauge. A leak is indicated either by the flow of bubbles in the impinger with liquid being drawn into the stem of the impinger or by a loss of vacuum. If a leak is present, tighten fittings, connections, and impingers, and restart the leak check procedure. After 2 minutes, record the pressure reading on the first vacuum gauge again. The leakage rate should not be in excess of 1 inch Hg (vacuum) in 2 minutes. Slowly and carefully remove the plug from the end of the probe, and turn the on/off valve back to the on position.

**2.4.2.4** Flow check procedure – If the flow is to be determined on site, check the flow rate at the probe inlet using a bubble flowmeter. The flow rate should be comparable to the flow rate of the critical orifice, measured with the impingers off-line. Record three to five measurements of the flow rate and turn off the pump. These measured flow rates (at ambient sampling conditions) should be corrected to dry standard conditions using Equation 4 in Section 2.6.1. The ambient temperature and barometric pressure measurements (Section 2.4.2.1) are used in order to calculate this correction factor.

When a calibrated critical orifice is used as the flow measurement device, two correction factors are applied:

1. The calibration flow rate of the critical orifice (at calibration conditions) is corrected for differences in orifice pressure and temperature between calibration and sampling conditions – Equation 1 in Section 2.6.1.

2. This sampling flow rate is subsequently corrected to dry standard conditions – Equation 2 in Section 2.6.1.

**2.4.2.5** Sample collection - Insert the probe into the stack and secure it. Start the pump, recording the time and the flow reading on the rotameter. Record the rotameter flow rate every ten minutes during sampling. (A significant flow decrease may invalidate the run; therefore, the sampling rate should be verified any time a decrease of five percent or more is noted during a run.) End the sampling after 60 minutes. Record the time and remove the tubing from the vent. If the flow is determined on site, recheck the sample flow rate at the probe inlet and turn off the pump. If the flow rate has changed significantly, redo sampling with fresh capture water. A slight variation (<5%) in flow can be averaged.

**2.4.3** Sample recovery

**2.4.3.1** Probe rinse - With the probe inlet end of the line elevated above the impingers, add approximately 5 mL of water into the inlet tip to rinse the line into the first impinger. Repeat this procedure twice in order to ensure adequate rinsing.

**2.4.3.2** Impinger Catch - Transfer the contents of the impingers into an appropriately labeled and pre-weighed sample storage bottle. The contents of both impingers can be combined into one bottle. If a large amount of water was collected in the dropout impinger, two bottles can be used. Store the impinger samples in a cooler with ice until they can be stored in a laboratory refrigerator at approximately 4°C.

Alternatively, the impinger catch may be transferred into an appropriate container (a volumetric flask) and subsequently adjusted to a predetermined constant total volume. This would allow for subsequent splitting of the samples before analysis.

**2.4.4** Field sampling quality assurance/quality control - 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 analyses meet the performance criteria of the method.

**2.4.4.1** Field blank samples - A field blank sample of water must be prepared to assure that the water being used in the impingers is not contaminated. It is made in the field by filling a 40 mL VOA vial or polyethylene bottle with the DI water being used to fill the impingers.

**2.4.4.2** Field spike sample - A field spike sample should be prepared by spiking the impinger with a known amount of methanol before sampling. After the impinger is spiked, a sample bottle containing DI water should also be spiked. This provides a check of the spiking solution and spiking procedure. The impinger spiking may be done on a duplicate sampling train if the equipment is available or may be done during a normal sampling run. This type of spiking is performed when a check of the complete sampling procedure, sample storage and sample analysis is desired.

**2.5 Analytical Procedures** - The analytical procedures are discussed in detail in NCASI Method DI/MEOH-94.03.

**2.5.1** Calibration and standardization – Refer to Section 10.0 in NCASI Method DI/MEOH-94.03.

**2.5.2** Quality control - Refer to Section 9.0 in NCASI Method DI/MEOH-94.03.

**2.5.2.1** Blank samples - Refer to Section 9.4.1 in NCASI Method DI/MEOH-94.03.

**2.5.2.2** Calibration verification - Refer to Section 9.4.2 in NCASI Method DI/MEOH-94.03.

**2.5.2.3** Replicates - Refer to Section 9.4.3 in NCASI Method DI/MEOH-94.03.

**2.5.2.4** Matrix spike recovery - Refer to Section 9.4.4 in NCASI Method DI/MEOH-94.03.

**2.5.3** Analytical range and minimum calibration level - Refer to Section 10.3 in NCASI Method DI/MEOH-94.03.

### 2.6 Calculations

**2.6.1** Nomenclature and calculations - Perform the calculations as follows:

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**Equation 1**

*Correcting for changes in critical orifice (CO) pressure and temperature under field sampling conditions:*

$$S_{field} = S_{calib} \left( \frac{P_{calib}}{P_{field}} x \frac{T_{field}}{T_{calib}} \right)^{\frac{1}{2}}$$

