Initial Performance Test Plan

Condensate Collection and Treatment

Revised May 2021

Submitted by:

New-Indy Catawba LLC – Catawba, SC Mill
5300 Cureton Ferry Road
Catawba, SC 29704

Submitted to:

SC Department of Health and Environmental Control
Bureau of Air Quality – Source Evaluation Section
2600 Bull Street
Columbia, SC 29201

ALL4 Contact Information: info@all4inc.com | 610.933.5246 | www.all4inc.com

TABLE OF CONTENTS

Section Name **Page Number**

LIST OF FIGURES

LIST OF TABLES

LIST OF APPENDICES

1. INTRODUCTION

The New-Indy Catawba LLC (New-Indy) operates a pulp and paper mill located in Catawba, South Carolina (Mill). In the Fall of 2020, the Mill was taken down for an extensive outage to convert the Mill from manufacturing bleached paper grades (lightweight coated paper and market pulp) to manufacturing unbleached or brown paper (linerboard and market pulp). New-Indy refers to this investment as Project Columbia. Concurrent with this conversion, the Mill installed a hard pipe from the foul condensate collection tank directly to the Mill's aerated stabilization basin (ASB), for the purpose of using the ASB to treat the foul condensates to comply with 40 CFR Part 63, Subpart S. No other physical changes were made to the ASB, with the exception of completion of planned dredging activities. The new hard pipe discharges the foul condensates below the liquid surface of the existing ASB per 40 CFR §63.446(e)(2) to allow for biological treatment of the hazardous air pollutants (HAPs) present in the condensates, primarily methanol (MeOH). Subpart S provides options for condensate collection and treatment; the Mill has chosen to comply with the following requirements, using both the existing Steam Stripper and the ASB for treatment:

- The Mill will collect 7.2 pounds of hazardous air pollutants (HAP) per oven-dried ton of pulp (lb HAP/ODTP) per 40 CFR §63.446(c)(3); and
- The Mill will treat 6.6 lb HAP/ton ODTP through treatment in the Steam Stripper and ASB (combined) per 40 CFR §63.446(e)(4).

40 CFR §63.7(a)(2) requires that an initial performance test (IPT) be conducted within 180 days of start-up to demonstrate compliance with the collection and treatment requirements of Subpart S. The Mill commenced post-project operations on February 1, 2021, so the Mill is required to conduct the performance test prior to July 31, 2021. The Mill plans to begin the IPT on June 14, 2021.

The Mill originally submitted an IPT plan on April 14, 2021, at least 60 days prior to the planned start date of the IPT in accordance with 40 CFR §63.7(b)(1) and (c). The initial IPT plan reflected that the ASB would be the sole control device used for treatment of foul condensates.

This IPT plan is an update to the initially submitted IPT plan and includes the ASB and the Steam Stripper historically used for treatment of foul condensates. Approximately half of the Mill's foul condensates, by volume, will be treated in the Mill's Steam Stripper, and the other half will be treated in the ASB.

Further, in accordance with the Order to Correct Undesirable Level of Air Contaminants (Order) issued by the South Carolina Department of Health and Environmental Control (SCDHEC) on May 7, 2021, this IPT plan has been updated to include hydrogen sulfide (H_2S) and methyl mercaptan (MMC) liquid testing requested in Item #2 of the Order. Note that this testing is not required by Subpart S but is being included in this IPT plan in response to the Order. At the time of submitting this IPT plan, the Mill has not been able to identify a certified laboratory able to conduct the liquid H_2S and MMC testing requested by DHEC using the preferred method [National Council of Air and Stream Improvement (NCASI) Reduced Sulfur Compounds (RSC) 02-02]. NCASI and ALS laboratory in Simi Valley, CA have previously conducted this testing; however, neither laboratory is set up with the proper equipment to conduct this testing for the Mill at this time. The Mill has identified the following alternatives to the NCASI RSC 02-02 method that may be used if ALS or NCASI is unable to support testing for MMC and H_2S at the time of the IPT:

- ALS Sulfur Liquid Method [derived from American Standards for Testing and Materials (ASTM) D 5504]
- H_2S may be analyzed onsite using a Hach 6000 analyzer.

All methods are discussed in this IPT plan. The Mill will continue to investigate these and other methods, and will select method(s) based on laboratory availability. The method used will be discussed in the IPT report submitted within 60 days of the conclusion of the IPT.

Regarding treatment of foul condensates in the ASB, this performance test plan was developed using guidance from the "Appendix C of Part 63 – Determination of the Fraction Biodegraded (Fbio) in a Biological Treatment Unit" and the "Technical Support Document for the Evaluation

of Aerobic Biological Treatment Units with Multiple Mixing Zones," hereafter referred to as Appendix C of Part 63 and Guidance Document, respectively.

1.1 DOCUMENT ORGANIZATION

This document is organized as follows:

- **Section 1 – Introduction:** provides an introduction, test plan objectives, program contacts, responsibilities, required elements of the test plan, and the test schedule.
- **Section 2 – Facility and Source Description:** provides a process description of Mill operations and summarizes the foul condensate streams collected.
- **Section 3 – Performance Test Plan:** presents the test procedures to be used in the IPT, including the sampling locations and test matrix, sample collection methodology, sample shipping and storage requirements, a summary of the sample analysis methodologies, test run criteria, and process data collection.
- **Section 4 – Internal Quality Assurance (QA)/Quality Control (QC):** presents internal QA/QC procedures for the test program.
- **Section 5 – Data Analysis and Calculations:** presents proposed calculation methods to be used to demonstrate compliance following the IPT.
- **Appendix A – Sampling Matrices:** presents detailed sampling matrices describing the test program.
- **Appendix B – Liquid Sampling Test Methods:** provides the test method procedures for analyses to be conducted during the test program.
- **Appendix C – CMS Matrices:** presents detailed continuous monitoring system (CMS) matrices for continuous monitoring parameters included in the test program.

1.2 PLAN OBJECTIVES

The objectives of this site-specific IPT plan are to provide the sampling and analytical methods used to ensure that representative emissions test results are obtained and to define and collect appropriate data to be used to demonstrate continuous compliance with the condensate collection and treatment requirements of Subpart S and to satisfy the request of the May 7, 2021 Order issued by SCDHEC regarding H_2S and MMC testing.

1.3 PROGRAM CONTACTS

New-Indy plans to contract with ALS Global's Kelso, WA lab to perform the liquid methanol and HAP and testing required for the IPT and with ALL4 to assist with the calculations required to determine the quantity of HAP collected and treated during the IPT. New-Indy has also contracted with Arcadis and TRC to assist with sample collection and with Pace Analytical for testing including chemical oxygen demand (COD). Liquid H_2S and MMC testing conducted per SCHDEC's Order may be conducted by ALS Global's Simi Valley, CA lab, NCASI, or another laboratory. Contact information for the source owner/operator, sampling, testing and consulting contractors are provided in Table 1-1.

Table 1-1
Test Program Contact Information

Owner/Operator	**New-Indy Containerboard – Catawba Mill** 5300 Cureton Ferry Road Catawba, SC 29704	**Point of Contact:** Dan Mallet Environmental Manager (803) 981-8010 Dan.Mallet@new-indycb.com
Liquid Sampling Contractor	**TRC** 50 International Drive, Suite 150 Greenville, SC 29615	**Point of Contact:** Jim Kirlin Senior Engineer (864) 421-3890 jkirlin@trcsolutions.com
	Arcadis 3109 West Dr. Martin Luther King Jr. Boulevard, Suite 350 Tampa, FL 33607	**Point of Contact:** Jason Diamond Licensed Remote Pilot (813) 353-5763 Jason.Diamond@arcadis.com
Analytical Testing Contractor	**ALS Kelso** 1317 South 13th Avenue Kelso, WA 98626	**Point of Contact:** Sydney A. Wolf Project Manager Sydney.Wolf@alsglobal.com
	Pace Analytical 106 Vantage Point Drive West Columbia, SC 29172	**Point of Contact:** Blaire Gagne Project Manager Blaire.Gagne@pacelabs.com

Table 1-1
Test Program Contact Information

	ALS Simi Valley 2655 Park Center Drive, Suite A Simi Valley, CA 93065	**Point of Contact:** Sue Anderson Project Manager (805) 577-2086 Sue.Anderson@alsglobal.com
	NCASI 402 SW 140th Terrace Newberry, FL 32669	**Point of Contact:** Zach Emerson Air Program Manager (352) 244-0909 zemerson@ncasi.org
Consulting Firm	**ALL4 LLC** 300 Chastain Center Blvd, Suite 395 Kennesaw, GA 30144	**Point of Contact:** Sheryl Watkins Sr. Technical Manager (678) 293-9428 swatkins@all4inc.com

1.4 RESPONSIBILITIES

In order to ensure that all of the necessary information is collected and quality assured during the performance test, various key responsibilities will be assigned to the Mill and the contracted firms. These responsibilities include, but are not limited to the following, organized by responsible party:

New-Indy Containerboard will be responsible for:

- Assuring the Mill is in a suitable operating condition for conducting the IPT per 40 CFR §63.7(e)(1).
- Collecting all Foul Condensate, Stripper Outlet, ASB Inlet, and ASB Effluent samples required for methanol, HAP, H_2S, MMC, or COD analysis and shipping to the testing contractor, on ice, such that they arrive within temperature and hold time constraints of applicable test methods.
- Conducting sample analysis for parameters including temperature, pH, mixed liquor volatile suspended solids (MLVSS), and biochemical oxygen demand (BOD_5) (Note: COD analysis will be performed by the testing contractor, Pace Analytical).

- Conducting onsite analysis for H_2S using Hach 6000 if this procedure is selected by the Mill.
- Completing chain-of-custody forms for test program samples.
- Retaining all necessary operational data (i.e. pulp production rates, foul condensate flow rates, stripper steam feed flow rates, stripped condensate temperature, inlet flow to the ASB, temperatures and pH within the ASB).
- Submitting the final test report to SCDHEC and the U.S. Environmental Protection Agency (U.S. EPA) per 40 CFR §63.7(g)(1).

The liquid sampling contractors will be responsible for:

- Collecting all samples within the ASB (center and/or outlet of each treatment zone) using a boat or drone and baler and taking initial measurement of temperature.

The testing contractors will be responsible for:

- Compositing samples prior to analysis as described in this IPT plan.
- Analyzing samples according to and within the hold time requirements of the applicable test methods, including all QA/QC procedures.
- Providing test results to the Mill and to the consulting firm.

The consulting firm will be responsible for:

- Conducting the required calculations to demonstrate compliance with the condensate collection and treatment requirements of Subpart S.
- Summarizing the results of the H_2S and MMC sampling for submittal to SCDHEC.
- Preparing the IPT report and providing to the Mill for submittal to SCDHEC and U.S. EPA.

1.5 SITE-SPECIFIC TEST PLAN ELEMENTS

Table 1-2 and Table 1-3 list each of the required elements of a performance test plan pursuant to 40 CFR Part 63, Subparts S and A, respectively, and identify where that information is presented within this document.

Table 1-2
Site-Specific IPT Plan Requirements
40 CFR Part 63, Subpart S

40 CFR Reference	Requirement	Document Section Number(s)
63.457(a)	*Performance tests.* Initial and repeat performance tests are required for the emissions sources specified in paragraphs (a)(1) and (a)(2) of this section, except for emissions sources controlled by a combustion device that is designed and operated as specified in §63.443(d)(3) or (4).	Section 1
63.457(a)(1)	Conduct an initial performance test for all emission sources subject to the limitations in §§63.443, 63.444, 63.445, 63.446, and 63.447.	Section 1
63.457(c), (c)(1)	*Liquid sampling locations and properties.* For purposes of selecting liquid sampling locations and for determining properties of liquid streams such as wastewaters, process waters, and condensates required in §§63.444, 63.446, and 63.447, the owner or operator shall comply with the following procedures: (1) Samples shall be collected using the sampling procedures of the test method listed in paragraph (c)(3) of this section selected to determine liquid stream HAP concentrations; (i) Where feasible, samples shall be taken from an enclosed pipe prior to the liquid stream being exposed to the atmosphere; and (ii) When sampling from an enclosed pipe is not feasible, samples shall be collected in a manner to minimize exposure of the sample to the atmosphere and loss of HAP compounds prior to sampling.	Sections 2 and 3
63.457(c)(2)	The volumetric flow rate of the entering and exiting liquid streams shall be determined using the inlet and outlet flow meters or other methods demonstrated to the Administrator's satisfaction. The volumetric flow rate measurements to determine actual mass removal shall be taken at the same time as the concentration measurements.	Section 3
63.457(c)(3)	The owner or operator shall conduct a minimum of three test runs that are representative of normal conditions and average the resulting pollutant concentrations. The minimum sampling time for each test run shall be 1 hour and the grab or composite samples shall be taken at approximately equally spaced intervals over the 1-hour test run period. The owner or operator shall use one of the following procedures to determine total HAP or methanol concentration… (ii) For determining methanol concentrations, NCASI Method DI/MeOH-94.03. This test method is incorporated by reference in §63.14(f)(1) of Subpart A of this part (iii) Any other method that measures total HAP concentration that has been demonstrated to the Administrator's satisfaction [Note: The Mill will utilize NCASI Method DI/HAPS-99.01, incorporated by reference under §63.14(p)(3)].	Sections 1, 3
63.457(c)(4)	To determine soluble BOD_5 in the effluent stream from an open biological treatment unit used to comply with §§63.446(e)(2) and 63.453(j), the owner or operator shall use Method 405.1 of part 136 of this chapter with	Section 3

Table 1-2
Site-Specific IPT Plan Requirements
40 CFR Part 63, Subpart S

40 CFR Reference	Requirement	Document Section Number(s)
	the following modifications [Note: The Mill will utilize Standard Method 5210, which is an approved method for BOD_5 under 40 CFR Part 136, Table B]: (i) Filter the sample through the filter paper, into an Erlenmeyer flask by applying a vacuum to the flask sidearm. Minimize the time for which vacuum is applied to prevent stripping of volatile organics from the sample. Replace filter paper as often as needed to in order to maintain filter times of less than approximately 30 seconds per filter paper. No rinsing of sample container or filter bowl into the Erlenmeyer flask is allowed. (ii) Perform Method 405.1 on the filtrate obtained in paragraph (c)(4) of this section. Dilution water shall be seeded with 1 milliliter of final effluent per liter of dilution water. Dilution ratios may require adjustment to reflect lower oxygen demand of the filtered sample in comparison to the total BOD_5. Three BOD_5 bottles and different dilutions shall be used for each sample.	
63.457(c)(5)	If the test method used to determine HAP concentration indicates that a specific HAP is not detectable, the value determined as the minimum measurement level (MML) of the selected test method for the specific HAP shall be used in the compliance demonstration calculations. To determine the MML for a specific HAP using one of the test methods specified in paragraph (c)(3) of this section, one of the procedures specified in paragraphs (c)(5)(i) and (ii) of this section shall be performed. The MML for a particular HAP must be determined only if the HAP is not detected in the normal working range of the method. (i) To determine the MML for a specific HAP, the following procedures shall be performed each time the method is setup. Set up is defined as the first time the analytical apparatus is placed in operation, after any shut down of 6 months or more, or any time a major component of the analytical apparatus is replaced. (A) Select a concentration value for the specific HAP in question to represent the MML. The value of the MML selected shall not be below the calibration standard of the selected test method. (B) Measure the concentration of the specific HAP in a minimum of three replicate samples using the selected test method. All replicate samples shall be run through the entire analytical procedure. The samples must contain the specific HAP at the selected MML concentration and should be representative of the liquid	Section 3, Appendix B

