Midwest Scaling Protocol for the Measurement of “VOC Mass Emissions”

VOC Sampling at Wet and Dry Grain Mills
and Ethanol Production Facilities

U.S. Environmental Protection Agency
Office of Air Quality Planning and Standards
Office of Regulatory Enforcement

August 2004
VOC Sampling from Wet and Dry Grain Mills and Ethanol Production Facilities

Introduction

This protocol is designed to determine the actual volatile organic compound (VOC) mass emission rates from sources where significant amounts of oxygen-containing organic compounds are emitted. Either U.S. EPA Method 25 or Method 25A is used to determine the total organic compound concentration of the emission samples. The concentration data are then converted to carbon mass (or propane mass) emission rates. Simultaneously, the concentrations of the most significant individual organic compounds in the emission sample are measured with Method 18.

This protocol is designed to be used in conjunction with Methods 25 or 25A to provide accurate VOC mass emission measurements from most air emission units at grain mills and ethanol production facilities. VOC mass emissions based on concentration measurements with Methods 25 or 25A reported “as carbon” or “as propane” results in reported VOC emission rates less than the actual emissions of the VOC pollutants. The Midwest Scaling Protocol (MSP) provides a way to convert the VOC results from “as carbon,” when Method 25 is used, or from “as propane,” when Method 25A is used, to “as VOC” emission rates.

Sources in this industry may opt to use a standard scaling factor (SF) of 2.2 pounds of VOC per pound of VOC as carbon instead of performing quantitative measurements of individual volatile organic compounds in order to derive individual scaling factors for each source. Alternatively, the MSP provides an acceptable means for the quantitative measurements of air emissions of individual volatile organic compounds from sources at grain mills and ethanol production facilities. The MSP also serves as a reference for equations used to convert VOC concentration measurements reported “as carbon” or “as propane” to actual VOC mass emissions.

The decision to use Method 25 or Method 25A to measure total VOC concentrations is source dependent. In general, Method 25 is applicable to all sources with total VOC concentrations >50 ppmC (parts per million carbon). Methane and carbon monoxide concentrations are also measured with Method 25. However, referring to Method 25A, section 1.1 of Method 25 states:

“Direct measurement of an effluent with a flame ionization detector (FID) analyzer may be appropriate with prior characterization of the gas stream and knowledge that the detector responds predictably to the organic compounds in the stream. If present, methane (CH4) will, of course, also be measured. The FID can be applied to the determination of the mass concentration of the total molecular structure of the organic emissions under any of the following limited conditions:
(1) Where only one compound is known to exist;
(2) when the organic compounds consist only of hydrogen and carbon;
(3) where the relative percentages of the compounds are known or can be determined, and the FID response to the compounds are known;

(4) where a consistent mixture of the compounds exist before and after emission control and only the relative concentrations are to be assessed; or

(5) where the FID can be calibrated against mass standards of the compounds emitted (solvent emissions, for example).”

The FID used in Method 25A has a depressed response to organic compounds that contain oxygen. The tester must determine, for the specific FID unit used for each test, the response factor for each organic compound that constitutes 5% or more of the total mass of the individual VOC species analyzed. A weighted average of these response factors shall be used to adjust the FID’s response to the actual emission samples. The tester shall adjust the analyzer’s response prior to converting the response to a mass emission rate.

If the tester uses Method 25A to measure VOC from a source where the moisture content is greater than 10%, then the tester must normally dilute the sample using the procedures in Method 205 to reduce the water content of the sample to less than 10%. The tester shall use a heated sample line to transport the sample from the stack to the analyzer to prevent condensation of water and organic compounds. At the time of this writing, at least one FID analyzer has a tolerance for moisture content up to 40%. The moisture content for which Method 205 dilution is required is analyzer-dependent.

One specific application of Method 18 for measuring the kinds of oxygen containing compounds that are most common in the emissions from grain mills is the impinger method developed by the National Council for Air and Stream Improvement, Inc. (NCASI). NCASI has designated this method as NCASI CI/SG/PULP-94.02, Chilled Impinger/Silica Gel Tube Test Method at Pulp Mill Sources for Methanol, Acetone, Acetaldehyde, Methyl Ethyl Ketone and Formaldehyde (NCASI 94.02). Water soluble organic compounds are collected in impingers filled with chilled laboratory grade water. Any target compounds that break through the chilled water are collected on organic grade silica gel. Method 18 analytical procedures, gas chromatography with flame ionization detection or mass spectrometric detection, are used to measure the target organic compounds listed in Table 1.1 that are collected in the sampling train, except for formaldehyde which is measured by a colorimetric procedure. The sample collection, recovery and preservation procedures for this specific application of Method 18 are described in Appendix B along with recommended GC/FID procedures for most target compounds. The analytical procedures to measure formaldehyde are described in Appendix C. Additional GC operating conditions may be necessary to quantify all of the water-soluble volatile organic compounds on the target list.

These data are used to calculate the weighted average ratio of the VOC molecular weight divided by the VOC carbon mass (or VOC propane mass). This SF is then used to convert the total organic carbon mass emission rate to the total VOC mass emission rate (i.e., the results are converted from “as carbon” or “as propane” to “as VOC”).
It should be noted that the VOC mass emission calculation based on a conversion of Method 25 or Method 25A data using Method 18 measurements of a specific list of oxygenated organic compounds may slightly bias the true total mass VOC emission rate compared to the use of a complete set of organic compound concentrations, including all non-oxygenated hydrocarbons. The source is allowed, at its discretion and with the EPA’s approval, to perform additional sampling and analysis to quantify the concentrations of other hydrocarbon compounds, including non-oxygenated compounds, and use the overall average molecular weight for all quantified organic compounds in the calculations discussed below. Failure to conduct additional testing indicates that the source accepts the oxygenated organics weighted average molecular weight to carbon weight ratio as representative of the actual average molecular weight to carbon weight ratio of all organic compounds present in the emissions from the specific unit being tested.