*where:*

$S_{field}$ = *Corrected critical orifice flow rate under field conditions, L/min*
$S_{calib}$ = *Critical orifice flow rate under calibration conditions, L/min*
$P_{field, calib}$ = *Critical orifice pressure under field and calibration conditions, mm Hg*
$T_{field, calib}$ = *Critical orifice temperature under field and calibration conditions, mm Hg*

## Equation 2

*Correcting critical orifice (CO) sampling flow rate (field conditions) to dry standard conditions (760mm Hg and 20ºC):*

$$S_C = S_{field}\left(\frac{P_{field} - PW_{4c}}{760}\right) x \left(\frac{293}{273 + T_{field}}\right)$$

*where:*

$S_C$ = Corrected (dry standard) sampling flow rate, L/min
$S_{field}$ = Critical orifice flow rate calculated in Equation 1, L/min
$P_{field}$ = Critical Orifice pressure under sampling conditions, mm Hg
$T_{field}$ = Average ambient temperature measured during the sampling run, ºC
$PW_{4c}$ = Saturated partial pressure of water vapor at 4ºC, mm Hg

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## Equation 3

*Correcting bubble tube meter sampling flow rate (measured at ambient temperature and pressure) to dry standard conditions (760mm Hg and 20ºC):*

$$S_C = S_U\left(\frac{BP - PW_t}{760}\right)\left(\frac{293}{273 + t}\right)$$

*where:*

$S_C$ = Corrected (dry standard) sampling flow rate, L/min
$S_U$ = Uncorrected sampling flow rate, L/min
$BP$ = Barometric pressure at time of sampling, mm Hg
$t$ = Average ambient temperature measured during the sampling run, ºC
$PW_t$ = Saturated partial pressure of water vapor at ambient temperature tºC, mm Hg

**Equation 4**

*Calculation of stack concentration:*

$$C_S = \left( \frac{g_X}{MW_X} \right) \left( \frac{24.04}{S_C \times S_T} \right) \times CF \times 10^6$$

*where:*

$C_S$ = *Stack concentration, ppmv*
$g_X$ = *Total amount of analyte collected in impingers and on sorbent tubes, grams*
$MW_X$ = *Molecular weight of analyte, grams/mole (= 32 for methanol)*
$S_C$ = *Corrected (dry standard) sampling flow rate, L/min*
$S_T$ = *Sampling time, min*
$CF$ = *Correction Factor from Table 1*

### 2.7 Alternative procedures - Not applicable to this method.

### 2.8 References

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

### 2.9 Tables, diagrams, flowcharts and validation data

**Table 1.** Method 301 Validation Results

| | **Brownstock Washer Hood** | | **Bleach Plant Scrubber Inlet** | | **Smelt Dissolving Tank** | | **Recovery Furnace** | |
|---|---|---|---|---|---|---|---|---|
| Pollutant | Validated | CF* | Validated | CF* | Validated | CF | Validated | CF |
| Methanol | Yes | 1.0 | Yes | 1.0 | Yes | 1.04 | Yes | 1.04 |