Table 1-2
Site-Specific IPT Plan Requirements
40 CFR Part 63, Subpart S

40 CFR Reference	Requirement	Document Section Number(s)
	streams to be analyzed in the compliance demonstration. Spiking of the liquid samples with a known concentration of the target HAP may be necessary to ensure that the HAP concentration in the three replicate samples is at the selected MML. The concentration of the HAP in the spiked sample must be within 50 percent of the proposed MML for the demonstration to be valid. As an alternative to spiking, a field sample above the MML may be diluted to produce a HAP concentration at the MML. To be a valid demonstration, the diluted sample must have a HAP concentration within 20 percent of the proposed MML, and the field sample must not be diluted by more than a factor of five. (C) Calculate the relative standard deviation (RSD) and the upper confidence limit at the 95 percent confidence level using the measured HAP concentrations determined in paragraph (c)(5)(i)(B) of this section. If the upper confidence limit of the RSD is less than 30 percent, then the selected MML is acceptable. If the upper confidence limit of the RSD is greater than or equal to 30 percent, then the selected MML is too low, and the procedures specified in paragraphs (c)(5)(i)(A) through (C) of this section must be repeated. (ii) Provide for the Administrator's approval the selected value of the MML for a specific HAP and the rationale for selecting the MML including all data and calculations used to determine the MML. The approved MML must be used in all applicable compliance demonstration calculations.	
63.457(c)(6)	When using the MML determined using the procedures in paragraph (c)(5)(ii) of this section or when using the MML determined using the procedures in paragraph (c)(5)(i), except during set up, the analytical laboratory conducting the analysis must perform and meet the following quality assurance procedures each time a set of samples is analyzed to determine compliance. (i) Using the selected test method, analyze in triplicate the concentration of the specific HAP in a representative sample. The sample must contain the specific HAP at a concentration that is within a factor of two of the MML. If there are no samples in the set being analyzed that contain the specific HAP at an appropriate concentration, then a sample below the MML may be spiked to produce the appropriate concentration, or a sample at a higher level may be diluted. After spiking, the sample must contain the specific HAP	Appendix B

Table 1-2
Site-Specific IPT Plan Requirements
40 CFR Part 63, Subpart S

40 CFR Reference	Requirement	Document Section Number(s)
	within 50 percent of the MML. If dilution is used instead, the diluted sample must contain the specific HAP within 20 percent of the MML and must not be diluted by more than a factor of five. (ii) Calculate the RSD using the measured HAP concentrations determined in paragraph (c)(6)(i) of this section. If the RSD is less than 20 percent, then the laboratory is performing acceptably.	
63.457(f)	*HAP concentration measurements.* For the purposes of complying with the requirements in §§63.443, 63.444, and 63.447, the owner or operator shall measure the total HAP concentration as one of the following: (1) As the sum of all individual HAPs; or (2) As methanol.	Section 3
63.457(g)	*Condensate HAP concentration measurement.* For purposes of complying with the kraft pulping condensate requirements in §63.446, the owner or operator shall measure the total HAP concentration as methanol. For biological treatment systems complying with §63.446(e)(2), the owner or operator shall measure total HAP as acetaldehyde, methanol, methyl ethyl ketone, and propionaldehyde and follow the procedures in §63.457(l)(1) or (2).	Section 3, Appendix B
63.457(j)	*Liquid stream calculations.* To demonstrate compliance with the mass flow rate, mass per megagram of ODP, and percent reduction requirements for liquid streams specified in §63.446, the owner or operator shall use the following: (1) The mass flow rates of total HAP or methanol entering and exiting the treatment process shall be calculated using the following equations: $E_b = \frac{K}{n \times 10^6}\left(\sum_{i=1}^{n} V_{bi} C_{bi}\right)$ $E_a = \frac{K}{n \times 10^6}\left(\sum_{i=1}^{n} V_{ai} C_{ai}\right)$ Where: E_b = Mass flow rate of total HAP or methanol in the liquid stream entering the treatment process, kilograms per hour. E_a = Mass flow rate of total HAP or methanol in the liquid exiting the treatment process, kilograms per hour.	Section 5

Table 1-2
Site-Specific IPT Plan Requirements
40 CFR Part 63, Subpart S

40 CFR Reference	Requirement	Document Section Number(s)
	K = Density of the liquid stream, kilograms per cubic meter. V_{bi} = Volumetric flow rate of liquid stream entering the treatment process during each run i, cubic meters per hour, determined as specified in paragraph (c) of this section. V_{ai} = Volumetric flow rate of liquid stream exiting the treatment process during each run i, cubic meters per hour, determined as specified in paragraph (c) of this section. C_{bi} = Concentration of total HAP or methanol in the stream entering the treatment process during each run i, parts per million by weight, determined as specified in paragraph (c) of this section. C_{ai} = Concentration of total HAP or methanol in the stream exiting the treatment process during each run i, parts per million by weight, determined as specified in paragraph (c) of this section. n = Number of runs. (2) The mass of total HAP or methanol per megagram ODP shall be calculated using the following equation: $F = \frac{E_a}{P}$ Where: F = Mass loading of total HAP or methanol in the sample, in kilograms per megagram of ODP. E_a = Mass flow rate of total HAP or methanol in the wastewater stream in kilograms per hour as determined using the procedures in paragraph (j)(1) of this section. P = The production rate of pulp during the sampling period in megagrams of ODP per hour. (3) The percent reduction of total HAP across the applicable treatment process shall be calculated using the following equation:	

Table 1-2
Site-Specific IPT Plan Requirements
40 CFR Part 63, Subpart S

40 CFR Reference	Requirement	Document Section Number(s)
	$$R = \frac{E_b - E_a}{E_b} \times 100$$ Where: R = Control efficiency of the treatment process, percent. E_b = Mass flow rate of total HAP in the stream entering the treatment process, kilograms per hour, as determined in paragraph (j)(1) of this section. E_a = Mass flow rate of total HAP in the stream exiting the treatment process, kilograms per hour, as determined in paragraph (j)(1) of this section. (4) Compounds that meet the requirements specified in paragraphs (j)(4)(i) or (4)(ii) of this section are not required to be included in the mass flow rate, mass per megagram of ODP, or the mass percent reduction determinations. (i) Compounds with concentrations at the point of determination that are below 1 part per million by weight; or (ii) Compounds with concentrations at the point of determination that are below the lower detection limit where the lower detection limit is greater than 1 part per million by weight.	
63.457(l)	*Biological treatment system percent reduction and mass removal calculations.* To demonstrate compliance with the condensate treatment standards specified in §63.446(e)(2) and the monitoring requirements specified in §63.453(j)(3) using a biological treatment system, the owner or operator shall use one of the procedures specified in paragraphs (1)(1) and (2) of this section. Owners or operators using a nonthoroughly mixed open biological treatment system shall also comply with paragraph (1)(3) of this section. (1) Percent reduction methanol procedure. For the purposes of complying with the condensate treatment requirements specified in §63.446(e)(2) and (3), the methanol percent reduction shall be calculated using the following equations:	Section 5

Table 1-2
Site-Specific IPT Plan Requirements
40 CFR Part 63, Subpart S

40 CFR Reference	Requirement	Document Section Number(s)
	$$R = \frac{f_{bio}(MeOH)}{(1+1.087(r))} * 100$$ $$r = \frac{F_{(nonmethanol)}}{F_{(methanol)}}$$ Where: R = Percent destruction. fbio(MeOH) = The fraction of methanol removed in the biological treatment system. The site-specific biorate constants shall be determined using the appropriate procedures specified in appendix C of this part. r = Ratio of the sum of acetaldehyde, methyl ethyl ketone, and propionaldehyde mass to methanol mass. F(nonmethanol) = The sum of acetaldehyde, methyl ethyl ketone, and propionaldehyde mass flow rates (kg/Mg ODP) entering the biological treatment system determined using the procedures in paragraph (j)(2) of this section. F(methanol) = The mass flow rate (kg/Mg ODP) of methanol entering the system determined using the procedures in paragraph (j)(2) of this section. (2) Mass removal methanol procedure. For the purposes of complying with the condensate treatment requirements specified in §63.446(e)(2) and (4), or §63.446(e)(2) and (5), the methanol mass removal shall be calculated using the following equation: $$F = F_b * \left(f_{bio}(MeOH) / (1+1.087(r))\right)$$ Where: F = Methanol mass removal (kg/Mg ODP). F_b = Inlet mass flow rate of methanol (kg/Mg ODP) determined using the procedures in paragraph (j)(2) of this section. f_{bio}(MeOH) = The fraction of methanol removed in the biological treatment system. The site-specific biorate constants shall be determined using the appropriate procedures specified in appendix C of this part.	

Table 1-2
Site-Specific IPT Plan Requirements
40 CFR Part 63, Subpart S

40 CFR Reference	Requirement	Document Section Number(s)
	r = Ratio of the sum of acetaldehyde, methyl ethyl ketone, and propionaldehyde mass to methanol mass determined using the procedures in paragraph (1) of this section. (3) The owner or operator of a nonthoroughly mixed open biological treatment system using the monitoring requirements specified in §63.453(p)(3) shall follow the procedures specified in Section III.B.1 of Appendix E of this part to determine the biorate constant, Ks, and characterize the open biological treatment system during the initial and any subsequent performance tests.	
63.457(n)	*Open biological treatment system monitoring sampling storage.* The inlet and outlet grab samples required to be collected in §63.453(j)(1)(ii) shall be stored at 4°C (40°F) to minimize the biodegradation of the organic compounds in the samples.	Section 3, Appendix B
63.457(o)	Performance tests shall be conducted under such conditions as the Administrator specifies to the owner or operator based on representative performance of the affected source for the period being tested. Upon request, the owner or operator shall make available to the Administrator such records as may be necessary to determine the conditions of performance tests.	Section 3

Table 1-3
Site-Specific IPT Plan Requirements
40 CFR Part 63, Subpart A

40 CFR §63.7 Reference	Requirement	Document Section Number(s)
(b)(1); (c)(2)(iv)	*Notification of performance test*. The owner or operator of an affected source must notify the Administrator in writing of his or her intention to conduct a performance test at least 60 calendar days before the performance test is initially scheduled to begin to allow the Administrator, upon request, to review and approve the site-specific test plan required under paragraph (c) of this section and to have an observer present during the test. The owner or operator of an affected source shall submit the site-specific test plan to the Administrator upon the Administrator's request at least 60 calendar days before the performance test is scheduled to take place, that is, simultaneously with the notification of intention to conduct a performance test required under paragraph (b) of this section, or on a mutually agreed upon date.	Intent to Test Notification Submitted with this IPT Plan

Table 1-3
Site-Specific IPT Plan Requirements
40 CFR Part 63, Subpart A

40 CFR §63.7 Reference	Requirement	Document Section Number(s)
(c)(2)(i)	*Submission of site-specific test plan*. Before conducting a required performance test, the owner or operator of an affected source shall develop and, if requested by the Administrator, shall submit a site-specific test plan to the Administrator for approval. The test plan shall include a test program summary, the test schedule, data quality objectives, and both an internal and external quality assurance (QA) program. Data quality objectives are the pretest expectations of precision, accuracy, and completeness of data.	Section 3
(c)(2)(ii)	The internal QA program shall include, at a minimum, the activities planned by routine operators and analysts to provide an assessment of test data precision; an example of internal QA is the sampling and analysis of replicate samples.	Section 4
(c)(2)(iii)	The external QA program shall include, at a minimum, application of plans for a test method performance audit (PA) during the performance test. The PA's consist of blind audit samples provided by the Administrator and analyzed during the performance test in order to provide a measure of test data bias. The external QA program may also include systems audits that include the opportunity for on-site evaluation by the Administrator of instrument calibration, data validation, sample logging, and documentation of quality control data and field maintenance activities.	Section 4
(c)(2)(iv)	The owner or operator of an affected source shall submit the site-specific test plan to the Administrator upon the Administrator's request at least 60 calendar days before the performance test is scheduled to take place, that is, simultaneously with the notification of intention to conduct a performance test required under paragraph (b) of this section, or on a mutually agreed upon date.	Document will be submitted to EPA upon request

Table 1-3
Site-Specific IPT Plan Requirements
40 CFR Part 63, Subpart A

40 CFR §63.7 Reference	Requirement	Document Section Number(s)
(d)	*Performance testing facilities*. The owner or operator shall provide performance testing facilities as follows: (1) Sampling ports adequate for test methods applicable to such source. This includes: (i) Constructing the air pollution control system such that volumetric flow rates and pollutant emissions rates can be accurately determined by applicable test methods and procedures; and (ii) Providing a stack or duct free of cyclonic flow during performance tests, as demonstrated by applicable test methods and procedures; (2) Safe sampling platform(s); (3) Safe access to sampling platform(s); (4) Utilities for sampling and testing equipment; and (5) Any other facilities that the Administrator deems necessary for safe and adequate testing of a source.	Section 3
(e)	*Conduct of performance test.* (2) Performance tests shall be conducted and data shall be reduced in accordance with the test methods and procedures set forth in this section, in each relevant standard, and, if required, in applicable appendices of parts 51, 60, 61, and 63 of this chapter. (3) Unless otherwise specified in a relevant standard or test method, each performance test shall consist of three (3) separate runs using the applicable test method. Each run shall be conducted for the time and under the conditions specified in the relevant standard. For the purpose of determining compliance with a relevant standard, the arithmetic mean of the results of the three (3) runs shall apply.	Section 5

1.6 TEST PROGRAM SCHEDULE

The emissions test program will begin on June 14, 2021. The total length of the sampling effort for condensate collection is expected to be 19 days, and the total length of the sampling effort for condensate treatment is expected to be a minimum of 5 days. In the event of a Mill upset or shutdown during the IPT, the IPT will be extended to include minimum of 15 days for condensate collection and 5 days for condensate treatment. Any changes in the tentative

schedule will be communicated via letter or email to SCDHEC. Please note the Mill may deviate from this schedule as appropriate. Samples will be taken during daylight hours due to personnel scheduling and, for condensate treatment testing, safety concerns with sampling from the ASB at night. Per 40 CFR §63.457(c)(3), a minimum of three sample runs under normal operating conditions is required, with each run having a minimum sampling time of one hour. To meet this requirement, samples will be obtained at least once per day for the duration of the performance test. Foul Condensate samples will be collected three times per day throughout the 19 days of the performance test; for the first 14 days (collection only), samples collected each day will be composited at the laboratory prior to analysis. During the collection and treatment portion of the test (last five days), Foul Condensate and Stripped Condensate samples will be collected three times per day for individual analysis, and ASB samples will be collected once per day.

2. GENERAL FACILITY AND SOURCE DESCRIPTION

Project Columbia converted the Mill from manufacturing bleached paper grades (lightweight coated paper and market pulp) to manufacturing unbleached or brown paper (linerboard and market pulp). The original Kraft continuous digester system was modified to produce a higher virgin pulp yield. Kappa number has been increased from less than 30 for bleached pulp to over 90 for unbleached pulp and the cook time in the continuous digester has been shortened. The higher Kappa produces more tons of virgin pulp using the same amount of raw materials (wood and cooking liquor).

The pulp slurry from the continuous digester is sent to the blow tank and through the diffusion washer system, then to one of two parallel pulping lines, each consisting of an enclosed deshive refiner and a 3-stage vacuum drum washer system and associated filtrate tanks. Weak black liquor from the washer filtrate tanks is stored before being recycled to chemical recovery. Rejects from the refiners are sent to the screw presses, with the filtrate being screened and stored before being recycled to chemical recovery. Washed pulp is stored and then sent to the Pulp Dryer Area to produce unbleached market pulp or to the No. 3 Paper Machine Area to produce linerboard. Note: The No. 2 Paper Machine may be used to produce an uncoated lightweight brown sheet, but is currently idle.