1.0 Scope and Applicability.

1.1 Analytes. The analytes in Table 1.1 must be measured from each source being tested. These compounds have been found to comprise the bulk of the identified VOC emitted from sources at grain mills and ethanol production facilities.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>CAS Number</th>
<th>Interference-Free Analytical Sensitivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Organic Compounds</td>
<td>NA</td>
<td>M25A ~3 ppmC, M25 ~50 ppmC</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>75070</td>
<td>~ 1 ug/ml</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>64197</td>
<td>~ 1 ug/ml</td>
</tr>
<tr>
<td>Ethanol</td>
<td>64175</td>
<td>~ 1 ug/ml</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>50000</td>
<td>~ 1 ug/ml</td>
</tr>
<tr>
<td>Formic Acid</td>
<td>64186</td>
<td>~ 1 ug/ml</td>
</tr>
<tr>
<td>2-Furaldehyde</td>
<td>98011</td>
<td>~ 1 ug/ml</td>
</tr>
<tr>
<td>Methanol</td>
<td>67561</td>
<td>~ 1 ug/ml</td>
</tr>
</tbody>
</table>

1.2 Applicability. This protocol is applicable to determining the actual VOC mass emission rates from sources at grain mills and ethanol production facilities.

1.3 Data Quality Objectives. The quality of the data needed is determined by the needs of the data user. If the test using this protocol is required as part of a regulatory process and if the
tester follows and meets the performance criteria in the protocol, including all Method 18 spike requirements, it is presumed that the MSP produces data of suitable quality to determine compliance with that regulation. The performance criteria in the protocol are set at levels that an operator properly using well designed equipment will consistently attain or exceed. However, because the protocol allows different options to comply with some of the performance criteria, it is the responsibility of the owner or operator of the emission unit, as the data provider, to identify the specific requirements in the protocol that were followed and document that the protocol’s performance criteria were met, or to identify deviations as an exception to the protocol. The regulatory agency is considered the data user and, therefore, is entitled to make the final assessment of data quality.

For the purpose of determining only the SF to be used in calculating VOC mass emissions, the spike requirements of Method 18 may be replaced with an analytical spike set consisting of one low concentration and one high concentration spike sample. These alternate spike samples shall be prepared in the field by spiking the first impinger of the sample collection train and drawing a measured amount of hydrocarbon-free air through the impinger train equivalent to the nominal sample volume. The spike samples shall be recovered and analyzed using the same procedures as those used to recover and analyze the source samples.

2.0 Summary of Protocol. Total organic emissions are measured based on the carbon content of the sample. The list of individual organic compounds that are present in significant quantities are measured individually by Method 18 (using the specific application described in Appendix B) and used to convert the total carbon based measurements to a true VOC mass.

3.0 Definitions. Use the definitions as specified in the following methods.

3.1 EPA Methods. These are methods found in 40 CFR Part 60, Appendix A, and 40 CFR Part 51, Appendix M.

3.1.1 Method 25 — Determination Of Total Gaseous Non-methane Organic Emissions As Carbon

3.1.2 Method 25A — Determination Of Total Gaseous Organic Concentration Using a Flame Ionization Analyzer

3.1.3 Method 18 — Measurement Of Gaseous Organic Compound Emissions By Gas Chromatography

3.1.4 Method 205 — Verification of Gas Dilution Systems for Field Instrument Calibrations

3.1.5 Method 5 — Determination Of Particulate Emissions From Stationary Sources
3.1.6 Method 1 — Sample And Velocity Traverses for Stationary Sources

3.1.7 Method 2 — Determination Of Stack Gas Velocity And Volumetric Flow Rate

3.1.8 Method 3A—Determination of Oxygen and Carbon Dioxide Concentrations in Emissions from Stationary Sources (Instrumental Analyzer Procedure).

3.1.9 Method 4—Determination of Moisture Content in Stack Gases.

3.1.10 Method 10 —Determination Of Carbon Monoxide Emissions From Stationary Sources

3.1.11 Method 10B —Determination Of Carbon Monoxide Emissions From Stationary Sources

4.0 Interference. Interference as specified in the methods in Section 3 and Appendix B.

5.0 Safety. Follow the safety precautions as specified in the methods in Section 3 and Appendix B.

Note that some sources and some areas of grain processing and ethanol production facilities may be fire or explosion hazards. Use appropriate caution and selection of sample collection procedures.

6.0 Equipment and Supplies. Equipment and supplies as specified in the methods in Section 3 and Appendix B.

7.0 Reagents and Standards. Reagents and standards as specified in the methods in Section 3 and Appendix B, with the following exception:

7.1 For Method 25A, obtain a calibration standard of all individual target analytes in Section 1.1 and/or other target analytes found in screening tests at significant levels (>5% of the total VOC). The standards shall be within the range of 25% to 200% of the expected concentration of the individual compound. These calibration standards will be used to develop response factors for each individual compound. These gases shall meet the specifications of Section 7.1 of Method 25A.

8.0 Sample Collection, Preservation, Storage and Transport.

8.1 Test Protocol (TP). The procedures in Appendix A, entitled “A Guide for Stack Test Protocol Development and Submittal For VOC Emission Tests at Grain Processing and Ethanol Production Facilities,” shall be used to assure consistency and adequacy. Failure to submit a complete TP could add cost and time due to postponements or additional submittals of the TP.
8.2 Operating Conditions. For the entire period of its performance test, each affected source shall operate at 90% to 100% of its maximum achievable capacity or its allowable/permitted capacity under representative conditions while maintaining safe and stable load conditions using the highest emitting fuel (normal power sources) and processing typical material resulting in normal product. Operational parameters shall be recorded at 15-minute intervals during the test to substantiate the load. The inlet and outlet gas temperatures of the dryers, syrup addition feed rate and solids content, wet cake feed rate (e.g. tons/hour) shall be recorded during the test.