*No correction factor required

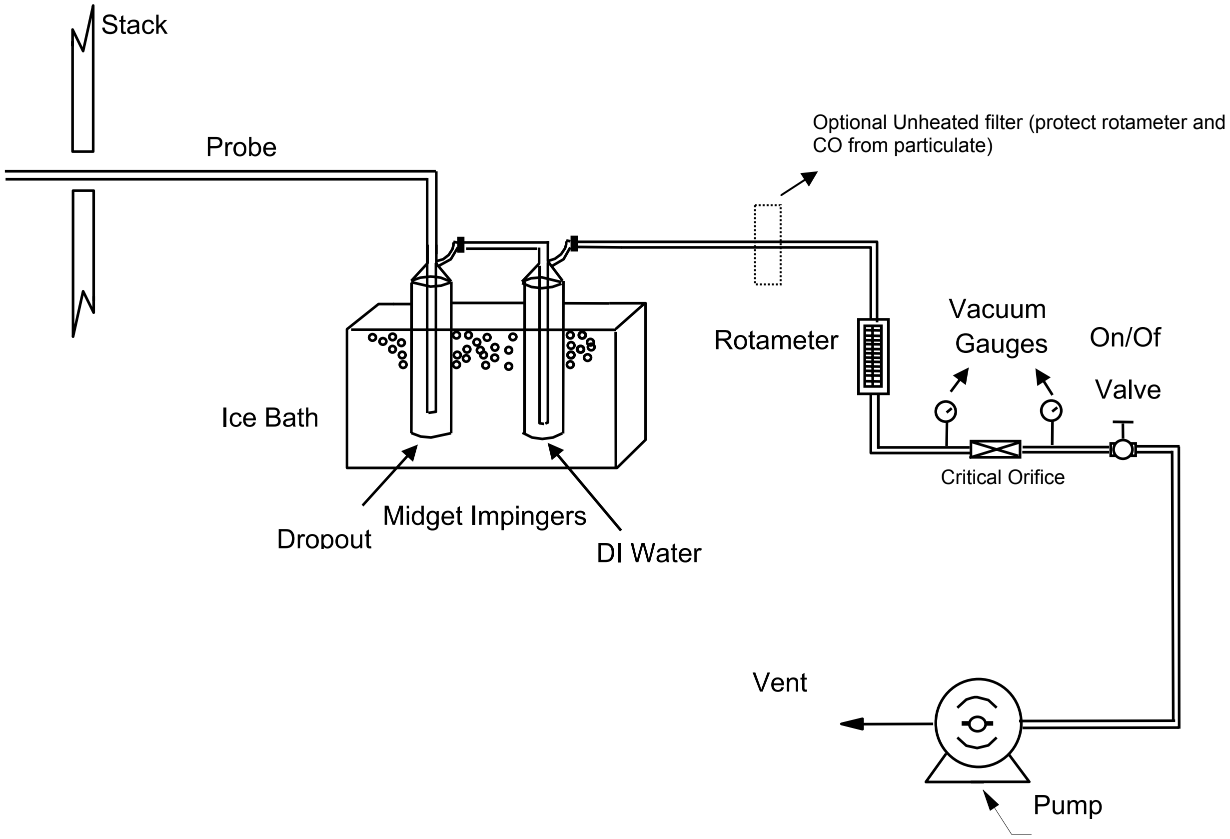


**Figure 1.** Chilled Impinger Sampling Train

*NCASI Chilled Impinger Test Method At Pulp Mill Sources for Methanol*

## Field Sampling Data Sheet

Mill Name:____________________ Date: ___________________________
City,State: ____________________ Sampler's Name: ________________
Source Name/Description: __________________________________________
______________________________________________________________
Run Number: _________________
Start Time: ___________________ Stop Time: ______________________
Ambient Temp at Start: _________ Ambient Temp at Stop: ____________
Barometric Pressure: ____________

***Leak Test***

Time:________________ Initial Measurement (in Hga): _______________
Time: ________________ Final Measurement (in Hga): _______________
*Leak Check Criteria*- Must not lose more than 1 inch of Hg (vacuum) in 2 minutes.
Meets Criteria? Yes No

***System Flow Rate Measurement***

Average of 5 flow measurements for Pre-Sample FlowRate:
1.________ 2.________ 3.________ 4.________ 5.________ Avg: ______________
Average of 5 flow measurements for Post-Sample Flow Rate:
1.________ 2.________ 3.________4.________ 5.________ Avg: ______________
Overall Average Sample Flow Rate: (indicate units!)
Avg: ______________

***Rotameter Readings***

Time: _______ Flow: _______
Time: _______ Flow: _______
Time: _______ Flow: _______
Time: _______ Flow: _______
Time: _______ Flow: _______
Time: _______ Flow: _______

***QA/QC Measures***

Train Spike Conducted? Yes No
Duplicate Conducted? Yes No
Spiked Duplicate Made? Yes No
Field Blank Made? Yes No
Field Spike Made? Yes No