The No. 1 Evaporator Set was modified to allow operation as a five-effect system design that addresses an increase the evaporation rate needed to account for the reduction in the solids content of the weak black liquor from the vacuum drum washers. No modifications were made to the No. 2 and No. 3 Evaporator Sets, No. 2 and No. 3 Recovery Furnaces, No. 2 and No. 3 Smelt Dissolving Tanks, No. 2 Lime Kiln or Causticizing Area as part of the conversion to unbleached pulp production.

As part of compliance with the pulping condensates collection and treatment under 40 CFR Part 63, Subpart S, the following streams are collected in the Foul Condensate Collection Tank and treated in the ASB or Steam Stripper:

- No. 1 Evaporator Pre-condenser, Intercondenser, and Aftercondenser Foul Condensates[1] [40 CFR §63.446(b)(3)(i and ii)];
- No. 2 Evaporator Intercondenser and Aftercondenser Foul Condensates[2] [40 CFR §63.446(b)(3)(i and ii)];
- No. 2 Evaporator - Surface Condenser Foul Condensates [40 CFR §63.446(b)(3)(ii)];
- No. 3 Evaporator Feed Effects (5th and 6th Effects) and Flash Tank Condensates [40 CFR §63.446(b)(3)(i)][3];
- HVLC Collection System Condensates [40 CFR §63.446(b)(4)]; and
- LVHC Collection System Condensates[4] [40 CFR §63.446(b)(5)].

The sampling location for the foul condensates collected and routed to treatment in either the ASB or the Steam Stripper is just ahead or downstream of the flow meter on the hardpipe to the ASB. This sample point is representative of condensates sent to the ASB and the Steam Stripper. The Mill has the following objectives under 40 CFR Part 63 Subpart S for the IPT:

- Demonstrate compliance with the condensate collection and treatment requirements of Subpart S;
- Establish a concentration factor to be used to determine continuous compliance with the condensate collection requirements of Subpart S and to be confirmed or re-established during quarterly performance testing; and
- Establish an operating parameter and limit to be used to determine continuous compliance with the condensate treatment requirements of Subpart S.

In addition, the Mill will collect H_2S and MMC samples to satisfy Item #2 of the May, 7, 2021 SCDHEC Order.

[1] No. 1 Evaporator Surface Condenser vents to the Pre-condenser, which vents to the Intercondenser and then the Aftercondenser. The No. 1 Evaporator Condensates are routed directly to the Foul Condensate Collection Tank.
[2] No. 2 Evaporator Surface Condenser vents to the Intercondenser, which vents to the Aftercondenser. The No. 2 Evaporator Condensates are routed directly to the Foul Condensate Collection Tank.
[3] Weak liquor feeds the 5th and 6th effects, which vent to a cooler and Flash Tank, which are routed directly to the Foul Condensate Collection Tank.
[4] The Evaporator Areas LVHC Condensates are collected in the Evaporator Area LVHC Condensate Tank and routed to the Foul Condensate Collection Tank.

3. PERFORMANCE TEST PLAN

This section addresses the key components of the IPT plan and describes the Mill operating conditions that will be maintained and monitored during the test program, the compliance demonstration parameters that will be monitored during the testing, the applicable test methods, and proposed QA and QC activities. This section also discusses the MMC and H_2S testing to be conducted during the IPT per the Order issued by SCDHEC.

3.1 TEST RUN CRITERIA

Sampling for the IPT will be conducted under stable Mill operations and normal operating conditions. The Mill will target to achieve at or above an average of 80% of the maximum pulp production during the sampling period. In the event of upset conditions resulting in process downtime or excess loading to the ASB, IPT sampling will be paused until the Mill is returned to stable operations. In the event of unplanned Steam Stripper downtime during the treatment portion of the IPT, sampling will be paused until the Steam Stripper is returned to stable operation.

3.2 SOURCE OPERATION AND PARAMETER MONITORING

To all extent practicable, all sources will be maintained at a normal operating rate during the IPT. During the condensate treatment performance test, the Mill proposes to limit aeration capacity within the designated zones to the proposed operating limit of aeration horsepower (such as 90% of the available aeration horsepower) to demonstrate the capability of the ASB to comply with the condensate treatment requirements at that level. The Mill will select a target aeration horsepower operating limit prior to the IPT based on ASB performance. The Mill plans to operate the ASB at the proposed operating limit of aeration horsepower for three days prior to the condensate treatment performance test. The Mill plans to operate the Steam Stripper at a range of effective steam to feed ratios (ESFR) during the IPT in order to establish a correlation between ESFR and methanol removal in the Steam Stripper. This correlation will be used

following the IPT to monitor compliance with the methanol treatment requirements of Subpart S. The method of calculating ESFR is discussed in Section 5.2.2.

Figure 3-1 below provides a simplified diagram of the Mill's foul condensate collection and treatment system, including flow meters and sample points applicable to this IPT plan.

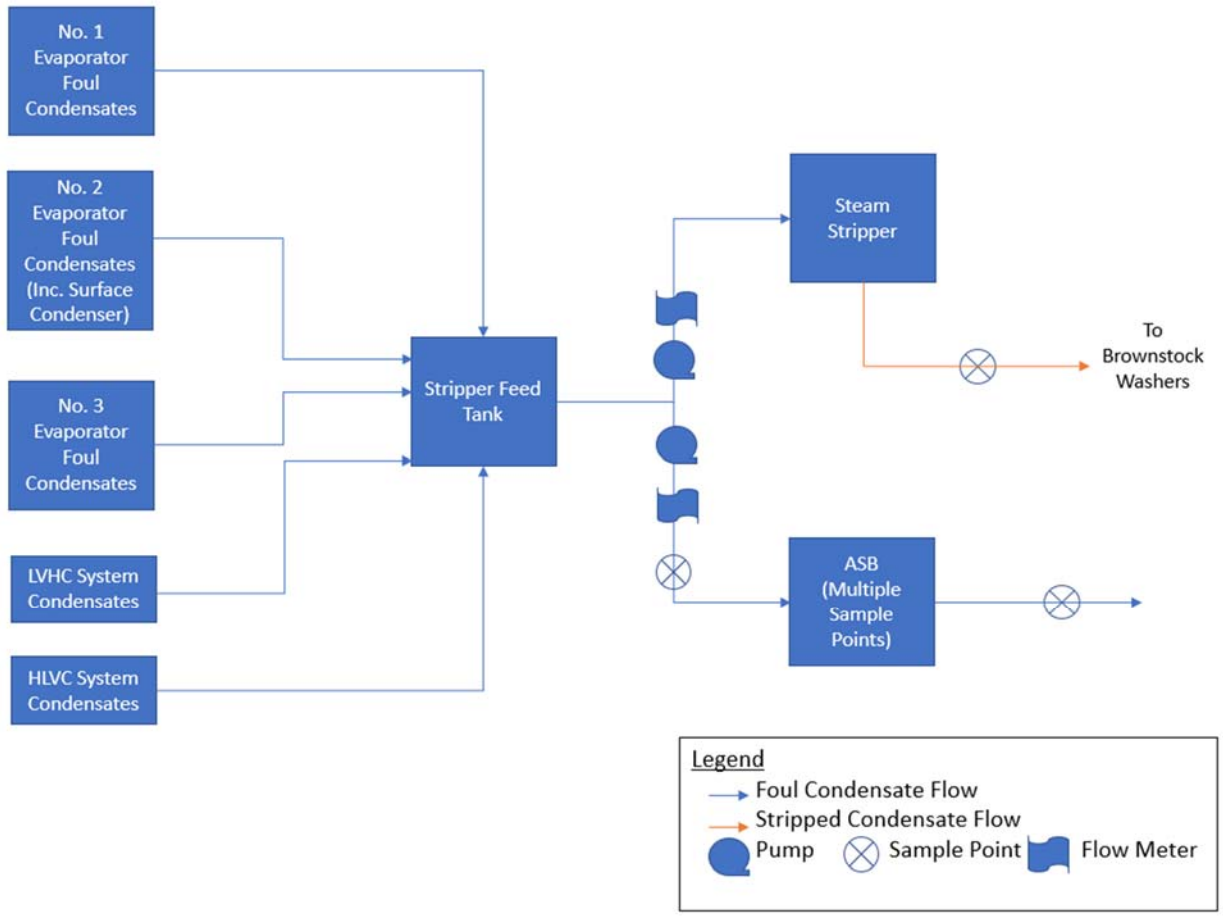


Figure 3-1
Foul Condensate Collection and Treatment System Diagram

Table 3-1 summarizes the parameters that the Mill proposes to monitor during the IPT and associated proposed calculation methods, which will be validated prior to or during the IPT. All of the instruments used for the monitoring parameters listed in Table 3-1 will undergo a

continuous monitoring system (CMS) performance evaluation/calibration prior to the IPT. Documentation of the performance evaluations will be included in the IPT report.

Table 3-1
Proposed Monitoring Parameters

Measurement Taken	Measurement Device	Calculation Method	Monitoring Period
Foul Condensate Hardpipe Flow	Continuous Flow Meter	Gallons per day (gpd) = Average gallons per minute (gpm) x Operating minutes per day	24-hour total
Steam Stripper Inlet Condensate Feed Flow	Continuous Flow Meter	Gallons per hour (gph) = Average gallons per minute (gpm) x Operating minutes per hour	1-hour average for each sampling event
Steam Stripper Steam Flow	Continuous Flow Meter	Average rate in pounds per hour (lb/hr)	1-hour average for each sampling event
Foul Condensate to Steam Stripper Feed Temperature	Continuous Temperature Probe	Average temperature in degrees Fahrenheit (°F)	1-hour average for each sampling event
Stripped Condensate Temperature	Continuous Temperature Probe	Average temperature in °F	1-hour average for each sampling event
Stripped Condensate Flow	Continuous Flow Meter	Gallons per hour (gph) = Average gallons per minute (gpm) x Operating minutes per hour	1-hour average for each sampling event
Digester production oven dried tons of pulp (ton ODTP)	Pulp Flow and Consistency Meters	ODTP = ADTUBP/d [Daily Average Flow, gpm x Daily Average Consistency, %/100 x (8.17 + 0.0333 x Daily Average Consistency, %) x 1440 minutes/day /1800] x 0.9	24-hour total

Table 3-1
Proposed Monitoring Parameters

Measurement Taken	Measurement Device	Calculation Method	Monitoring Period
ASB Wastewater Inlet Flow (based on Fresh Water Intake Flow)	Continuous Flow Meter, Evaporation Factor	Wastewater inlet flow rate to ASB, gpd = Average gpm Fresh Water Intake flow x [1 – Evaporation Rate] x Flow Meter Operational Minutes per Day	24-hour total
Number of Aerators Operating per Zone	Readout in Pi and calculated total	Sum of aerators running in each zone during each day of the condensate treatment performance test	24-hour average
ASB Total Aerator hp-hrs	Readout in Pi or calculated value	Total daily hp-hrs = Sum for all aerators (hp x daily runtime, hrs)	24-hour total

3.3 SAMPLE COLLECTION AND TESTING

The following subsections describe sampling conducted for purposes of demonstrating compliance with the foul condensate collection and treatment requirements of Subpart S and the RSC testing conducted in accordance with SCDHEC's Order. Table 3-2 contains an overall sampling matrix for the liquid sampling proposed for the IPT, and Appendix A contains detailed sampling matrices.

Table 3-2
Proposed Condensate Collection and Treatment IPT Sampling Matrix
New-Indy Catawba, SC Mill
Green shading indicates monitoring to be conducted per DHEC order that is not required by Subpart S

Sample Location	Sampling Start Date	Sampling End Date	Number of Daily Samples	Analytes Tested	Who Will Collect Samples?	Who Will Analyze Samples?
Foul Condensate Collection Tank to Hardpipe (also representative of Foul Condensate to Steam Stripper)	14-Jun-2021	27-Jun-2021	(3) per day	Methanol, NCASI MeOH-94.03	Catawba Mill Lab Technicians	ALS Kelso
	28-Jun-2021	2-Jul-2021	(1) per day	Total HAPs; NCASI HAPS-99.01	Catawba Mill Lab Technicians	ALS Kelso
	28-Jun-2021	2-Jul-2021	(2) per day	Methanol, NCASI MeOH-94.03	Catawba Mill Lab Technicians	ALS Kelso
	28-Jun-2021	2-Jul-2021	(3) per day	COD	Catawba Mill Lab Technicians	Pace Analytical
	28-Jun-2021	2-Jul-2021	(3) per day	Methyl Mercaptan (MMC)	Catawba Mill Lab Technicians	To Be Determined
	28-Jun-2021	2-Jul-2021	(3) per day	Hydrogen sulfite (H_2S)	Catawba Mill Lab Technicians	
Steam Stripper Outlet	28-Jun-2021	2-Jul-2021	(3) per day	Methanol, NCASI MeOH-94.03	Catawba Mill Lab Technicians	ALS Kelso
	28-Jun-2021	2-Jul-2021	(3) per day	MMC	Catawba Mill Lab Technicians	To Be Determined
	28-Jun-2021	2-Jul-2021	(3) per day	H_2S	Catawba Mill Lab Technicians	
ASB Inlet Wastewater Stream	28-Jun-2021	2-Jul-2021	(1) per day	Total HAPs; NCASI HAPS-99.01	Catawba Mill Lab Technicians	ALS Kelso
	28-Jun-2021	2-Jul-2021	(1) per day	Liquid Temperature	Catawba Mill Lab Technicians	Catawba Mill Lab Technicians
	28-Jun-2021	2-Jul-2021	(1) per day	COD	Catawba Mill Lab Technicians	Pace Analytical
	28-Jun-2021	2-Jul-2021	(3) per day	MMC	Catawba Mill Lab Technicians	To Be Determined
	28-Jun-2021	2-Jul-2021	(3) per day	H_2S	Catawba Mill Lab Technicians	
ASB Samples: Zone 1 Center and Outlet; Zone 2 Center and Outlet; Zone 3 Center[a]	28-Jun-2021	2-Jul-2021	(1) per day	Methanol, NCASI MeOH-94.03	Arcadis/TRC	NCASI
	28-Jun-2021	2-Jul-2021	(1) per day	Liquid Temperature	Arcadis/TRC	Catawba Mill Lab Technicians
	28-Jun-2021	2-Jul-2021	(1) per day	MLVSS	Arcadis/TRC	Catawba Mill Lab Technicians
ASB Effluent (Zone 3 Outlet)	28-Jun-2021	2-Jul-2021	(1) per day	Methanol, NCASI MeOH-94.03	Catawba Mill Lab Technicians	NCASI
	28-Jun-2021	2-Jul-2021	(1) per day	Liquid Temperature	Catawba Mill Lab Technicians	Catawba Mill Lab Technicians
	28-Jun-2021	2-Jul-2021	(1) per day	Soluble BOD_5	Catawba Mill Lab Technicians	Catawba Mill Lab Technicians
	28-Jun-2021	2-Jul-2021	(3) per day	MMC	Catawba Mill Lab Technicians	To Be Determined
	28-Jun-2021	2-Jul-2021	(3) per day	H_2S	Catawba Mill Lab Technicians	

[a] Pending results of grid sampling and the tracer study anticipated prior to the IPT, there may be more or less than the anticipated three zones. The Mill will provide an update to SCDHEC prior to the IPT, as necessary. Additionally, if the results of the grid study show that there is no significant variation between samples collected at the center and outlet of the treatment zones, only the outlet of the zones will be monitored during the IPT and subsequent quarterly sampling events for performance testing due to the relative increased safety and ease of access of obtaining samples from these points.