8.3 The samples shall be collected using the following parameters:

8.3.1 Sources Without Entrained Water Droplets or Aerosols. If the tester intends to use procedures for sources that do not have entrained water droplets, the tester shall conduct a visual inspection and a saturation test of the exhaust gases immediately prior to testing to demonstrate the stack gas is not saturated. A saturation test consists of measuring the moisture content of the exhaust gases using Method 4 and comparing the measured moisture results to tabulated values for moisture content at 100 % relative humidity at the average temperature of the stack gas. If the measured moisture content exceeds the moisture content from the tabulated values, then the stack gas shall be considered to be saturated and to contain water droplets. If the stack gas does not contain water droplets or visible aerosols, collect the samples directly from the stack gas using the procedures in Method 25 or Method 25A and Method 18 as described in Appendix B. Use appropriate caution and unheated sample trains when collecting samples from explosion or fire hazard rated sources regardless of aerosol or water droplet content.

The need for unheated sample trains may dictate the requirement for using Method 25 if the Method 25A sample train would be subject to sample condensation.

8.3.2 Sources That Contain Entrained Water Droplets. If the stack gas contains entrained water droplets, the sample shall be extracted directly from it using the isokinetic sampling procedures described in Method 5 with the exception that the sample shall be drawn from a single representative point, preferably near the center of the stack or duct. Use Method 1 to determine the appropriate sampling location. The tester shall maintain the probe and filter of the Method 5 sampling train at 250° F ± 25° F. Between 20 and 30 dry standard cubic feet (dscf) shall be drawn through the Method 5 sampling train over a one-hour period for each of the three runs.

Use two stainless steel compression fittings behind the filter in the heated filter box of the Method 5 sampling train to withdraw the sample for the total organic compound quantification test (Method 25 or 25A) and for the individual organic compound analysis (Method 18 as described in Appendix B). Place a valve between the Method 5 and the Method 25 or 25A sampling system, and between the Method 5 and the Method 18 sampling systems to isolate each of the sampling systems for leak checks. The tester shall account for the amount of sample diverted to the total organic quantification test and to the Method 18 sampling trains when...
calculating the isokinetic sampling rates. Method 25 samples require ~5 dry standard liters (~0.2 dscf) per sample, and the Method 18 train requires ~30 dry standard liters (~1.1 dscf) per sample. Method 25A analyzers have different flow requirements and must be determined individually.

8.4.3 All Sources. Measure stack gas velocity according to the procedures in Methods 2 and 3 at the beginning and the end of each test. Measure the moisture content of the stack during each test according to the procedures in Method 4. If the moisture content of the sample stream is greater than 10% (or as otherwise specified for the specific FID used) and if the tester is measuring total organic compounds by Method 25A, the tester shall use the procedures in Method 205 to dilute the sample to reduce the moisture content to within the linear and unbiased operating range of the FID. The tester shall conduct cyclonic flow tests prior to the commencement of testing at all sampling locations. If cyclonic flow is determined, appropriate corrections must be conducted.

8.4.4 Dryers and Combustion Sources. Measure the carbon monoxide content of emissions from dryers and combustion sources using the procedures in Method 10 or Method 10B.

8.5 Sample Recovery.

8.5.1 If using Method 25 for the total organic compound quantification test, follow the procedures in that method to recover the sample, store it and transport it to the laboratory.

8.5.2 Follow the recovery procedures in Method 18 as described in Appendix B with the following exception: If the tester uses an empty impinger as the final impinger in the sample train to collect any carryover impinger solution due to high moisture content in the stack, the tester shall recover any liquid in the final impinger and treat it as part of the sample. The tester may combine this recovered liquid with the sample from the impinger immediately in front of the final impinger or may recover it in a separate container.

9.0 Quality Control. Follow the quality control procedures as specified in the methods in Section 3 and Appendix B.

10.0 Calibration and Standardization. Follow the procedures for calibration and standardization as specified in the methods in Section 3 and Appendix B with the following exceptions:

10.1 For Method 25A, the tester shall determine the response factor of the actual instrument used for measuring the total organic compound concentration to each of the individual compounds in Section 1.1 that comprise >5% of the identifiable VOC in the sample. The response factor shall be determined by the instrument’s response to the calibration gas used during the emissions test. The tester may determine the response factor in the laboratory, at the test site prior to the testing, or in the laboratory within 45 days after the first day of the testing.
provided that the instrument has not been modified or repaired in the interim. The response factor shall not be acceptable if the instrument is modified, repaired or adjusted between the test date and the date that the response factors are determined. After the tester has determined the response factor for an individual instrument, the tester may use this response factor for other tests on the same emission unit using the same instrument until the instrument is modified or repaired.

Immediately prior to determining the response factors, the tester must introduce zero gas and high-level calibration gas at the calibration valve assembly. The analyzer output shall be adjusted to the appropriate levels, if necessary. The predicted response as carbon shall be calculated for the compound for which a response factor is being determined by multiplying the concentration of the compound by the number of carbon atoms in each molecule of the compound. Then, the tester shall introduce the calibration gas to the measurement system, record the analyzer response, and calculate the response factor using the equation in Section 12.7.

11.0 Analytical Procedure. Follow the analytical procedures as specified in the methods in Section 3 and Appendix B.

12.0 Calculations and Data Analysis. Follow the calculation and data analysis procedures as specified in the methods in Section 3 and Appendix B with the following additions:

12.1 Scaling Factor, SF. Calculate the scaling factor using the following equation.

\[ SF = \sum_{i=1}^{N} \frac{MW_i}{MWC_i} \times MFC_i \]  

Equation 1

Where

SF = Factor used to correct mass as carbon to “as VOC” or actual mass (expected to be 1.9-2.6)  
N = Total number of compounds  
MW_i = Molecular weight of compound i  
MWC_i = Molecular weight of carbon per mole of compound i  
MFC_i = Mole fraction of carbon contributed by compound i

12.2 Mole Fraction of Carbon.
Where

\[ M_{FC_i} = \frac{m_{c_i}}{\sum_{i=1}^{N} m_{c_i}} \]  

Equation 2

\[ m_{c_i} = \text{Milligrams of carbon contributed by compound } i \text{ in the Method 18 sample.} \]