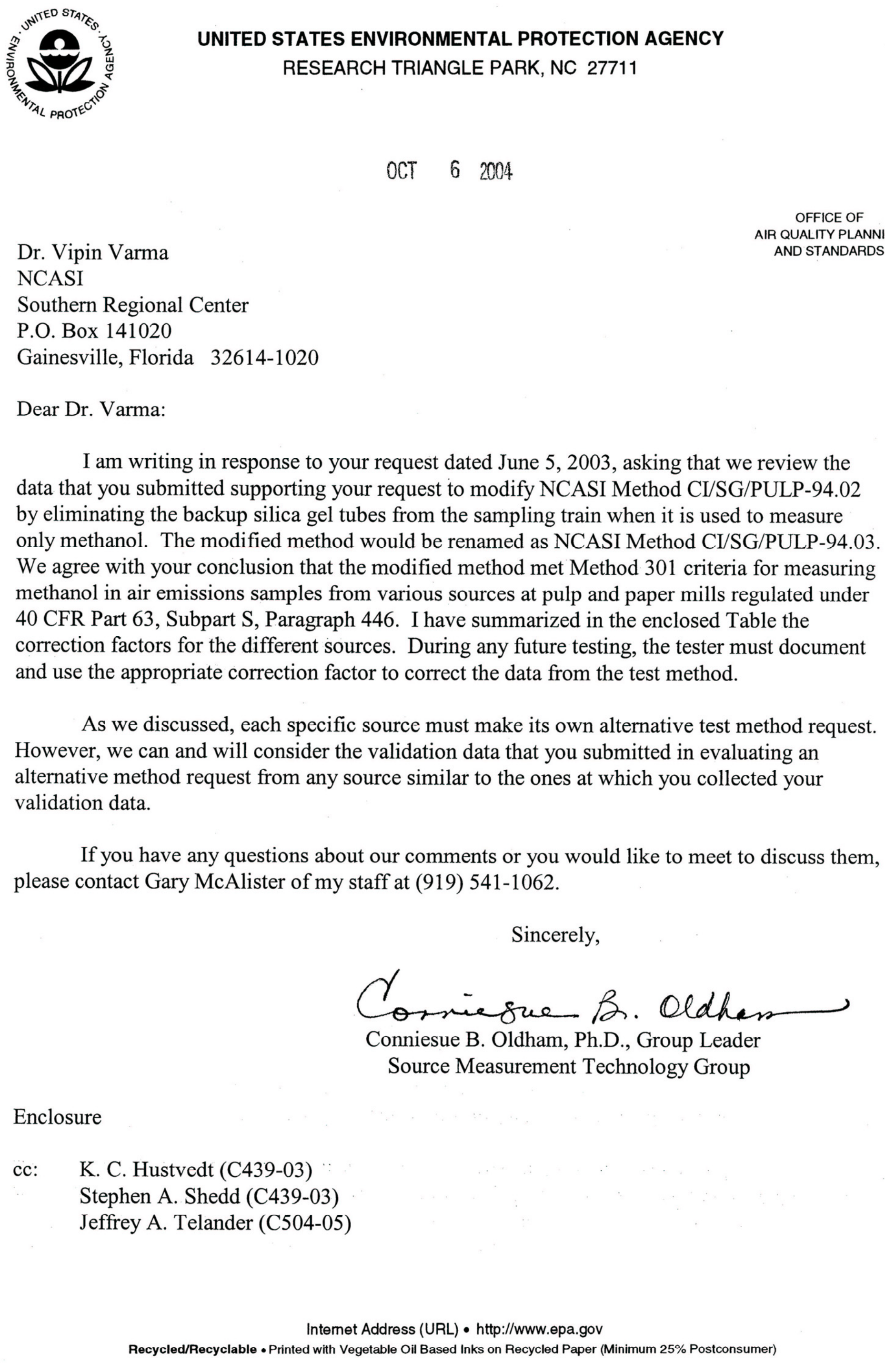
***Sample Bottle Weight(s):***

Bottle 1: Initial Weight: ________ Bottle 2: Initial Weight: _________
Final Weight:_________ Final Weight:_________

***Notes/Comments***

______________________________________________________________

**Figure 2.** Example Field Sampling Data Sheet



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

OCT 6 2004

OFFICE OF
AIR QUALITY PLANNING
AND STANDARDS

Dr. Vipin Varma
NCASI
Southern Regional Center
P.O. Box 141020
Gainesville, Florida 32614-1020

Dear Dr. Varma:

I am writing in response to your request dated June 5, 2003, asking that we review the data that you submitted supporting your request to modify NCASI Method CI/SG/PULP-94.02 by eliminating the backup silica gel tubes from the sampling train when it is used to measure only methanol. The modified method would be renamed as NCASI Method CI/SG/PULP-94.03. We agree with your conclusion that the modified method met Method 301 criteria for measuring methanol in air emissions samples from various sources at pulp and paper mills regulated under 40 CFR Part 63, Subpart S, Paragraph 446. I have summarized in the enclosed Table the correction factors for the different sources. During any future testing, the tester must document and use the appropriate correction factor to correct the data from the test method.

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

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,

Conniesue B. Oldham

Conniesue B. Oldham, Ph.D., Group Leader
Source Measurement Technology Group

Enclosure

cc: K. C. Hustvedt (C439-03)
Stephen A. Shedd (C439-03)
Jeffrey A. Telander (C504-05)

**Figure 3.** EPA Approval Letter - Page 1

**Table.** NCASI Method CI/SG/PULP-94.03

| Source | Validated | Correction Factor |
|---|---|---|
| Brownstock Washer Hood | Yes | None (1.0) |
| Bleach Plant Scrubber Inlet | Yes | None (1.0) |
| Smelt Dissolving Tank | Yes | 1.04 |
| Recovery Furnace | Yes | 1.04 |

**Figure 3.** EPA Approval Letter - Page 2