3.3.1 Condensate Collection Sampling

During the IPT, the Catawba Mill lab technicians will collect grab samples from the outlet of the Foul Condensate Collection tank three times a day for the full duration of the performance test (19 days). For the first 14 days of the performance test, samples will be composited at the lab prior to analysis, and each day will be considered a test run. For the remaining 5 days, each of the three daily samples will be analyzed individually, and sample results will be averaged for the purposes of condensate collection calculations. Samples will be shipped to the laboratories at least once every seven days for analysis, and results will be provided to the Mill and ALL4.

3.3.1.1 Methanol – NCASI MeOH-94.03

Samples will be collected three times daily from the sampling locations identified in Table 3-2 in accordance with the requirements of NCASI MeOH 94.03 test method, which is included in Appendix B. Samples must be collected in 40 milliliter (mL) glass vials, with zero headspace. ALS will provide sample vials to the Mill to use for sample collection. Two vials will be filled for every sample that is collected; one to be sent to the lab for analysis, and one to be retained by the Mill as a back-up in case the original sample is lost or damaged. The pH and temperature for each sample will be measured upon collection and recorded on the chain of custody (COC) form provided by ALS. (Note: If there is headspace greater than the size of a pea, additional sample will be added). Samples will be stored in a refrigerator between 0 and 6 ºC until they are shipped for analysis. Samples must be shipped overnight, in a cooler on ice and must arrive at the lab within 0-6 ºC. Sample shipment will be coordinated with ALS to ensure someone will be present to receive the samples on the day they arrive.

3.3.1.2 Acetaldehyde, Methanol, Methyl Ethyl Ketone, Propionaldehyde – NCASI-HAPS-99.01

During the last week of the IPT, samples will be collected at the sampling locations and frequencies identified in Table 3-2 in accordance with the requirements of NCASI MeOH 99.01 test method, which is included in Appendix B. Samples must be collected in 40 milliliter (mL) glass vials, with zero headspace. ALS will provide sample vials to the Mill to use for sample

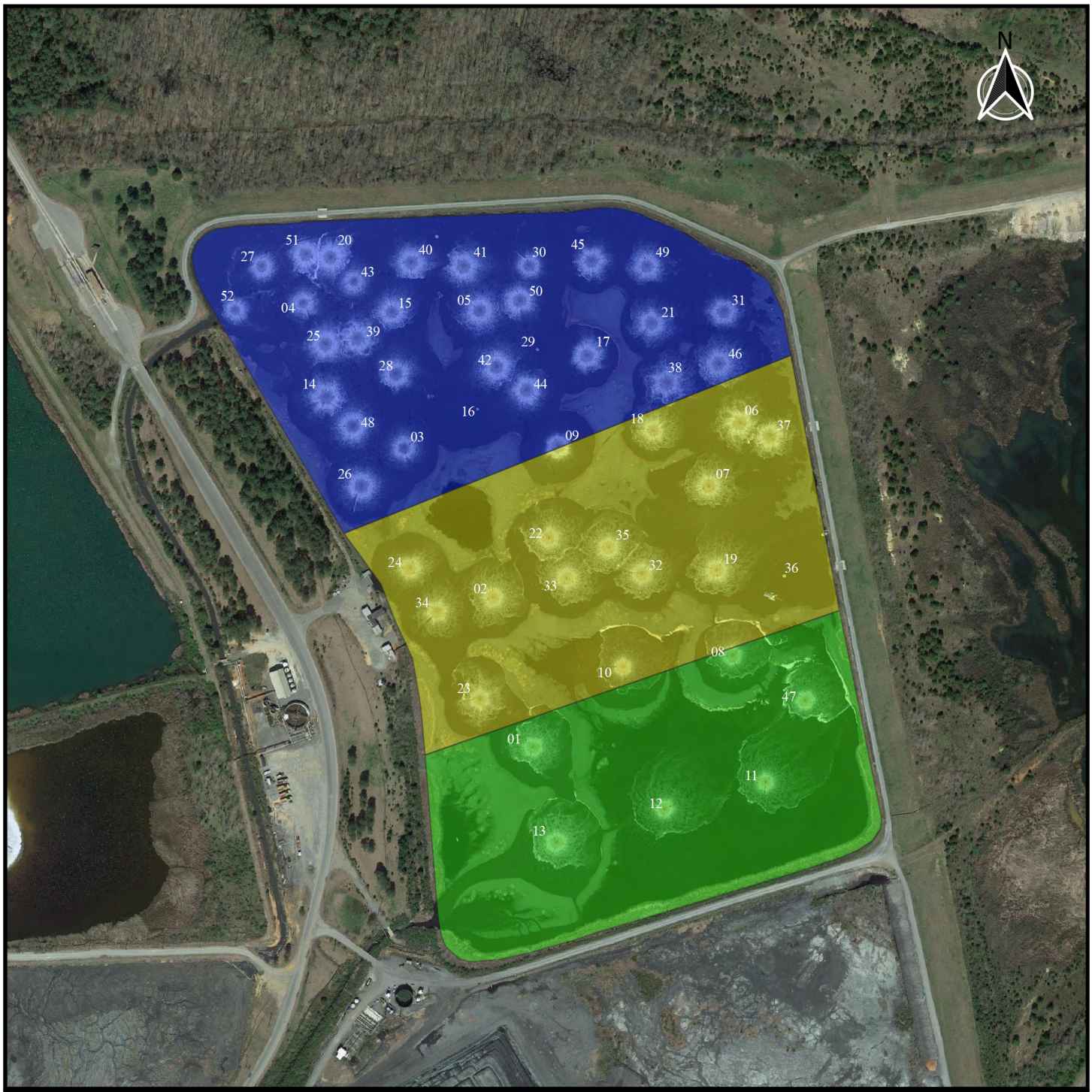
collection. Two vials will be filled for every sample that is collected; one to be sent to the lab for analysis, and one to be retained by the Mill as a back-up in case the original sample is lost or damaged. The pH and temperature for each sample will be measured upon collection and recorded on the chain of custody (COC) form provided by ALS. Drops of acid will need to be added upon sample collection until the sample reaches a pH of 2-3. The sampler will then fill the vial to zero headspace (Note: If there is headspace greater than the size of a pea, additional sample will be added). Samples will be stored in a refrigerator between 0 and 6 ºC until they are shipped for analysis. Samples must be shipped overnight, in a cooler on ice and must arrive at the lab within 0-6 ºC. Sample shipment will be coordinated with ALS to ensure someone will be present to receive the samples on the day they arrive. Note that only the methanol results from this analysis will be used for purposes of determining compliance with condensate collection requirements of Subpart S. The remaining data will be used in the calculations for condensate treatment, as discussed in Section 5.2.

3.3.2 Condensate Treatment Sampling

3.3.2.1 ASB Sampling

Based on observation of flow patterns within the ASB, the Mill believes the ASB to be a non-thoroughly mixed basin. As a result, the ASB will likely be mathematically subdivided into a series of zones for the purposes of the IPT and subsequent performance testing. The Mill plans to conduct a grid study and a tracer study of the ASB prior to the IPT to confirm that the ASB is non-thoroughly mixed and, if so, to mathematically subdivide the ASB into zones for the purposes of the condensate treatment calculations. The Mill has assumed that the ASB will be subdivided into three zones, approximately as shown in Figure 3-2. The Mill will submit updated information to SCDHEC following the tracer study, as needed.

Sampling locations within the ASB were determined using guidance from the Guidance Document and with respect to where future quarterly performance test samples would be obtained. For samples collected from the ASB, the Mill will use a boat or a drone. If the identified ASB sample points cannot be safely accessed by a boat, a drone with a sample baler



Zone 1
Zone 2
Zone 3

0 75 150 225 300 m

Figure 3-2
Anticipated ASB
Zones

New-Indy Catawba
Catawba, SC

Aerial Imagery courtesy of Google Satellite © Maxar Technologies, Orbis Inc, USDA Farm Service Agency, York County Government, SC

will be used to collect the samples. The drone will be operated by Arcadis. Once the drone has collected a sample from a given sample location, the drone will return to shore where the TRC technician will measure temperature of the sample and fill sample vials and containers for the analyses to be conducted. The Guidance Document suggests the following sampling locations in order to accurately characterize the concentration of the target compound (methanol):

- ASB Inlet;
- ASB Effluent;
- Approximate center of each of the three zones; and/or
- Outlet of each of the three zones.

The Guidance Document advises to avoid sampling edge, bottom, or surface effects. During grid and tracer studies conducted prior to the IPT, the Mill will determine whether there is significant variation between the center and outlet of the mixing zones. If no significant variation is observed, the locations at the outlet of the mixing zones will be used for the IPT and subsequent quarterly sampling events for performance testing due to the relative increased safety and ease of access of obtaining samples from these points.

3.3.2.2 Steam Stripper Sampling

Samples will be collected at the inlet and outlet of the Steam Stripper three times a day during the last week of the IPT and will be analyzed individually for methanol via NCASI MeOH 94.03.

3.3.3 Reduced Sulfur Compounds Sampling

Per the Order issued by DHEC, samples will be collected at the locations and frequencies described in Table 3-2 and analyzed for MMC and H_2S. As discussed in Section 1.2, the Mill is not certain at this time which test method(s) will be used for this testing. The sampling procedures for each test method are summarized in the following subsections.

3.3.3.1 NCASI Method RSC 02-02

Method RSC 02-02, including sample collection procedures, is provided in Appendix B. The sample pH and temperature will be determined and recorded on the chain of custody (COC) form specifically tailored for the RSC, provided in Appendix D. The aliquot used for determining temperature and pH will be discarded and a fresh portion of sample will be collected.

Sample vials will be provided by the lab conducting the RSC analysis. The vials contain preservative as delivered by the laboratory and must not be overfilled. The sampler must leave approximately 1 mL of headspace for addition of preservation stocks. Once the preservative is added, the sampler will then fill the vial to zero headspace (Note: If there is headspace greater than the size of a pea, additional sample will be added). For the grab sampling locations, the sampler will collect four aliquots of each sample using 40 mL amber vials. At each sampling point, two vials will be used for analysis (one for MMC and one for H_2S), and two vials will be held at the Mill as backups. Each sample will be preserved as discussed in the following subsections; samples will be stored and shipped at 4°C using ice packs.

3.3.3.1.1.1 MMC Sample Preservation

Per Method RSC-02.02, Section 8.2.1, each of the two vials collected for MMC analysis (including one backup vial) will be prefilled with 120 g of ascorbic acid. The sampler will fill the vial up to 38-39 mL and then will add 300 µL of phosphoric acid solution using a plastic pipette. The cap to the vial will then be secured and the vial mixed thoroughly. The sampler will then use pH test strips to verify that the pH is below 3. The final adjusted pH and volume of phosphoric acid used for the adjustment are then recorded on the COC for RSC. The remaining vial is adjusted using the same amount of phosphoric acid solution.

3.3.3.1.2 H_2S Sample Preservation

Per Method RSC-02.02, Section 8.2.2, each of the two vials collected for H2S analysis (including one backup vial) will be prefilled with 5 mL of a zinc acetate/sodium hydroxide (NaOH) solution as prepared by the laboratory. The sampler will add the process water sample to the vial up to approximately 39 mL, cap and mix thoroughly. The sampler must then verify

that the pH is greater than 10. If the pH is not in this range, it will be adjusted by adding portions of 1N NaOH solution using plastic pipettes. The sampler will then record the final pH and the volume of the 1N NaOH used for the adjustment on the COC for RSC. The remaining vial will be adjusted using the same amount of 1N NaOH solution.

3.3.3.2 H_2S Only – Hach 6000 Onsite Analyzer

Hach documentation describing the procedures for sampling and analysis for the Hach 6000 method are provided in Appendix B. Sample pH and temperature will be determined and recorded for each sample collected. The ASB effluent sample may be filtered prior to analysis if the solids content appears too high for the analyzer. A color blank will be needed for each sample taken.

Samples will be collected in clean glass or plastic bottles with tight-fitting caps. The bottle will be completely filled and the cap will be tightened immediately. 10 mL of sample will be transferred to a 10-mL sample cell for analysis. Samples will be analyzed within two hours of collection if possible but will be analyzed during the same day as collection.

3.3.3.3 ALS Sulfur Liquid Method (Derived from ASTM D 5504)

In lieu of NCASI RSC 02-02 method, ALS has developed an in-house method derived from ASTM D 5504 using a gas chromatograph equipped with a sulfur chemiluminescence detector (SCD). If the Mill selects this method for MMC and H_2S analysis, two to three 40 mL glass vials with zero headspace will be collected at the sample locations and frequencies specified in Table 3-2. Samples collected from the ASB influent and effluent will be filtered to remove sediment.

3.3.4 Sample Collection Methodology

This section summarizes sample container size requirements, sample preparation (i.e. required preservatives), sample storage temperature, sample hold times, and additional details on sample collection procedures.

3.3.4.1 MLVSS – U.S. EPA Method 1684

Samples collected from within the ASB will be analyzed for MLVSS content via U.S. EPA Method 1684 by the Catawba Mill Lab Technicians. Sufficient sample volume for conducting the test will be collected via the drone. Samples will be stored in a refrigerator at 4°C until they are analyzed, and all samples will be analyzed within seven days of collection.

3.3.4.2 Acetaldehyde, Methanol, Methyl Ethyl Ketone, Propionaldehyde – NCASI-HAPS-99.01

Samples will be collected from the sampling locations and frequencies identified in Table 3-2 in accordance with the requirements of NCASI MeOH 99.01 test method, which is included in Appendix B. Samples must be collected in 40 milliliter (mL) glass vials, with zero headspace. ALS will provide sample vials to the Mill to use for sample collection. Two vials will be filled for every sample that is collected; one to be sent to the lab for analysis, and one to be retained by the Mill as a back-up in case the original sample is lost or damaged. The pH and temperature for each sample will be measured upon collection and recorded on the chain of custody (COC) form provided by ALS. All samples collected from the ASB, including ASB inlet wastewater samples, will need to be preserved with 1N hydrochloric acid (HCl) or sulfuric acid (H_2SO_4) that will be provided by ALS. Drops of acid will need to be added upon sample collection until the sample reaches a pH of 2-3. The sampler will then fill the vial to zero headspace (Note: If there is headspace greater than the size of a pea, additional sample will be added). Samples will be stored in a refrigerator between 0 and 6 ºC until they are shipped for analysis. Samples must be shipped overnight, in a cooler on ice and must arrive at the lab within 0-6 ºC. Sample shipment will be coordinated with ALS to ensure someone will be present to receive the samples on the day they arrive.

3.3.4.3 Methanol – NCASI MeOH-94.03

Samples will be collected from the sampling locations and frequencies identified in Table 3-2 in accordance with the requirements of NCASI MeOH 94.03 test method, which is included in Appendix B. Samples must be collected in 40 milliliter (mL) glass vials, with zero headspace.

ALS will provide sample vials to the Mill to use for sample collection. Two vials will be filled for every sample that is collected; one to be sent to the lab for analysis, and one to be retained by the Mill as a back-up in case the original sample is lost or damaged. The pH and temperature for each sample will be measured upon collection and recorded on the chain of custody (COC) form provided by ALS. All samples collected from the ASB, including ASB inlet wastewater samples, will need to be preserved with 1N hydrochloric acid (HCl) or sulfuric acid (H_2SO_4) that will be provided by ALS. Drops of acid will need to be added upon sample collection until the sample reaches a pH of 2-3. (Note: If there is headspace greater than the size of a pea, additional sample will be added). Samples will be stored in a refrigerator between 0 and 6 ºC until they are shipped for analysis. Samples must be shipped overnight, in a cooler on ice and must arrive at the lab within 0-6 ºC. Sample shipment will be coordinated with ALS to ensure someone will be present to receive the samples on the day they arrive.