12.3 Mass of Carbon Contributed by Each Compound.

\[ m_{c_i} = m_i \times \frac{MW_{c_i}}{MW_i} \]  

Equation 3

Where

\[ m_i = \text{Milligrams of compound } i \text{ in the Method 18 sample.} \]

12.4 Actual Mass Concentration VOC in the Sample Gas. Calculate the actual mass concentration of VOC in the sample gas from the measured VOC concentration as carbon using the following equation.

\[ m_a = m_c \times SF \]  

Equation 4

Where

\[ m_a = \text{Actual mass concentration of VOC in the sample} \]
\[ m_c = \text{Measured carbon mass concentration of VOC in the sample, mg/dscm.} \]

12.5 Carbon Mass in the Sample Based on Method 25A Measurement. For Method 25A, calculate the carbon mass in the Method 25A measured sample using the following equation.

\[ m_c = 0.4993 \times C \times RF_{ave} \]  

Equation 5

Where

\[ m_c = \text{Organic concentration as carbon, ppmv from Method 25A.} \]
\[ RF_{ave} = \text{Weighted average response factor from Equation 6.} \]

12.6 Average Response Factor for Method 25A. Calculate the weighted average response factor, RF_{ave}, for Method 25A using the following equation.
Where

\[ RF_{\text{ave}} = \frac{\sum_{i=1}^{N} C_i}{\sum_{i=1}^{N} C_i / RF_i} \]  

Equation 6

\[ RF_i = \frac{C_{ci}}{C_{mi}} \]  

Equation 7

Where

\( C_i = \) Concentration in ppm carbon of organic compound \( i \)

\( RF_i = \) Response Factor of organic compound \( i \)

12.7 Response Factor for Individual Compounds. Calculate the response factor for individual organic, \( RF_i \), compounds using the following equation.

\[ RF_i = \frac{C_{ci}}{C_{mi}} \]

Where

\( C_{ci} = \) Concentration in ppmv carbon of organic compound \( i \) as certified by the manufacturer of the standard

\( C_{mi} = \) Measured concentration in ppm carbon of organic compound \( i \) from Section 10.1
Appendix A

A Guide for
Stack Test Protocol Development and Submittal
For VOC Emission Tests at Grain Processing and Ethanol Production Facilities

PROTOCOL DEVELOPMENT

A detailed protocol, describing all test equipment, procedures, and quality assurance (QA) measures to be utilized, will help ensure that a complete and representative stack test is performed. The protocol must be specific for the test, facility, operating conditions, and parameters to be measured. Adherence to the protocol should eliminate unnecessary delays and costs in the performance of the test, whether the work is done in-house or by a consultant.

The term "tester" will be used to refer to the individual(s) performing the emission test, whether in-house or a consultant. The tester should make at least one on-site inspection of the emission point(s), testing ports, stack access and other parameters in order to prepare the protocol.

The following provides specific guidance pertinent to the major elements of the stack test protocol.

1. Project Description

Provides a general description of the project. This should include sufficient detail to allow those individuals responsible for review and approval to perform their tasks. Where appropriate, the following shall be included:

a. Intended end use of the acquired data.

b. Dates anticipated for the beginning and the completion of testing.

c. Description of plant processes and control equipment, including flow diagrams and permitted, or maximum achievable, process rates.

d. Description of plant operating conditions, including but not limited to production rate, fuel rate, process data (including relevant temperatures and/or flow rates), and pollution control operational data.
2. Project Organization and Responsibility

Include a table or chart showing the project organization and line of authority. List the key individuals, including the Quality Assurance Officer (QAO), who are responsible for ensuring the collection of valid measurement data and the routine assessment of measurement systems for precision and accuracy.

3. QA Objectives for Measuring Data

All measurements must be made to ensure that results are representative of the normal, or permitted, maximum operating conditions of the facility. Data quality objectives will be determined for each measurement and compared with the requirements for the specific project. This will ensure that the data collected will be appropriate for their intended use.

4. Sampling Procedure

For each major measurement parameter, provide a description of the sampling procedures to be used. Officially approved EPA procedures and Reference Methods should be used where applicable. The protocol should include the following:

a. A stack diagram showing test ports, their distances from upstream and downstream disturbances, the stack diameter, planned sampling equipment and monitoring locations.

b. The proposed method for the determination of the presence and quantification of cyclonic flow.

c. The proposed number of sample flow measurement points and the total sample volume.

d. A detailed description of all sampling, sample recovery, and analytical procedures. In the case of non-standard procedures or modifications to standard procedures, the entire procedure should be described with justifications and necessary data for backup. Options offered by the Reference Method should be selected and justified.
e. Any special conditions for the preparation of the sampling equipment and containers to avoid sample contamination.

f. Samples of forms to be used to record sample history, sampling conditions, and plant operating conditions.

g. The methodology for measurement of plant and pollution control device operating conditions.

h. If more than one sampling train is to be used, a detailed description of the relevant sequencing and logistics.

i. If Continuous Emission Monitors (CEMs) are to be used, a detailed description of the operating and data logging procedures.

5. Sampling Procedures for Ethanol Production Facility Dryers

The protocol for the emission test should include the following test methods to accurately characterize the VOC emissions from dryers:

Test Methods -

USEPA Method 1: Sampling Location and Cyclonic Flow Determination
USEPA Method 2: Stack Gas Velocity and Volumetric Flow Rate
USEPA Method 3: Stack Gas Molecular Weight
USEPA Method 4: Stack Gas Moisture Content
USEPA Method 18: Gas Chromatography
   The preferred application of Method 18 based on similar sources is the NCASI Method CI/SG/PULP-94.02: Chilled Impinger/Silica Gel Tube Test Method at Pulp Mill Sources for Methanol, Acetone, Acetaldehyde, Methyl Ethyl Ketone and Formaldehyde

USEPA Method 25: Determination of Total Gaseous Non-Methane Emissions as Carbon
USEPA Method 25A: Determination Of Total Gaseous Organic Concentration Using A Flame Ionization Analyzer

Location - Sampling shall be performed at the exit of each stack. If the stack has a control device for VOC emissions, sampling shall occur before and after the control device where applicable and consistent with the Project Description listed above.

Isokinetics - Sample shall be drawn isokinetically from a single representative point for all methods in any stack that contains uncombined water or organic aerosols.
Detection Limits - The limits of detection for each targeted compound and for total VOC shall be calculated in Kg/hr and/or lbs/hr.

6. Sample Custody

Sample custody is a part of any good laboratory or field operation. At a minimum, the following sample custody procedures shall be addressed in the protocol:

a. Documentation of procedures for preparation of reagents or supplies that become an integral part of the sample (e.g., filters and absorbing reagents).

b. Procedures and forms for recording the exact location and specific considerations associated with sample acquisitions. As samples are transferred between individuals, the individuals should sign and date their relinquishing of, or receipt of, the samples on the Chain of Custody form.

c. Prepared sample labels containing all information necessary for effective sample tracking. Labels or custody seals should cover the sample container cap such that it would be evident if the sample was opened by a person other than the laboratory analyst.

7. Calibration Procedures and Frequency

Include calibration procedures and information for each major measurement device, including coefficients, by reference to a standard method or by providing written description. Provide the frequency planned for recalibration during the test and a list of all calibration standards, including their source and traceability. Equipment to be calibrated would include, for example, dry gas meters, orifice meters, pitot tubes, thermometers/thermocouples, nozzles, flow meters as well as all process parameter monitors. Also include a detailed description of spike preparation procedures.

8. Documentation

Include sample copies of all data log sheets and examples of any calculations that will be performed on the raw data. **Note:** copies of all raw data sheets, including manually and automatically recorded data (strip charts and data logger or computer printouts) will be submitted with the test report and copies must be available at the end of the day's testing.
Appendix B
Method 18 for Oxygenated Organics Other Than Formaldehyde

Introduction.
This appendix describes a specific application of the general Method 18 procedures to measure the individual oxygenated organic compounds other than formaldehyde that are required by the Midwest Scaling Protocol. Formaldehyde is collected in the same Method 18 sample, but is analyzed by a separate procedure found in Appendix C. Both this specific application of Method 18 and the formaldehyde procedure in Appendix C were developed by the NCASI and validated for their use at pulp mills. The NCASI identifies the procedure as NCASI Method CI/SG/PULP-94.02, Chilled Impinger/Silica Gel Tube Test Method at Pulp Mill Sources for Methanol, Acetone, Acetaldehyde, Methyl Ethyl Ketone and Formaldehyde.

Acknowledgment
This method was prepared by Dr. MaryAnn Gunshefski, Senior Research Scientist, and Ward Dickens, Research Associate, at the NCASI Southern Regional Center. Other assistance was provided by Terry Bousquet, Senior Research Scientist, with the NCASI West Coast Regional Center.

This specific application follows the general Method 18 procedure with the following additions to Method 18 taken directly from the NCASI Method CI/SG/PULP-94.02.

1.0 Scope and Application. Same as Method 18 with the following addition:
Stability - The stability of acetaldehyde in the impinger catch was found to be 10 days, with refrigeration at approximately 4°C. The stability of acetone, methyl ethyl ketone, and methanol was found to be 21 days, with refrigeration at approximately 4°C. The stability of acetaldehyde, acetone, methyl ethyl ketone, and methanol on the silica gel sorbent tubes was found to be approximately 10 days, with refrigeration at approximately 4°C. Once desorbed in 3% n-propanol, these same compounds are stable for up to 21 days, with refrigeration at approximately 4°C.

2.0 Summary of Method. Same as Method 18 with the following addition:
This method involves collection of an air sample by drawing it through a midget impinger, which is filled with water, and then through two 2-section silica gel sorbent tubes. The impinger is kept in an ice water bath during sampling to enhance collection efficiency. The impinger catch is analyzed for methanol, acetaldehyde, ethanol, formic acid, acetic acid, 2-furaldehyde, by direct injection into a gas chromatograph equipped with a flame ionization detector (GC/FID). The silica gel sorbent is desorbed with a 3% (v/v) solution of n-propanol. The desorbate is injected directly into the GC/FID for analysis of methanol, acetaldehyde, ethanol, formic acid, acetic acid, and 2-furaldehyde. Alternative GC procedures may be used with prior approval.

3.0 Definitions. Same as Method 18.

Version 1.6
August 2004
4.0 Interferences. Same as Method 18 with the following addition: method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing hardware. Clean all glassware by detergent washing with hot water and rinsing with tap water. The glassware should then be drained dry and baked at greater than 100°C for over 2 hours.

5.0 Safety. Same as Method 18.

6.0 Equipment and Supplies. Same as Method 18 with the following additions:

6.1.1 Sampling apparatus. A diagram of the sampling train is shown in Figure 1 (see below).

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

6.1.1.2 Impinger train. Three 30 mL capacity midget impingers are connected in series to the sampling probe. The impingers should have regular tapered stems. All impinger train connectors should be glass and/or Teflon.

6.1.1.3 Sorbent tubes. Two 2-section silica gel sorbent tubes (SKC #226-15 GWS) are placed in line after the impingers.

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

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

6.1.1.6 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.

6.1.1.7 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.

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

6.1.1.9 Flowmeter. A bubble tube flowmeter is used to measure flow at the sampling line tip prior to and after sampling. Alternatively, a dry gas meter may be used.
**Alternative Sampling Apparatus.** An equivalent sample gas collection system may be proposed by the tester (e.g., use of a volumetrically calibrated evacuated vessel and controller consisting of a needle valve and rotameter along with pre- and post-tank temperature and absolute pressure measurements, or use of a Volatile Organic Sampling Train [VOST] console with its low-flow calibrated dry gas meter.)

6.1.1.10 Thermometer - An accurate thermometer is used to measure ambient temperature.

6.1.1.11 Barometer - A barometer is used to measure barometric pressure.

6.1.1.12 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.