3.3.4.4 BOD_5 – Standard Methods 5210

Soluble (filtered) BOD_5 will be monitored at the ASB effluent every day during the condensate treatment performance test by Standard Methods 5210. A composite sampler will be used at the ASB effluent to collect samples. Ice will be applied at the composite sampler to chill samples upon collection. Catawba Lab Technicians will collect sufficient sample for the necessary dilutions and will set up the samples within the required 48-hour hold time. Note that for composite samples, the 48-hour hold time begins when the composite sampler begins sampling such that once a 24-hour composite sample is collected, 24 hours of the hold time is remaining. Samples will be pH-adjusted in the laboratory as needed prior to analysis.

3.3.4.5 COD – Standard Methods 5220

Soluble (filtered) COD of the ASB influent and the Foul Condensate will be monitored every day during the condensate treatment performance test by Standard Methods 5220. A composite sample will be taken of the ASB influent, and a grab sample will be taken of the Foul Condensate stream. Catawba Lab Technicians will collect sufficient sample volume for the test. Samples will be provided to Pace Analytical for testing.

3.3.4.6 Reduced Sulfur Compounds

Per the Order issued by SCDHEC, samples will be collected for MMC and H_2S analysis during the condensate treatment performance test. All samples collected for MMC and H_2S analysis will be grab samples. As discussed in Section 1.2, the Mill is not certain at this time which test method(s) will be used for this testing, however proper sample collection methods will be followed for the test method(s) selected.

3.3.5 Sample Shipping and Storage

The MeOH and HAP samples will be stored on ice or in a controlled temperature refrigerator prior to shipping at the temperatures indicated in Section 3.3. Vial samples should be carefully packaged in foam sleeves when shipping. Samples will ship via overnight delivery under chain of custody to the laboratory for analysis (ALS – Kelso, WA). Sample holding time is 14 days for NCASI HAPS-99.01 and 30 days for NCASI MeOH-94.03. Sample shipment and receipt times should be coordinated with ALS. Samples will not be shipped on Fridays or days prior to holidays unless ALS has confirmed that someone will be able to receive the samples upon arrival.

Samples collected for MMC and H2S analysis per the Order issued by SCDHEC will be stored and shipped in accordance with the requirements of the test method(s) selected, as applicable. The Mill anticipates that samples will be stored on ice or in a controlled temperature refrigerator prior to shipping in coolers overnight.

3.3.6 Sample Analysis Methodology

The following sections present a summary of the test methods to be utilized for the liquid samples to be collected as part of this liquid sampling effort.

3.3.6.1 Methanol – NCASI MeOH-94.03

Methanol will be measured using the NCASI Method DI/MEOH 94.03 - Methanol in Process Liquids by gas chromatography/flame ionization detection (GC/FID), May 2000 in accordance

with 40 CFR §63.457(c)(3)(ii). This method was validated on February 24, 1998 to meet the U.S. Environmental Protection Agency (U.S. EPA) Method 301 criteria for measuring methanol in process liquids from the sources specified in the method. The NCASI MeOH-94.03 test method is provided in Appendix B.

3.3.6.2 Acetaldehyde, Methanol, Methyl Ethyl Ketone, Propionaldehyde – NCASI HAPS-99.01

Total HAP will be measured using the NCASI HAPS-99.01 Method, February 2000, by GC/FID. The method has been validated in two laboratories using U.S. EPA Method 301, Field Validation of Emission Concentrations from Stationary Sources (Appendix A to 40 CFR 63) and is a validated method. The NCASI HAP-99.01 test method is provided in Appendix B. Foul Condensate samples will be analyzed by this method during the last week of the IPT for purposes of calculating the "r" factor for the foul condensate treatment calculations, as discussed in Section 5.2. Additionally, the methanol results from this test method will be used for purposes of calculating methanol collection, as discussed in Section 5.1.

3.3.6.3 Reduced Sulfur Compounds

The reduced sulfur compounds MMC and H_2S will be measured using one of the methods discussed in previous sections. As stated previously, this analysis is not required for Subpart S but is included in this IPT plan per the Order issued by SCDHEC.

3.3.6.4 BOD_5 – Standard Method 5210

Soluble (filtered) BOD_5 will be measured using Standard Method 5210. This method has been approved by U.S. EPA.

3.3.6.5 COD – Standard Method 5220

Soluble (filtered) COD will be measured using Standard Method 5220. This method has been approved by U.S. EPA.

3.3.6.6 MLVSS – U.S. EPA Method 1684

MLVSS will be measured using U.S. EPA Method 1684.

4. QA/QC PROGRAM

4.1 QA/QC PROCEDURES

The test program shall incorporate the appropriate QA/QC procedures specified in respective test methods (NCASI Method DI/MEOH 94.03, NCASI Method HAPS-99.01, Standard Methods 5210, and Standards Methods 5220). The complete NCASI test methods are provided in Appendix B. The following sections summarize the overall data quality objectives and internal and external QA for the condensate program.

4.2 DATA QUALITY OBJECTIVES

Quality assurance procedures are designed to assess and document data accuracy, precision, and completeness. Accuracy is the percent difference between a measurement and a reference or standard value. Precision is a measure of mutual agreement of replicate measurements. Completeness is a measure of the amount of valid data compared to the amount that was expected to be obtained under correct operating conditions.

4.3 INTERNAL QA PROGRAM

Test data precision will be measured using replicate sample runs and analysis. For each week of foul condensate collection and treatment testing for methanol, one duplicate sample will be analyzed for each sample point. The Catawba Mill Laboratory Technicians will follow Mill procedures regarding QA for BOD_5 samples in accordance with Standard Methods 5210, such as running blanks, standards, and duplicate samples at specified frequencies.

4.4 EXTERNAL QA PROGRAM

Test data accuracy for methanol and HAP testing will be determined through preparation of field matrix spikes. The matrix spike is a separate aliquot of the sample spiked with known concentrations of the analytes of interest. It is analyzed to determine, including the matrix interferences, if the procedure is working within established control limits. It is carried through the complete preparation and analytical procedure. The recoveries of the spiked analytes are

evaluated to determine accuracy in a given matrix. ALS will prepare matrix spikes as per their operating protocol and the selected analytical method. The lab will provide the appropriate number of trip blanks with the shipped bottles and the Mill will return those with the collected liquid samples.

Test data accuracy for COD testing will be determined using replicate sample runs and analysis. Pace will follow laboratory procedures regarding QA for COD samples in accordance with Standard Methods 5220, such as running blanks, standards, and duplicate samples at specified frequencies.

Test data accuracy for RSC testing will be determined in accordance with the test method(s) selected and the practices of the contract laboratory conducting the analysis.

4.5 SAMPLE IDENTIFICATION AND CHAIN OF CUSTODY

The Mill technician(s) and TRC are responsible for collecting the samples and ensuring that the samples are accounted for and that proper custody procedures are followed. ALS will supply sample bottles and labels for all samples collected for methanol and HAP analysis. The Mill anticipates that the contract laboratory performing RSC testing will supply sample bottles and labels for all samples collected for RSC analysis.

4.6 PROCESS DATA QUALITY ASSURANCE

The Mill will establish continuous monitoring systems (CMS) for the process data parameters discussed in Section 3.2. CMS matrices, including thresholds for CMS downtime and the definition of good data quality, are provided in Appendix C.

5. DATA ANALYSIS AND CALCULATIONS

All data will be reviewed for validity and accuracy. This section describes the proposed calculations that will be performed to determine compliance with the methanol collection and treatment requirements of Subpart S.

5.1 HAP COLLECTION CALCULATIONS

The Mill pulp production rate, condensate flow rate to the ASB and Steam Stripper in million gallons per day (MGD), and foul condensate methanol concentration will be used to calculate methanol collection in terms of lb HAP/ODTP, with HAP measured as methanol. Daily pulp production will be calculated as presented in Table 3-1. The 15-day average methanol collection will be calculated using the equation below, in accordance with 40 CFR §63.457(j).

$$15\ day\ average\ lb\ \frac{HAP}{ODTP} = lb\ \frac{HAP}{ODTP}\ to\ ASB + lb\ \frac{HAP}{ODTP}\ to\ Steam\ Stripper$$

Where:

$$15\ day\ average\ \ lb\frac{HAP}{ODTP}\ to\ ASB$$

$$= \frac{\sum_{i=1}^{15}[Methanol\ Concentration\ (ppm) \times Flow\ to\ ASB\ (MGD)\ \times 8.34\ \frac{lb}{gal}]}{\sum_{i=1}^{15} ODTP}$$

$$15\ day\ average\ \ lb\frac{HAP}{ODTP}\ to\ Steam\ Stripper$$

$$= \frac{\sum_{i=1}^{15}[Methanol\ Concentration\ (ppm) \times Flow\ to\ Steam\ Stripper\ (MGD)\ \times 8.34\ \frac{lb}{gal}]}{\sum_{i=1}^{15} ODTP}$$

The 15-day rolling average lb HAP/ODTP will be calculated for days 15-19 of the IPT. Following the IPT, the Mill will develop a methanol concentration factor determined from the

methanol concentration data collected prior to and during the IPT and documented in the IPT report. The methanol concentration factor will be re-established or confirmed during subsequent quarterly performance testing.

5.2 HAP TREATMENT CALCULATIONS

The total HAP treatment will be calculated daily as the sum of the lb HAP/ODTP treated in the ASB and the lb HAP/ODTP (measured as methanol) treated by the Steam Stripper, as discussed in the following subsections. The lb HAP/ODTP treated results for the five days of the treatment IPT will be averaged to determine compliance with the condensate treatment requirements of Subpart S. The IPT report submitted to DHEC following the IPT will include a detailed description of the calculation methods used. This section also describes calculations to be used for monitoring ongoing compliance with the treatment requirements of Subpart S.

5.2.1 ASB Treatment Calculations

HAP treatment in the ASB on a lb HAP/ODTP basis will be determined using the calculations provided in Appendix C to Part 63 and 40 CFR §63.457(l). The fraction of methanol biodegraded (Fbio) in the ASB will be calculated per Appendix C, as well as the ratio of the sum of acetaldehyde, methyl ethyl ketone, and propionaldehyde mass to the ratio of methanol mass in the foul condensate stream, and then applied to the 15-day rolling average methanol collection in lb HAP/ODTP to determine the HAP treated, per the equations below:

$$r = \frac{F(nonmethanol), \frac{lb}{ODTP}}{F(methanol), \frac{lb}{ODTP}}$$

$$lb\,\frac{HAP}{ODTP}\,Treated\ in\ ASB = lb\,\frac{HAP}{ODTP}\,to\ ASB\ (15\ day\ average)\ \times \left[\frac{Fbio(Methanol)}{(1 + 1.087 \times r)}\right]$$

The daily lb HAP/ODTP treated will be calculated for the five days of the condensate treatment performance test. The Mill plans to use published meteorological data from the same month of

the previous year for the Fbio calculations or June 2021 meteorological data if it is published in time to be used in the report.

Following the IPT, the Mill plans to establish a site-specific operating parameter for monitoring continuous compliance with the ASB condensate treatment portion of the requirements of Subpart S. The Mill anticipates that the proposed operating parameter will either be aerator horsepower or COD to aerator horsepower ratio (COD/HP). In the IPT report submitted to DHEC following the IPT, the Mill will provide the rationale for the selected monitoring parameter, the operating parameter value, monitoring frequency, averaging time, all data and calculations used to develop the value and a description of why the value, monitoring frequency, and averaging time demonstrate continuous compliance with the condensate treatment standard. The Mill will continue to operate according to the proposed parameter(s) following the IPT while awaiting approval from SCDHEC.

5.2.2 Steam Stripper Treatment Calculations

The methanol removed in the Steam Stripper will be calculated according to the equation below for each set of samples collected:

$$lb\,\frac{HAP}{ODTP}\ Treated\ in\ Steam\ Stripper = \frac{Steam\ Stripper\ Inlet, lbs\ MeOH - Steam\ Stripper\ Outlet, lbs\ MeOH}{ODTP}$$

Following the IPT, the Mill plans to establish a correlation between ESFR and methanol removal efficiency for purposes of demonstrating continuous compliance with the treatment requirements of Subpart S. The mass percent HAP reduction across the Steam Stripper for each set of samples collected (three samples per day during the five days of the treatment test) will be calculated as follows:

$$Ri = \{[E(bi) - E(ai)] \div E(bi) \times 100\}$$

Where:

Ri = Methanol removal efficiency of the Steam Stripper, percent

E(bi) = Mass flow rate of total methanol in the liquid stream entering the Steam Stripper for each hour “i" (lb/hr)

E(ai) = Mass flow rate of total methanol in liquid stream exiting the Steam Stripper for each hour “i" (lb/hr)

ESFR will be calculated during each hour of sampling according to the equation below:

$$ESFRi = [Msi - Mf(STi)] \times \frac{(Tsc - Tcf)/100}{Vb(SFTi)}$$

Where:

MSi = Mass steam rate entering the Steam Stripper for each hour “i" (lbs/hr)

Mf(SFTi) = Mass rate of the condensate liquid stream entering the Steam Stripper for each hour “i" (lbs/hr)

Tsc = Temperature of stripped condensate (°F)

Tcf = Temperature of condensate feed to the stripper (°F)

Vb(STFi) = Volumetric flow rate of the liquid stream entering the Steam Stripper for each hour “i" (gph)

In the IPT report submitted to DHEC following the IPT, the Mill will provide the calculated ESFR values and their correlation to methanol removal in the Steam Stripper, as well as the Mill’s proposal for using this correlation to demonstrate continuous compliance with the methanol treatment requirements of Subpart S.