6.1.2 GC/FID analysis apparatus

6.1.2.1 Laboratory glassware. Volumetric pipets, volumetric flasks, autosampler vials, syringes, and cuvettes necessary for standards preparation and analysis.

6.1.2.2 NCASI-recommended gas chromatography system. Gas chromatography/flame ionization detector system, complete with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories including syringes, analytical columns and gases. Note that we suspect systems with EPC are not designed to handle aqueous injections, and as a result the FID flame may begin to go out during the runs. This could be due to the water which builds up in the GC system after several injections on any type of GC. Bakeouts are necessary for any type of GC system, but more frequent bakeouts of a system with EPC may need to be performed.

6.1.2.3 Column - 30 m x 0.53 mm x 1 μm bonded phase DB-WAX fused silica capillary column (J&W Scientific or equivalent); 30 m x 0.32 mm x 0.25 μm bonded phase DB-WAX fused silica capillary column (J&W Scientific or equivalent); 30 m x 0.53 mm x 3 μm bonded phase DB-624 fused silica capillary column (J&W Scientific or equivalent); or other column shown to be capable of separating methanol, acetone, acetaldehyde, methyl ethyl ketone and n-propanol.

6.1.2.4 GC detector - Flame ionization detector with appropriate data system.

7.0 Reagents and Standards

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

7.2 Pure compounds - Reagent grade methanol, acetaldehyde, ethanol, formic acid, acetic acid, 2-furaldehyde, formaldehyde solution in water (stabilized with methanol) for preparation of
standard and spike solutions. Be sure to account for the methanol in the formaldehyde solution when calculating spike concentrations.

7.3 GC/FID calibration primary stock solution - Prepare stock solution by diluting 0.126 mL of pure methanol, 0.128 mL of pure acetaldehyde, 0.073 mL of glacial acetic acid, 0.127 mL of pure ethanol, 0.082 mL of pure formic acid, 0.086 mL of pure 2-furaldehyde, and 0.270 ml of 37% formaldehyde solution in 100 ml volumetric flask with DI water (1000 mg/L plus the methanol in the formaldehyde solution).

7.4 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.

7.5 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.

7.6 n-propanol - Prepare a 3% (v/v) n-propanol/water solution for desorption of the analytes from the silica gel sorbent tubes.

8.0 Sample Collection, Preservation, Storage, and Transport. Same as Method 18, Sections 8.2.4, 8.3, and 8.4.3 with the following additions:

8.1.1 Sample bottle preparation - Determine the number of sample bottles required for the sampling trip. Weigh each bottle and record the pre-sampling weight on the bottle.

8.1.2 Sampling.

8.1.2.1 Measure and record ambient temperature and barometric pressure.

8.1.2.2 Preparation of collection train. Measure 20 mL of DI water into each of the first and second impingers and assemble the sampling train.

8.1.2.3 Leak and flow check procedure. Make sure that the on/off valve is in the on position, close the valve to the M-5 train and turn on pump to draw a vacuum. When the vacuum reading is approximately 25 inches of Hg, turn the pump on/off valve to the off position, then record time and pressure reading on first pressure gauge. A leak is indicated by a flow of bubbles in the impinger, liquid being drawn into the stem of the impinger or 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 pressure gauge again. The leakage rate should
not be in excess of 1 inch Hg (vacuum) in 2 minutes. Slowly and carefully open the valve to the M-5 train, and turn the on/off valve back to the on position. If using the critical orifice procedure, check the flow rate at the probe inlet with a bubble flowmeter. The flow rate should be comparable to the flow rate of the critical orifice with the impingers off-line. Record five measurements of the flow rate and turn off the pump.

8.1.2.4 Sample collection - Insert the probe into the stack and secure it. Start the pump, recording the time and the flow reading on the rotameter. End the sampling after 60 minutes. Record the time and remove the tubing from the vent. 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. With the probe inlet end of the line elevated above the impinges, add about 5 mL of water into the inlet tip to rinse the line into the first impinger.

8.1.3 Sample recovery - 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. Remove the silica gel tubes from the sampling train, cap ends (tape caps on if necessary), and label. Store both impinger and sorbent tube samples in a cooler with ice until they can be stored in a laboratory refrigerator at approximately 4°C.

9.0 Quality Control. Same as Method 18 with the following exception: for the purpose of determining only the Scaling Factor to be used in calculating VOC mass emissions, the spike requirements of Method 18 may be replaced with an analytical spike set consisting of one low concentration and one high concentration spike sample. These alternate spike samples shall be prepared in the field by spiking the first impinger of the sample collection train and drawing a measured amount of filtered air through the impinger train equivalent to the nominal sample volume. The spike samples shall be recovered and analyzed using the same procedures as those used to recover and analyze the source samples.

10.0 Calibration and Standardization. Obtain calibration standards for each target compound to be analyzed. Prepare or obtain enough calibration standards so that there are three different concentrations of each organic compound expected to be measured in the source sample. For each organic compound, select those concentrations that bracket the concentrations expected in the source samples. A calibration standard may contain more than one organic compound. Prepare or obtain standards in the same solvent used for the sample extraction procedure. Verify the stability of all standards for the time periods they are used. Analyze each standard in triplicate.

10.1 GC/FID analysis of calibration standards.

10.1.1 Internal standard calibration.
10.1.1.1 Inject 1 μL of a methanol, acetaldehyde, ethanol, formic acid, acetic acid, and 2-furaldehyde calibration solution containing the internal standard and determine the retention time of the analytes relative to the internal standard. Each analyst should optimize the temperature program or instrument conditions, as necessary, to establish distinct separate peaks.

10.1.1.2 Calculate the relative response factor for the analytes (RRF$_M$) using Equation 1 (section 12.1, below). If the average of the relative response factor for the analytes is constant, i.e., exhibits a coefficient of variation less than 20%, the calibration is acceptable and the average RRF$_M$ can be used in all subsequent calculations; otherwise, the calibration curve solutions must be reanalyzed and reevaluated. It may be necessary to perform instrument maintenance prior to reanalysis. If reanalysis also fails to produce a linear curve, new calibration standards must be prepared and analyzed.

10.1.1.3 Analyze and calculate the relative response factor of a midrange calibration standard daily, prior to each sample set, using Equation 2 (section 12.2, below) to verify the calibration. The relative response factors must be within an acceptable range. If they are not, either prepare a new standard or perform instrument maintenance. If necessary, re-calibrate the instrument.

10.2.2 External standard calibration

10.2.2.1 Inject 1 μL of a methanol, acetaldehyde, ethanol, formic acid, acetic acid, and 2-furaldehyde calibration solution and determine the retention time of each analyte. Each analyst should optimize the temperature program or instrument conditions, as necessary, to establish distinct separate peaks.

10.2.2.2 Measure and plot the response of each analyte vs. concentration. If the correlation coefficient of the graph is greater than 0.99, the calibration is acceptable and the equation of the curve can be used in all subsequent calculations; otherwise, the calibration curve solutions must be reanalyzed and reevaluated. It may be necessary to perform instrument maintenance prior to reanalysis. If reanalysis also fails to produce a correlated curve, new calibration standards must be prepared and analyzed.

10.2.2.3 Analyze and calculate the concentration of a mid-range calibration standard daily, prior to each sample set, to verify the calibration. The recovery should be between 70 and 130%. If it is not, either prepare a new standard or perform instrument maintenance. If necessary, re-calibrate the instrument.

10.3 Analytical range and minimum calibration level

10.3.1 Demonstrate that the calibration curve is acceptable (relative response factors exhibit a coefficient of variation less than 20%, or correlation coefficient greater than 0.99) throughout the range of the calibration curve.
10.3.2 Demonstrate that the analytes are detectable at the minimum levels using the lowest level calibration curve solution.

11.0 Analytical Procedures.

11.1 Preparation of impinger samples. Remove bottles from refrigerator. Weigh the sample bottles and record weights on the bottle. Transcribe initial and final bottle weight to sample field data sheet. Bottles do not need to be at room temperature before weighing. Remove an aliquot of sample and place in the sampler vial, add 10 μL of internal standard solution (if using internal standard calibration curve), and cap vial.

11.2 Preparation of sorbent tube samples. Remove sorbent tubes from refrigerator. Remove end caps and score glass to remove the silica gel from one section. All sections of the silica gel tubes can be combined and analyzed together. This is considered the “back half” of the sample collection train. Pour into a 4.0 mL screw-capped vial and add 3.0 mL of a 3% (v/v) n-propanol/water desorption solution. Allow to sit for 30 minutes, with occasional light shaking. Vigorous shaking causes the silica gel particles to adhere to the cap and walls of the vial. Remove an aliquot of the desorption solution and place in an autosampler vial. Add 10 μL of internal standard solution (if using internal standard calibration curve) and cap vial.

11.3 GC/FID analysis. Analysis is performed by direct aqueous injection into the GC/FID. Representative conditions for the GC/FID analysis are given in Tables 1, 2 and 3 (section 18, below). Other chromatographic columns and conditions may be used if it has been established that the compounds are separated and quality control parameters are met. Once the GC/FID system is optimized for analytical separation and sensitivity, the sample operating conditions must be used to analyze all samples, blanks, calibration standards and quality assurance samples. Note that constant injections of aqueous samples can cause water to build up in the system. This will cause the retention times to shift, and the peaks to broaden. It is recommended that after approximately 50 injections a bakeout of the system be performed. This should consist of heating the injector to 250°C, the oven to over 200°C and the detector to 275°C for at least several hours.

12.0 Data Analysis and Calculations. Same as Method 18 Sections 12.7 -12.9 with the following additions:

12.1 Relative Response Factor. Calculate the relative response factor (RRF\textsubscript{M} using the following equation.

\[
RRF\textsubscript{M} = \frac{C\textsubscript{M}A\textsubscript{IS}}{C\textsubscript{IS}A\textsubscript{M}}
\]

Where:

\(A\textsubscript{M}\) = area of analyte peak

Version 1.6
August 2004
\[ C_M = \frac{R RF_M A_M C_{IS}}{A_{IS}} \]  

Equation 2

Where:
\( A_M \) = Area of the analyte peak  
\( C_{IS} \) = Concentration of the internal standard (mg/L)  
\( A_{IS} \) = Area of the internal standard peak  
\( RRF_M \) = Relative response factor of analyte

12.2 Calibration Verification. Calculate the concentration of the midrange standard using the following equation.

13.0 Method Performance. Same as Method 18.

14.0 Pollution Prevention. [Reserved]

15.0 Waste Management. [Reserved]

16.0 Alternative Procedures. [Reserved]

17.0 References. Same as Method 18 with the following addition:

18.0 Tables, Diagrams, Flowcharts, and Validation Data.

Table 1: GC/FID Operating Conditions for Methanol, Acetaldehyde, Acetone and Methyl Ethyl Ketone Analysis-DB-WAX Column  
Injection: Direct  
Injector Temperature: 150°C  
Injection Volume: 1 μL  
FID Detector Temperature: 250°C  
Carrier Gas: Helium  
Column: DB-WAX, 30 m x 0.53 mm id x 1 micron fused silica capillary column  
Temperature Program °C:
Initial: 18vC for 8 min
Ramp 1: 3°C/min to 20°C for 2 minutes
Ramp 2: 50°C/min to 220°C
Ramp 3: [deliberately blank]
Final Hold Time: 5 minutes
Retention Time Order: acetaldehyde, acetone, methyl ethyl ketone, methanol, n-propanol, cyclohexanol

Table 2: GC/FID Operating Conditions for Methanol, Acetaldehyde, Acetone and Methyl Ethyl Ketone Analysis-DB-WAX Column
Injection: Direct
Injector Temperature: 170°C
Injection Volume: 1 μL
FID Detector Temperature: 275°C
Carrier Gas: Helium
Column: DB-WAX, 30 m x 0.32 mm id x 0.25 micron fused silica capillary column
Temperature Program °C:
Initial: 0°C for 3 min
Ramp 1: 5°C/min to 50°C for 4 minutes
Ramp 2: 70°C/min to 100°C for 10 min
Ramp 3: 70°C/min to 200°C
Final Hold Time: 4 minutes
Retention Time Order: acetaldehyde, acetone, methyl ethyl ketone, methanol, n-propanol, cyclohexanol