APPENDIX A – SAMPLING MATRIX

Table A-1
Condensate Collection and Treatment IPT Sampling Matrix
New-Indy Catawba, SC Mill

Green shading indicates monitoring to be conducted per DHEC Order that is not required by Subpart S

Description of Source/ Location of Sample	Analyte/ Pollutant	Test/Sampling Method	Sampling Start Date	Sampling End Date	Type of Sample (Grab/ Composite Sampler)	No. of Days Sampled	Samples Collected per Day	Field Back-Up Samples	Weekly Duplicate Analysis	Sample Bottles Per Sample Needed[a]	Total No. of Bottles Needed[b]	Composite Daily Samples Before Analysis in Lab (Y/N)?	Total No. of Analyses Needed[c]	Method Reporting Limit (MRL)	Container Size	Preservative Added	Hold Time	Sample Storage Requirements	Quality Assurance/ Quality Control	Data to Collect with Sample/Comments
Foul Condensate to Hardpipe (also representative of Foul Condensate to Steam Stripper)	Methanol[d]	NCASI MeOH-94.03	14-Jun-21	27-Jun-21	Grab	19	3	1	1	2	116	N	21	0.5 mg/L	40 mL glass vials, zero headspace required	None	30 days	<6ºC	In accordance with test method	Liquid Temperature, pH
	Methanol, Acetaldehyde, Methyl Ethyl Ketone, Propionaldehyde	NCASI HAPS-99.01	28-Jun-21	2-Jul-21	Grab	5	1	1	1	2	11	N	6	1 mg/L	40 mL glass vials, zero headspace required	None	15 days	<4ºC	In accordance with test method	
	Methanol	NCASI MeOH-94.03	28-Jun-21	2-Jul-21	Grab	5	2	1	1	2	21	N	11	0.5 mg/L	40 mL glass vials, zero headspace required	None	30 days	<6ºC	In accordance with test method	
	COD	Standard Methods 5220	28-Jun-21	2-Jul-21	Grab	5	1	0	1	1	6	N	6	Depends on dilutions used	Sufficient volume for dilutions	None	28 days	<4ºC	In accordance with test method	
	Methyl Mercaptan (MMC) - One of the methods listed will be used	Method RSC-02.02	28-Jun-21	2-Jul-21	Grab	5	3	1	1	2	31	N	16	20 ug S/L	Two 40 mL amber glass vials, zero headspace required	To container: 120 g ascorbic acid Upon Collection: 300 uL phosphoric acid until pH <3 (record amount of acid and final pH on COC)	14 days	<4ºC	In accordance with test method	
		ALS Sulfur Liquid	28-Jun-21	2-Jul-21	Grab	5	3	1	1	2	31	N	16	1.2 ug/L	Two 40 mL glass vials, zero headspace	None	N/A	<4ºC	In accordance with test method	
	Hydrogen Sulfide (H_2S) - One of the methods listed will be used	Method RSC-02.02	28-Jun-21	2-Jul-21	Grab	5	3	1	1	2	31	N	16	20 ug S/L	Two 40 mL amber glass vials, zero headspace required	To container: 5 mL of zinc acetate/sodium hydroxide Upon collection: 1 N NaOH until pH is 9-11 (record amount of NaOH added and final pH on COC)	14 days	<6ºC	In accordance with test method	
		Hach 6000 Analyzer	28-Jun-21	2-Jul-21	Grab	5	3	0	1	1	16	N	16	N/A	Clean glass or plastic bottle with tight-fitting cap	N/A	Immediately upon collection, same day	N/A	In accordance with test method	
		ALS Sulfur Liquid	28-Jun-21	2-Jul-21	Grab	5	3	1	1	2	31	N	16	0.84 ug/L	Two 40 mL glass vials, zero headspace	None	N/A	<4ºC	In accordance with test method	
Steam Stripper Outlet	Methanol	NCASI MeOH-94.03	28-Jun-21	2-Jul-21	Grab	5	3	1	1	2	31	N	16	0.5 mg/L	40 mL glass vials, zero headspace required	None	30 days	<6ºC	In accordance with test method	Liquid Temperature, pH
	MMC - One of the methods listed will be used	Method RSC-02.02	28-Jun-21	2-Jul-21	Grab	5	3	1	1	2	31	N	16	20 ug S/L	Two 40 mL amber glass vials, zero headspace required	To container: 120 g ascorbic acid Upon Collection: 300 uL phosphoric acid until pH <3 (record amount of acid and final pH on COC)	14 days	<4ºC	In accordance with test method	
		ALS Sulfur Liquid	28-Jun-21	2-Jul-21	Grab	5	3	1	1	2	31	N	16	1.2 ug/L	Two 40 mL glass vials, zero headspace	None	N/A	<4ºC	In accordance with test method	
	H_2S - One of the methods listed will be used	Method RSC-02.02	28-Jun-21	2-Jul-21	Grab	5	3	1	1	2	31	N	16	20 ug S/L	Two 40 mL amber glass vials, zero headspace required	To container: 5 mL of zinc acetate/sodium hydroxide Upon collection: 1 N NaOH until pH is 9-11 (record amount of NaOH added and final pH on COC)	14 days	<6ºC	In accordance with test method	
		Hach 6000 Analyzer	28-Jun-21	2-Jul-21	Grab	5	3	0	1	1	16	N	16	N/A	Clean glass or plastic bottle with tight-fitting cap	N/A	Immediately upon collection, same day	N/A	In accordance with test method	
		ALS Sulfur Liquid	28-Jun-21	2-Jul-21	Grab	5	3	1	1	2	31	N	16	0.84 ug/L	Two 40 mL glass vials, zero headspace	None	N/A	<4ºC	In accordance with test method	
ASB Influent	COD	Standard Methods 5220	28-Jun-21	2-Jul-21	Composite	5	1	0	1	1	6	Automatic Sampler	6	Depends on dilutions used	Sufficient volume for dilutions	N/A	28 days	<4ºC	In accordance with test method	
	Methanol, Acetaldehyde, Methyl Ethyl Ketone, Propionaldehyde	NCASI HAPS-99.01	28-Jun-21	2-Jul-21	Grab	5	1	1	1	2	11	N	6	1 mg/L	40 mL glass vials, zero headspace required	1 N HCl or H_2SO_4	15 days	<4ºC	In accordance with test method	Liquid Temperature, pH
	MMC - One of the methods listed will be used	Method RSC-02.02	28-Jun-21	2-Jul-21	Grab	5	1	1	1	2	11	N	6	20 ug S/L	Two 40 mL amber glass vials, zero headspace required	To container: 120 g ascorbic acid Upon Collection: 300 uL phosphoric acid until pH <3 (record amount of acid and final pH on COC)	14 days	<4ºC	In accordance with test method	
		ALS Sulfur Liquid	28-Jun-21	2-Jul-21	Grab	5	3	1	1	2	33	N	16	1.2 ug/L	Two 40 mL glass vials, zero headspace	None	N/A	<4ºC	In accordance with test method	
	H_2S - One of the methods listed will be used	Method RSC-02.02	28-Jun-21	2-Jul-21	Grab	5	1	1	1	2	41	N	6	20 ug S/L	Two 40 mL amber glass vials, zero headspace required	To container: 5 mL of zinc acetate/sodium hydroxide Upon collection: 1 N NaOH until pH is 9-11 (record amount of NaOH added and final pH on COC)	14 days	<6ºC	In accordance with test method	
		Hach 6000 Analyzer	28-Jun-21	2-Jul-21	Grab	5	1	0	1	1	6	N	6	N/A	Clean glass or plastic bottle with tight-fitting cap	N/A	Immediately upon collection, same day	N/A	In accordance with test method	
		ALS Sulfur Liquid	28-Jun-21	2-Jul-21	Grab	5	3	1	1	2	31	N	16	0.84 ug/L	Two 40 mL glass vials, zero headspace	None	N/A	<4ºC	In accordance with test method	

Table A-1
Condensate Collection and Treatment IPT Sampling Matrix
New-Indy Catawba, SC Mill

Green shading indicates monitoring to be conducted per DHEC Order that is not required by Subpart S

Description of Source/ Location of Sample	Analyte/ Pollutant	Test/Sampling Method	Sampling Start Date	Sampling End Date	Type of Sample (Grab/ Composite Sampler)	No. of Days Sampled	Samples Collected per Day	Field Back-Up Samples	Weekly Duplicate Analysis	Sample Bottles Per Sample Needed[a]	Total No. of Bottles Needed[b]	Composite Daily Samples Before Analysis in Lab (Y/N)?	Total No. of Analyses Needed[c]	Method Reporting Limit (MRL)	Container Size	Preservative Added	Hold Time	Sample Storage Requirements	Quality Assurance/ Quality Control	Data to Collect with Sample/Comments
Zone 1 Center and/or Outlet	Methanol	NCASI MEOH-94.03	28-Jun-21	2-Jul-21	Grab	5	1	1	1	2	11	N	6	0.5 mg/L	40 mL glass vials, zero headspace required	1 N HCl or H_2SO_4	30 days	<6ºC	In accordance with test method	Liquid Temperature, pH
	MLVSS	U.S. EPA Method 1684	28-Jun-21	2-Jul-21	Grab	5	1	0	1	1	6	N	6	Depends on dilutions used	Sufficient volume for dilutions	N/A	7 days	<4ºC	In accordance with test method	
Zone 2 Center and/or Outlet	Methanol	NCASI MEOH-94.03	28-Jun-21	2-Jul-21	Grab	5	1	1	1	2	11	N	6	0.5 mg/L	40 mL glass vials, zero headspace required	1 N HCl or H_2SO_4	30 days	<6ºC	In accordance with test method	
	MLVSS	U.S. EPA Method 1684	28-Jun-21	2-Jul-21	Grab	5	1	0	1	1	6	N	6	Depends on dilutions used	Sufficient volume for dilutions	N/A	7 days	<4ºC	In accordance with test method	
Zone 3 Center and/or Outlet	Methanol	NCASI MEOH-94.03	28-Jun-21	2-Jul-21	Grab	5	1	1	1	2	11	N	6	0.5 mg/L	40 mL glass vials, zero headspace required	1 N HCl or H_2SO_4	30 days	<6ºC	In accordance with test method	
	MLVSS	U.S. EPA Method 1684	28-Jun-21	2-Jul-21	Grab	5	1	0	1	1	6	N	6	Depends on dilutions used	Sufficient volume for dilutions	N/A	7 days	<4ºC	In accordance with test method	
ASB Effluent	Methanol	NCASI MEOH-94.03	28-Jun-21	2-Jul-21	Grab	5	1	1	1	2	11	N	6	0.5 mg/L	40 mL glass vials, zero headspace required	1 N HCl or H_2SO_4	30 days	<6ºC	In accordance with test method	Liquid Temperature, pH
	Soluble BOD_5	Standard Methods 5210	28-Jun-21	2-Jul-21	Composite	5	1	0	1	1	6	Automatic Sampler	6	Depends on dilutions used	Sufficient volume for dilutions	N/A	48 hours	<4ºC	In accordance with test method	Liquid Temperature, pH
	MMC - One of the methods listed will be used	Method RSC-02.02	28-Jun-21	2-Jul-21	Grab	5	1	1	1	2	11	N	6	20 ug S/L	Two 40 mL amber glass vials, zero headspace required	To container: 120 g ascorbic acid Upon Collection: 300 uL phosphoric acid until pH <3 (record amount of acid and final pH on COC)	14 days	<4ºC	In accordance with test method	
		ALS Sulfur Liquid	28-Jun-21	2-Jul-21	Grab	5	3	1	1	2	31	N	16	1.2 ug/L	Two 40 mL glass vials, zero headspace	None	N/A	<4ºC	In accordance with test method	
	H_2S - One of the methods listed will be used	Method RSC-02.02	28-Jun-21	2-Jul-21	Grab	5	1	1	1	2	11	N	6	20 ug S/L	Two 40 mL amber glass vials, zero headspace required	To container: 5 mL of zinc acetate/sodium hydroxide Upon collection: 1 N NaOH until pH is 9-11 (record amount of NaOH added and final pH on COC)	14 days	<6ºC	In accordance with test method	
		Hach 6000 Analyzer	28-Jun-21	2-Jul-21	Grab	5	1	0	1	1	6	N	6	N/A	Clean glass or plastic bottle with tight-fitting cap	N/A	Immediately upon collection, same day	N/A	In accordance with test method	
		ALS Sulfur Liquid	28-Jun-21	2-Jul-21	Grab	5	3	1	1	2	31	N	16	0.84 ug/L	Two 40 mL glass vials, zero headspace	None	N/A	<4ºC	In accordance with test method	

[a] Two sample bottles will be collected at each sampling event for methanol and HAPs samples; an original and a duplicate as back-up in the event of sample damage or loss. No back-up samples will be collected for BOD_5, COD, or MLVSS.

[b] For methanol and HAPs, total number of bottles needed = [(Number of days sampled) * (Samples collected per day) * (Sample bottles per sample)] + [(Number of weekly duplicate analysis samples) x (Number of weeks of study)]

[c] For methanol and HAPs, number of analyses needed = [(Number of days sampled) * (Samples collected per day)] + [Weekly duplicate analysis x Number of weeks of study)]. Back-ups will only be analyzed in the event of damage to the original sample. Back-ups can be discarded upon receipt of valid laboratory results.

[d] The three daily samples collected will be composited at the lab for one analysis per day.

APPENDIX B – LIQUID SAMPLING TEST METHODS

NCASI METHOD DI/MEOH-94.03

METHANOL IN PROCESS LIQUIDS AND WASTEWATERS BY GC/FID

NCASI
Southern Regional Center
May 2000

Acknowledgements

This method was prepared by Dr. MaryAnn Gunshefski, Senior Research Scientist, and Jim Stainfield, 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.

For more information about this method, contact:

MaryAnn Gunshefski, Ph.D.
Senior Research Scientist
NCASI Southern Regional Center
P.O. Box 141020
Gainesville, FL 32614
(352) 377-4708 ext. 244
mgunshefski@ncasi.org

For more information about NCASI publications, contact:

Publications Coordinator
NCASI
P.O. Box 13318
Research Triangle Park, NC 27709-3318
(919) 558-1999
publications@ncasi.org

National Council for Air and Stream Improvement, Inc. (NCASI). 2000. *Methods Manual - Methanol in process liquids and wastewaters by GC/FID*. Research Triangle Park, N.C.: National Council for Air and Stream Improvement, Inc.

© 2000 by the National Council for Air and Stream Improvement, Inc.

Disclaimer:

The mention of trade names or commercial products does not constitute endorsement or recommendation for use.

NCASI METHOD DI/MEOH-94.03

METHANOL IN PROCESS LIQUIDS AND WASTEWATERS BY GC/FID

1.0 Scope and Application

1.1 This method is used for the analysis of methanol (CAS # 67-56-1) in process liquid samples from pulp and paper mills by gas chromatography/flame ionization detection (GC/FID). This is an update of the NCASI Method DI/MEOH-94.02. An older version of this method was published in Appendix I of NCASI Technical Bulletin 684 as *Method for Methanol, Acetone, Acetaldehyde, and Methyl Ethyl Ketone in Liquid Samples*, and has been rewritten to conform with the contents and format established by the EMMC for EPA wastewater methods. This version includes only methanol, since methanol is the only compound for which the method has been validated at this time.

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

1.3 The method has been single laboratory validated using the United States Environmental Protection Agency (EPA) Method 301, *Field Validation of Emission Concentrations from Stationary Sources* (Appendix A to CFR 63), and is a validated method.

1.4 This method is applicable for detecting methanol in process liquids at the part per million (ppm) level.

1.5 This method is restricted to use by, or under the supervision of, analysts experienced in the use of gas chromatographs and skilled in the interpretation of chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 Summary of the Method

2.1 Samples are collected directly from the process liquid stream using an appropriate collection vessel. For sample streams which are extremely hot, a cooling coil is used to lower the temperature of the sample to below 160°F. Effluent samples must be preserved with acid to pH 2-3 upon collection. The samples are kept refrigerated until analysis.

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

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

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

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

2.5 Quality is assured through testing of the analytical systems. This is accomplished by using a second source reference material, calibration check samples and spike recovery samples. Method blanks, duplicates and matrix spikes should also be analyzed with each analytical batch to ensure data quality.

3.0 Definitions

3.1 The definitions below are specific to this method, but conform to common usage as much as possible.

3.1.1 Batch - grouping of samples, not more than 20

3.1.2 mg/L - milligrams per liter

3.1.3 May - This action, activity, or procedural step is neither required nor prohibited.

3.1.4 Must not - This action, activity, or procedural step is prohibited.

3.1.5 Must - This action, activity, or procedural step is required.

3.1.6 Should - This action, activity, or procedural step is suggested, but not required.

4.0 Interferences

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing hardware. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analyses by running laboratory blanks as described in Section 9.4.1.

4.2 Glassware must be scrupulously cleaned. Clean all glassware by detergent washing with hot water and rinsing with tap water. The glassware should then be drained dry and baked at over 100°C for several hours.

4.3 Injections into the GC must be made with a clean syringe. Carryover of analytes from previously injected high level standards or samples can have a large influence on the measured values of subsequent samples or standards. After injection of the sample, the syringe should be cleaned immediately by rinsing the syringe ten times with VOC-free DI water.

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

4.5 Compounds may interfere with the internal standard. When initially analyzing samples of unknown composition, an injection without internal standard can be performed to determine if an interference exists.

5.0 Safety

5.1 All chemicals should be treated as a potential health hazard. It is recommended that prudent practices for handling chemicals in the laboratory be employed.

5.2 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness of OSHA regulations regarding safe handling of chemicals used in this method. Material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

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

6.0 Equipment and Supplies

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

6.2 Sampling equipment

6.2.1 Samples are to be collected in glass or plastic bottles to zero headspace. It is recommended that 40 mL glass vials with Teflon™ faced silicone backed lids (VOA vials) be used.

6.2.2 Figure 1 shows the configuration of a VOA sample cooling train. Valve sizes should be small enough to yield controllable low flow rates (i.e., <1000 mL per minute). The diameter of the tubing should be small (i.e., around 0.25 inch inside diameter).

6.3 Laboratory glassware and supplies

6.3.1 Autosampler vials capable of holding 2 mL

6.3.2 Volumetric flasks

6.3.3 Volumetric pipets

6.3.4 Syringes

6.4 Analytical equipment

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

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

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

6.4.4 GC detector - Flame ionization with appropriate data system ; a large-bore jet tip is recommended, capillary jet tips were found to result in frequent flame-outs.

7.0 Reagents and Standards

7.1 **Deionized water -** Deionized water should be tested immediately before use to verify the absence of any target analytes. If it is found to be contaminated, it may be necessary to prepare fresh deionized water, purge the water with nitrogen or helium, or boil the water to remove the contaminant(s).

7.2 **Analytical standards** - Reagent grade or the highest purity methanol and cyclohexanol must be used.

7.3 **Internal standard primary spiking solution**- Prepare primary stock solution by adding 0.312 mL cyclohexanol to a tared 100 mL ground glass stoppered volumetric flask. Weigh the flask after the addition of the internal standard and record the weight to the nearest 0.1 mg. Fill the flask to 100 mL with DI water. This will result in a nominal 3,000 mg/L primary stock solution. Compute the exact concentration (mg/L) using the weight gain. The solution can be stored at room temperature for over 6 months. A higher concentration of internal standard should be prepared and used if the upper limit of the calibration curve being used is above 100 mg/L. Additionally, another internal standard material could be used if it is demonstrated that it does not interfere with any other peaks in the chromatogram.

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

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

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

8.0 Sample Collection, Preservation and Storage

8.1 **Collection** - Grab samples are collected directly from the process liquid stream using an appropriate collection vessel, typically a 40 mL VOA vial. For sample streams which are greater than 160^{o}F, a cooling coil is used to lower the temperature of the sample to below 160°F. The cooling coil tubing should be flushed for two to three minutes with the wastewater to be sampled prior to collecting a sample. This is done by opening both valves and allowing the sample to run through the tubing. After the line is flushed, valves are restricted to slow the flow rate. The temperature of the liquid to be sampled should be checked to be sure it is cool prior to collecting the sample. Use caution when sampling even moderately hot streams into glass vials, since the heat may cause the glass to break. Fill the vial to zero headspace with the sample.

8.2 **Preservation** - Effluent samples must be preserved with acid upon collection. This can be accomplished by adding several drops of dilute (1N) acid (i.e., HCl, H_2SO_4) to

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

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

9.0 Quality Control

9.1 Each field sampling program or laboratory that uses this method is required to operate a formal quality assurance program. Laboratory or field performance is compared to established criteria to determine if the results of the analyses meet the performance criteria of the method.

9.2 GC Maintenance

9.2.1 Injector maintenance - The septum and injection liner should be replaced when necessary. If this is not done, retention time shifts, peak broadening and low continuing calibration verification recoveries can occur.

9.2.2 Bakeouts - Water can build up in the GC, causing peak broadening and FID flame out. Frequent bakeouts of the system help to purge the system of excess water.

9.3 Initial GC/FID performance

9.3.1 Second source or certified reference material - A second source or certified reference material must be evaluated after each recalibration of the instrument. Recoveries between 85 and 115% are required for methanol.

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

9.4 Continuing GC/FID performance

9.4.1 Blanks - One method blank must be prepared per analytical batch to demonstrate that all materials are interference free. The concentration of methanol in the blank must be below 0.5 mg/L.

9.4.2 Calibration verification - Before each set of samples is analyzed, a calibration check is done to determine that the GC/FID system is operating within acceptable parameters. The calibration check must involve the analysis of a calibration standard in the mid-range of the calibration curve. The concentration of methanol must be within ±10% of the expected concentration. If the calibration fails to meet these expected criteria, the

GC/FID system may require maintenance. If routine maintenance does not correct the problem, a new standard prepared from a fresh calibration stock solution should be run. If this still fails, the instrument will need to be recalibrated.

9.4.3 Replicates - Replicates consist of running two or more separate aliquots of the sample through the entire analytical procedure. A duplicate must be performed for each batch of samples. The relative percent difference and the mean should be tabulated in a method precision log.

9.4.4 Matrix spike recovery - A matrix spike may be prepared for each batch of samples. Using the mean concentration determined by the replicate analyses or the level determined from a single measurement, determine the spiking level which will give at least three times the sample concentration. If the sample does not have detectable levels of analytes, spike the sample at approximately five times the lowest calibration level of the instrument. Spike the sample with the determined amount of the calibration standard or matrix spike solution and analyze the sample in the normal manner. Calculate the percent recovery using Equation 1.

Equation 1

$$R = \left(\frac{C_S - C_N}{C_T} \right) \times 100$$

Where:

R = percent recovery of matrix spike
C_S = measured concentration of spiked sample
C_N = measured concentration of native sample
C_T = theoretical concentration of spike

10.0 Calibration and Standardization

10.1 FID operating conditions

Assemble the GC/FID and establish the operating conditions outlined in Table 1, 2, or 3. Other chromatographic columns and conditions may be used if it has been established that methanol is separated from compounds which may cause interference, and quality control parameters are met. Once the GC/FID system is optimized for analytical separation and sensitivity, the sample operating conditions must be used to analyze all samples, blanks, calibration standards and quality assurance samples. Note that constant injections of aqueous samples can cause water to build up in the system. This will cause the retention times to shift and the peaks to broaden. It is recommended that after approximately 50 injections a bakeout of the system be performed. This should consist of heating the injector to 250°C, the oven to over 200°C and the detector to 350°C for at least several hours.

10.2 GC/ FID analysis of calibration standards

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

10.2.2 Prepare a five-point calibration curve for methanol by taking 2.0 mL of each calibration solution and adding the internal standard solution as described above. The calibration range is defined in Section 7.5. Use of an internal standard for calibration is required.

10.2.3 Calculate the relative response factor (RRF_M) for methanol using Equation 3. If the relative standard deviation (RSD) of the average RRF_M is less than 10% for methanol, the calibration is acceptable. The average RRF_M can be used in all subsequent calculations. If the calibration does not pass the criteria the calibration curve solutions must be reanalyzed and reevaluated. It may be necessary to perform instrument maintenance prior to reanalysis. If reanalysis also fails to produce a linear curve, new calibration standards must be prepared and analyzed.

10.2.4 Analyze and calculate the concentration of the mid-range calibration standard daily, prior to each sample set, using Equation 4. Calculate the percent recovery of the standard using Equation 5 to verify the calibration. In-house percent recovery control limits must be determined, and are not to exceed

±10% for methanol. If the limits are exceeded, either prepare a new standard or perform instrument maintenance. If necessary, recalibrate the instrument.

Equation 2

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

Where:

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

Equation 3

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

Where:

A_M = area of methanol peak
A_{IS} = area of internal standard peak
C_M = concentration of methanol injected
C_{IS} = concentration of internal standard injected

Equation 4

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

Where:

C_M = concentration of methanol in sample (mg/L)
A_M = area of methanol peak in the sample
C_{IS} = concentration of the internal standard (mg/L)
A_{IS} = area of the internal standard peak
RRF_M = relative response factor of methanol (Section 10.2.3)

Equation 5

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

Where:

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

10.3 Analytical range and minimum calibration level

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

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

11.0 Procedure

11.1 Transfer an aliquot (2.0 mL) of the sample to an autosampler vial. Add 10 µL of the internal standard primary spike solution to each of the autosampler vials. Perform the analysis by direct aqueous injection into the GC/FID. If the concentration of an analyte is more that 10% above the calibrated range, the sample should be diluted and reanalyzed to measure the analyte concentration.

11.2 If dilution is necessary, volumetric flasks can be utilized to achieve the desired concentrations. An aliquot of the diluted sample is then analyzed as described in Section 11.1. Calculate the dilution factor using Equation 6.

Equation 6

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

Where:

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

12.0 Data Analysis and Calculations

12.1 GC/FID data analysis

12.1.1 The analytes are identified by comparison of the relative retention times established in the calibration to the retention times in the samples. The sample component relative retention time (RRT) should fall within ±0.01 RRT units of the RRT of the standard component.

12.1.2 Calculate the sample concentration, using the internal standard response factors established in Section 10.2.3, according to Equation 7.

Equation 7

$$C_A = \left[\frac{A_A \times C_{IS} \times CF \times DF}{A_{IS} \times RRF_A} \right]$$

Where:

C_A = concentration of compound A in sample (mg/L)
A_A = area of the compound A peak in the sample
C_{IS} = concentration of the internal standard (mg/L)
A_{IS} = area of the internal standard peak
RRF_M = relative response factor of compound A (Section 10.3)
CF = correction factor from Method 301 validation (Table 3)
DF = dilution factor

12.2 Data review requirements

12.2.1 The data are reviewed for accuracy of the identification, GC problems, interferences and bias. Any problems should be corrected prior to reporting of analytical results.

12.2.2 All chromatograms must be manually reviewed to confirm internal standard and analyte identification and area integrations. As part of this review, the analyst assesses whether or not the concentration is within the calibration range of the instrument. The analyst should determine if the level of interferences and baseline noise can be corrected with dilution of the samples. Another tool that can be utilized to identify the analyte peaks is to overlay the sample chromatogram with the standard chromatogram.

12.2.3 The internal standard area counts must be reviewed and added to a control chart. The in-house determined control limits must not exceed ±20% of the mean.

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

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

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

12.2.7 Where analytes are not detected or are detected below the lowest calibration standard, report the Minimum Measurement Level. Report a revised Minimum Measurement Level in accordance with Section 12.1.3 for any dilute analyses where less dilute samples were not run and for any analyte that was not detected.

12.3 Data reporting requirements

12.3.1 Report results in mg/L to appropriate number of significant figures for individual situations.

12.3.2 Report all corresponding blanks, replicates and matrix spikes recoveries for each analytical batch of samples.

13.0 Method Performance

13.1 Single laboratory method validation studies were performed during the development of the method, and included evaluation based on the United States Environmental Protection Agency (EPA) Method 301, *Field Validation of Emission Concentrations from Stationary Sources* (Appendix A to CFR 63). The method performance data are presented in Section 17, Table 4.

14.0 Pollution Prevention

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

15.0 Waste Management

15.1 It is the responsibility of the laboratory to comply with all federal, state and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and lands by minimizing releases into the environment. Compliance with all sewage discharge permits and regulations is also required.

16.0 References

16.1 National Council of the Paper Industry for Air and Stream Improvement, Inc. (NCASI). 1994. *Volatile Organic Emissions from Pulp and Paper Mill Sources, Part X - Test Methods, Quality Assurance/Quality Control Procedures, and Data Analysis Protocols*. Technical Bulletin No. 684. Research Triangle Park, NC: National Council of the Paper Industry for Air and Stream Improvement, Inc.

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

17.0 Tables, Diagrams, Flowcharts And Validation Data

17.1 Through the use of the EPA Method 301 validation procedure, this method has been shown to be a valid method for measurement of methanol in treated effluent, untreated effluent, stripped condensate, foul condensate and weak wash from kraft mill sources; and condensate, evaporator condensate, influent to sludge and dirty hot water plants from sulfite mill sources. A summary of these validation data are presented in Table 4.

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

Injection:	Direct (Splitless)
Injector Temperature:	110°C
Injection Volume:	1 μL
Injection Liner Size:	2 mm id (no packing)
Syringe Rinse	10 rinses with VOC free DI water
FID Detector Temperature:	275°C
H_2 Flow Rate:	approx. 50 mL/min
Air Flow Rate:	approx. 500 mL/min
Makeup Gas:	Nitrogen or Helium
Makeup Gas Flow Rate:	approx. 25 mL/min
Carrier Gas:	Helium
Carrier Gas Flow Rate:	constant pressure mode to give 6 mL/min at room temperature, or use constant flow mode at 6 mL/min
Column:	J&W DB-624, 30 m x 0.53 mm id x 3 micron fused silica capillary column with 10 m deactivated fused silica guard column
Cryogenics:	On
Temperature Program °C:	
Initial:	0°C for 3 min
Ramp 1:	5°C/min to 50°C for 0 minutes
Ramp 2:	70°C/min to 105°C for 17 minutes
Ramp 3:	70°C/min to 220°C for 3 minutes
Retention Time Order:	Acetaldehyde, Methyl Mercaptan, Methanol, Ethanol, Propionaldehyde, Methyl Ethyl Ketone, Cyclohexanol
Relative Retention Time:	Methanol - 0.260

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

Injection:	Direct (Splitless)
Injector Temperature:	110°C
Injection Volume:	1 μL
Injection Liner Size:	2 mm id (no packing)
Syringe Rinse	10 rinses with VOC free DI water
FID Detector Temperature:	275°C
H_2 Flow Rate:	approx. 50 mL/min
Air Flow Rate:	approx. 500 mL/min
Makeup Gas:	Nitrogen or Helium
Makeup Gas Flow Rate:	approx. 25 mL/min
Carrier Gas:	Helium
Carrier Gas Flow Rate:	constant pressure mode to give 6 mL/min at room temperature, or use constant flow mode at 6 mL/min
Column:	J&W DB-WAX, 30 m x 0.32 mm id x 025 micron fused silica capillary column with 10 m deactivated fused silica guard column
Cryogenics:	On
Temperature Program °C:	
Initial:	0°C for 3 min
Ramp 1:	5°C/min to 50°C for 4 minutes
Ramp 2:	70°C/min to 100°C for 10 minutes
Ramp 3:	70°C/min to 200°C for 4 minutes
Retention Time Order:	Acetaldehyde, Acetone, Methyl Ethyl Ketone, Methanol, Cyclohexanol
Relative Retention Time:	Methanol - 0.235

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

Injection:	Direct (Splitless)
Injector Temperature:	110°C
Injection Volume:	1 μL
Injection Liner Size:	2 mm id (no packing)
Syringe Rinse	10 rinses with VOC free DI water
FID Detector Temperature:	275°C
H_2 Flow Rate:	approx. 50 mL/min
Air Flow Rate:	approx. 500 mL/min
Makeup Gas:	Nitrogen or Helium
Makeup Gas Flow Rate:	approx. 25 mL/min
Carrier Gas:	Helium
Carrier Gas Flow Rate:	constant pressure mode to give 6 mL/min at room temperature, or use constant flow mode at 6 mL/min
Column:	J&W DB-624, 75 m x 0.53 mm id x 3 micron fused silica capillary column with 10 m deactivated fused silica guard column
Cryogenics:	Off
Temperature Program °C:	
Initial:	35°C for 1 min
Ramp 1:	6°C/min to 90°C for 0 minutes
Ramp 2:	70°C/min to 150°C for 10 minutes
Ramp 3:	70°C/min to 220°C for 3 minutes
Retention Time Order:	Acetaldehyde, Methyl Mercaptan, Methanol, Ethanol, Propionaldehyde, Methyl Ethyl Ketone, Cyclohexanol
Relative Retention Time:	Methanol - 0.260

Table 4. Method 301 Validation Results for Methanol

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

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

Figure 1. VOA Sample Cooling Train

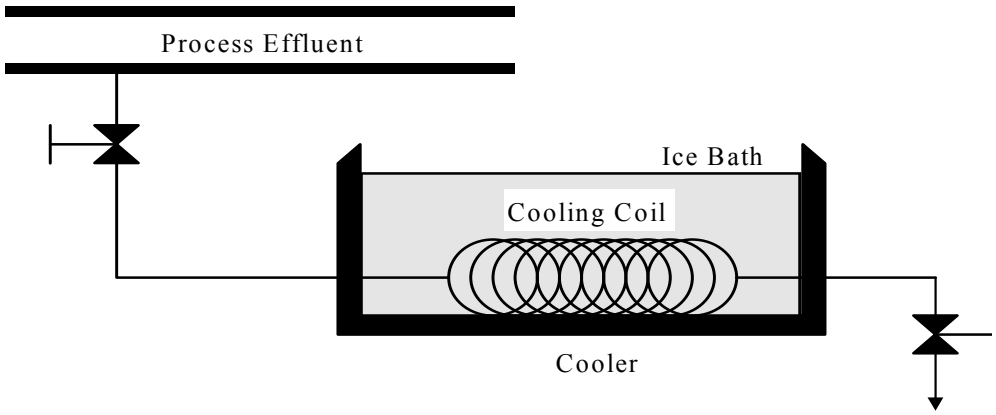


Figure 2: Approval Letter from EPA - Page 1

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

FEB 24 1998

OFFICE OF
AIR QUALITY PLANNING
AND STANDARDS

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

Dear Ms. Gunshefski:

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

To complete the approval process, we would like to have an electronic file copy of the test method and the supporting report in Wordperfect 6.x format.