Table 3: GC/FID Operating Conditions for Methanol, Acetaldehyde, Acetone and Methyl Ethyl Ketone Analysis-DB-624 Column
Injection: Direct
Injector Temperature: 170°C
Injection Volume: 1 μL
FID Detector Temperature: 275°C
Carrier Gas: Helium
Column: DB-624, 30 m x 0.53 mm id x 3 micron fused silica capillary column
Temperature Program °C:
Initial: 0°C for 3 min
Ramp 1: 5°C/min to 50°C for 0 minutes
Ramp 2: 70°C/min to 105°C for 17 min
Ramp 3: 70°C/min to 220°C
Final Hold Time: 3 minutes
Retention Time Order: acetaldehyde, methanol, acetone, n-propanol, methyl ethyl ketone, cyclohexanol

Version 1.6
August 2004
Figure 1. NCASI Formaldehyde Sampling Train
Appendix C
Analysis of Method 18 Samples for Formaldehyde

1.0 Scope and Application. Same as Appendix B with the following addition:
The stability of formaldehyde was found to be 21 days, with refrigeration at approximately 4°C.

2.0 Summary of Method.
This method contains procedures for analyzing the samples collected by the Method 18
procedure described in Appendix B for formaldehyde. To analyze for formaldehyde, the
acetylacetone derivatization/spectrophotometric analysis method is used on an aliquot of the
impinger solution collected according to Appendix B.

3.0 Definitions. Same as Appendix B.

4. Interferences. Same as Appendix B with the following addition:
Interferences with the formaldehyde analysis can be caused by the presence of sulfur compounds
(i.e. SO₂) in the source gas.

5.0 Safety. Same as Appendix B.

6.0 Equipment and Supplies. Same as Appendix B with the following addition:

6.1. Formaldehyde analysis apparatus

6.1.1 Spectrophotometer - A spectrophotometer capable of
measuring absorbance at 412 nm.

7.0 Reagents and Standards.

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

7.2 Pure compound. Reagent grade 37% formaldehyde solution (formalin) for preparation of
standard and spike solutions.

7.3 Acetylacetone reagent. Prepare by dissolving 15.4 g of ammonium acetate in about 50 mL
of DI water in a 100 mL volumetric flask. Add 0.20 mL of acetylacetone to this solution, along
with 0.30 mL of glacial acetic acid. Mix thoroughly and dilute to 100 mL with DI water. Store
reagent in a brown glass bottle in the refrigerator. Reagent is stable for at least two weeks.

7.4 Formaldehyde analysis primary stock solution. Prepare stock solution by diluting 2.7 mL of
formalin in a 1000 mL volumetric flask with DI water (1000 mg/L formaldehyde).
7.4.1 Formaldehyde analysis calibration standard solution. Prepare standard solution by diluting 1.0 mL of primary stock solution in a 100 mL volumetric flask with DI water (10 mg/L formaldehyde).

8.0 Sample Collection, Preservation, Storage, and Transport. The sample is collected according to the procedures in Appendix B.

9.0 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.

9.1 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 same water being used to fill the impingers.

9.2 Field spike sample. A field spike sample should be prepared by spiking the impinger with a known amount of analyte before sampling. The spike solution described in Appendix A should be used for this purpose. 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.

9.3 Laboratory blank sample. A laboratory blank sample should be analyzed with each batch of samples. A batch is considered no more than 10 samples of similar matrix type.

9.4 Laboratory duplicates. A replicate injection of one sample in the analytical batch should be performed. The results of the duplicate analysis should be within 10% of the mean of the original and duplicate sample analysis.

9.5 Laboratory matrix spike samples. A laboratory matrix spike sample may be prepared with each group of similar matrix type. Using the mean concentration determined by the replicate analyses or the background level determined from a single measurement, determine the spiking level which will give one to four times the background. If the background sample does not have detectable levels of analytes, spike the sample at approximately five times the lowest calibration level of the instrument. Spike the sample with the determined amount of the calibration standard/matrix spike solution and proceed to analyze the sample in the normal manner. The results can be considered acceptable if the calculated spike recovery is 70 to 130%. In cases where multiple analytes are present, the analyte with the highest concentration should govern the acceptance criteria.

Version 1.6
August 2004
10.0 Calibration and Standardization.

10.1 Formaldehyde analysis calibration solutions. A series of calibration standards are made from the standard solution (Section 7.1.4.1) by adding 0, 0.1, 0.2, 0.4, 1.0 and 1.5 mL of the standard solution to individual screw-capped vials. The volume in each vial is adjusted to 2.0 mL with DI water. This corresponds to 0, 0.5, 1, 2, 5 and 7.5 mg/L calibration solutions. To each vial, 2.0 mL of the acetylacetone reagent is added, and the procedure described in Section 11.1 is then followed.

11.0 Analytical Procedures.

11.1 Formaldehyde sample analysis. Remove a 2.0 mL aliquot of the impinger sample and transfer to a screw-capped vial. Add 2.0 mL of the acetylacetone reagent and mix thoroughly. Place vial in a water bath at 60°C for 10 minutes. Allow vials to cool to room temperature. Transfer the solution to a cuvette and measure the absorbance at 412 nm. If the sample solution concentration is above the calibration curve, dilute original sample and repeat entire procedure. Do not dilute colored (derivitized) samples.

12.0 Data Analysis and Calculations.

13.0 Method Performance. [Reserved]

14.0 Pollution Prevention. [Reserved]

15.0 Waste Management. [Reserved]

16.0 Alternative Procedures. [Reserved]

17.0 References. Same as Appendix B.

18.0 Tables, Diagrams, Flowcharts, and Validation Data. [Reserved]