If you have any questions about our comments or you would like to meet to discuss them, please contact Gary McAlister of my staff at (919) 541-1062.

Sincerely,

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

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

Enclosure

Internet Address (URL) • http://www.epa.gov
Recycled/Recyclable • Printed with Vegetable Oil Based Inks on Recycled Paper (Minimum 25% Postconsumer)

Figure 3: Approval Letter form EPA - Page 2

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

NCASI METHOD DI/HAPS-99.01

SELECTED HAPS IN CONDENSATES BY GC/FID

NCASI
Southern Regional Center
February 2000

Acknowledgements

This method was prepared by Dr. MaryAnn Gunshefski, Senior Research Scientist at the NCASI Southern Regional Center. Other assistance was provided by Alex Gholson, Senior Research Scientist, Dean Hoy, Research Associate, and Larry LaFleur, NCASI Fellow, at the NCASI West Coast Regional Center.

NCASI would like to acknowledge the following laboratories and individuals for their voluntary participation in the interlaboratory validation of this method:

- Columbia Analytical Services, Jacksonville FL, Ward Dickens and Josh Apple
- Columbia Analytical Services, Kelso WA, Ed Wallace and Loren Portwood
- Data Analysis Technologies, Inc. Dublin OH, Ron Mitchum
- Performance Analytical Inc. (a division of Columbia Analytical Services), Simi Valley CA, Michael Tuday and John Yokoyama
- STL-Savannah Labs, Savannah GA, Craig Ratkey and Myron Young
- Weyerhaeuser Co., Federal Way WA, Rick Bogar and Mike Grove

For more information about this method, contact:

MaryAnn Gunshefski, Ph.D.
Senior Research Scientist
NCASI Southern Regional Center
P.O. Box 141020
Gainesville FL 32614
(352) 377-4708, ext. 244
mgunshefski@ncasi.org

For more information about NCASI publications, contact:

Publications Coordinator
NCASI
P.O. Box 13318
Research Triangle Park NC 27709-3318
(919) 558-1999
publications@ncasi.org

National Council for Air and Stream Improvement, Inc. (NCASI). 2000. *Methods Manual - Selected HAPS in Condensates by GC/FID*. Research Triangle Park, NC: National Council for Air and Stream Improvement, Inc.

© 2000 by the National Council for Air and Stream Improvement, Inc.

Disclaimer

The mention of trade names or commercial products does not constitute endorsement or recommendation for use.

NCASI METHOD DI/HAPS-99.01

SELECTED HAPS IN CONDENSATES BY GC/FID

1.0 Scope and Application

1.1 This method is used for the analysis of methanol (CAS # 67-56-1), acetaldehyde (CAS # 75-07-7), methyl ethyl ketone (CAS # 78-93-3), and propionaldehyde (CAS # 123-38-6) in condensate samples from pulp and paper mills by gas chromatography/flame ionization detection (GC/FID). A version of this method was published as Appendix I of NCASI Technical Bulletin No. 684, *Method for Analysis of Methanol, Acetone, Acetaldehyde and Methyl Ethyl Ketone in Liquid Samples*, and has been rewritten to conform with the contents and format established by the EMMC for EPA wastewater methods.

1.2 Types of condensates for which this method can be used include condensate to be piped to a biological treatment system and condensate entering the stripper system.

1.3 The method has been validated in two laboratories using United States Environmental Protection Agency (EPA) Method 301, *Field Validation of Emission Concentrations from Stationary Sources* (Appendix A to CFR 63), and is a validated method.

1.4 This method is applicable for detecting methanol, acetaldehyde, MEK, and propionaldehyde in condensates at the parts per million (ppm) level. A correction factor may be needed. All correction factors are given in Section 17.0.

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 condensate 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 an autosampler vial. An aliquot of an internal standard solution is added to each of the autosampler vials. The internal standard is also used as a time reference peak. An aliquot of a surrogate solution can also be added. The aqueous samples are then introduced directly into 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 a flame ionization detector which is interfaced to the gas chromatograph.

2.3 Identification of the analytes is determined by comparison of their relative retention times with the relative retention times of a known standard. If the results are questionable, confirmation may be performed by using a mass spectrometer as the detector.

2.4 The sensitivity of the method is defined as the minimum measurement level (MML) and for undiluted samples is set at 1 mg/L for this method.

2.5 Quality is assured through frequent testing of the analytical systems. This is accomplished by using a second source reference material, a resolution test mixture, calibration check samples and spike recovery samples. Method blanks , duplicates, and matrix spikes must also be analyzed with each analytical batch to ensure data quality.

3.0 Definitions

3.1 The definitions below are specific to this method, but conform to common usage as much as possible.

3.1.1 Batch - grouping of samples, not more than 20

3.1.2 mg/L - milligrams per liter

3.1.3 May - This action, activity, or procedural step is neither required nor prohibited.

3.1.4 Must not - This action, activity, or procedural step is prohibited.

3.1.5 Must - This action, activity, or procedural step is required.

3.1.6 Should - This action, activity, or procedural step is suggested, but not required.

4.0 Interferences

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analyses by running laboratory blanks as described in Section 9.2.6.

4.2 Glassware must be scrupulously cleaned. Clean all glassware by detergent washing with hot water and rinsing with tap water. The glassware should then be drained dry and baked at over 100°C for several hours.

4.3 Injections into the GC must be made with a clean syringe. Carryover of analytes from previously injected high level standards or samples can have a large influence on the measured values of subsequent samples or standards. After injection of the sample, the syringe should be cleaned immediately by rinsing the syringe ten times with VOC-free DI water.

4.4 Several compounds which are not HAPs can interfere with the chromatography if the separation is not efficient. These compounds include methyl mercaptan, ethanol, acetone, and dimethyl sulfide. When performed properly, this method does sufficiently separate these compounds from the analytes of interest at concentrations found in condensates.

4.5 Compounds may interfere with the internal standard. Two internal standards are specified by the method so that one free of interference can be selected. When initially analyzing samples of unknown composition, an injection without internal standard can be performed to determine if an interference exists.

5.0 Safety

5.1 All chemicals should be treated as 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, MEK, propionaldehyde, and acetaldehyde are flammable liquids which may be harmful if inhaled or ingested. Use in a laboratory fume hood and wear appropriate gloves, eye protection, and other protective clothing.

6.0 Equipment and Supplies

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

6.2 Sampling equipment

6.2.1 Samples are to be collected in glass bottles to zero headspace. It is recommended that 40 mL glass vials with Teflon™ faced silicone backed lids (VOA vials) be used.

6.2.2 Figure 1 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).

6.3 Laboratory glassware and supplies

6.3.1 Autosampler vials capable of holding 2 mL[1]

6.3.2 Volumetric flasks

6.3.3 Volumetric pipets

6.3.4 Syringes (including gas-tight syringes)

6.4 Analytical equipment

6.4.1 Gas chromatography system - gas chromatography analytical system complete with a cryogenically cooled temperature-programmable gas chromatograph with either a purge-packed or split/splitless injection port

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

6.4.3 Column - 75 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)

6.4.4 GC detector - flame ionization with appropriate data system; a large-bore jet tip is recommended, capillary jet tips were found to result in frequent flame-outs

7.0 Reagents and Standards

7.1 **Deionized water** - Deionized water should be tested immediately before use to verify the absence of any target analytes. If it is found to be contaminated, it may be necessary to prepare fresh deionized water, purge the water with nitrogen or helium, or boil the water to remove the contaminant(s).

7.2 **Analytical standards** - Reagent grade or the highest purity methanol, acetaldehyde, propionaldehyde, methyl ethyl ketone, cyclohexanol, 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

[1] It was found that a small bubble in the vial allowed rapid mixing of the sample to disperse the internal standard.

standards. The minimum acceptable purity is 95%. Some suppliers of propionaldehyde report 97% purity and upon inquiry indicate there may be from 1 to 2% water.

7.3 Internal standard primary spiking solution - Cyclohexanol or 2,2,2-trifluoroethanol can be used as the internal standard.

7.3.1 Prepare primary stock solution by adding 1.56 mL cyclohexanol to a tared 50 mL ground glass stoppered volumetric flask. Weigh the flask after the addition of the internal standard and record the weight to the nearest 0.1 mg. Fill the flask to 50 mL with DI water. This will result in a nominal 30,000 mg/L primary stock solution. Compute the exact concentration (mg/L) using the weight gain. The solution can be stored at room temperature for over 6 months.

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. This should result in a nominal 40,000 mg/L primary stock solution. Compute the exact concentration (mg/L) using the weight gain. 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. After each addition of analyte, weigh and record the weight gain to the nearest 0.1 mg. 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. In a like manner, add 64 µL of acetaldehyde, 62 µL of propionaldehyde, and 62 µL of methyl ethyl ketone. Once all the analytes have been added, fill the flask to the mark. This will result in a nominal 50,000 mg/L methanol, 1000 mg/L acetaldehyde, 1,000 mg/L propionaldehyde, and 1000 mg/L methyl ethyl ketone primary stock solution. Use this weight gain to compute the exact analyte concentrations. Note that acetaldehyde and propionaldehyde are extremely volatile and degrade in the neat solutions over time. A chilled gas-tight syringe must be used to deliver the neat compounds to the volumetric flask. New neat standards for acetaldehyde and propionaldehyde should be obtained when the second source standard requirement is not met using freshly prepared standards. An alternative would be to purchase a primary stock solution from a chemical reference supply company. The primary stock must be stored in the refrigerator and must be re-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 supports it.

7.5 Calibration and matrix spike solutions - Prepare standard solutions by dilutions of the stock solution using gas-tight syringes to measure the required aliquots of primary standard. The required dilutions are shown below. Prepare matrix spike solutions by

calculating the concentration of analytes desired and diluting the primary stock solution.

µL of stock solution to add to 10 mL volumetric flask	Resulting acetaldehyde, MEK, and propionaldehyde concentration (mg/L)	Resulting methanol concentration (mg/L)
2,000	200	10,000
500	50	2,500
200	20	1,000
50	5	250
10	1	50

7.6 **Second source standard or certified reference standard** - A second source standard or certified reference standard containing the analytes in an aqueous solution must be prepared or obtained and analyzed after every recalibration of the instrument. The standard must be stored in a refrigerator and must be re-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 supports it.

7.7 **Resolution test mixture** - Prepare a resolution test mixture containing the analytes of interest along with the possible interferences described in Section 4.3. This mixture can be prepared by first preparing a resolution stock solution by adding 2.5 mL of dimethyl sulfide, 1.0 mL of acetone, and 0.5 mL of ethanol to a 25 mL volumetric flask and diluting with methanol. Then add 10µL of the primary stock solution and 50 µL of resolution stock solution to 10 mL of DI water. Analyze 2.0 mL of this mixture as if it were a sample.

8.0 Sample Collection, Preservation, and Storage

8.1 **Collection** - Grab samples are collected directly from the process liquid stream using an appropriate collection vessel, typically a 40 mL VOA vial. For sample streams which are greater than 160°C, 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 condensate 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 to zero headspace with the sample.

8.2 **Preservation** - No preservation is necessary for condensate samples.

8.3 **Storage** - All samples must be stored in a refrigerator (4°C) until analysis. Samples may be stored for 14 days, at which time the recovery of acetaldehyde may fall to less than 80%.

9.0 Quality Control

9.1 Each field sampling program or laboratory that uses this method is required to operate a formal quality assurance program. Laboratory or field performance is compared to established criteria to determine if the results of the analyses meet the performance criteria of the method.

9.2 GC Maintenance

9.2.1 Injector maintenance - The septum and injection liner should be replaced when necessary. If this is not done, retention time shifts and peak broadening can occur.

9.2.2 Bakeouts - Water can build up in the GC, causing peak broadening and FID flame out. Frequent bakeouts of the system help to purge the system of excess water. Keeping the injection port purge flowing throughout the chromatographic run will help to remove water from the system (e.g., disable "gas saver" on HP 6890 systems).

9.3 Initial GC/FID performance

9.3.1 Second source or certified reference material - A second source or certified reference material must be evaluated after each recalibration of the instrument. Recoveries between 85 and 115% are required for methanol, and between 80 and 120% for the other three analytes.

9.3.2 Resolution test mixture - The resolution test mixture described in Section 7.6 must be analyzed after each recalibration, and weekly thereafter. This is to assure that the chromatography system is working appropriately. Baseline resolution between acetaldehyde/methanol and ethanol/propionaldehyde/ acetone is required. The dimethyl sulfide and acetone need not be baseline resolved. Figures 2 and 3 contain sample chromatograms.

9.3.3 Reproducibility check - When the instrument is set up to perform this method a reproducibility/sensitivity check must be performed. Seven aliquots of the resolution test mix must be analyzed. The %RSD of the seven analyses must be less that 14% for acetaldehyde and less than 10% for propionaldehyde and MEK.

9.4 Continuing GC/FID performance

9.4.1 Blanks - One method blank must be prepared per analytical batch to demonstrate that all materials are interference free. The concentration of the analytes in the blank must be below 0.5 mg/L.

9.4.2 Calibration verification - Before each set of samples is analyzed, a calibration check is done to determine that the GC/FID system is operating within acceptable parameters. The calibration check must involve the analysis of a calibration standard in the mid-range of the calibration curve. The concentrations of the analytes must be within ±15% of the expected concentration for acetaldehyde, propionaldehyde, and MEK, and ±10% for methanol. If the calibration fails to meet these expected criteria, the GC/FID system may require maintenance. If routine maintenance does not correct the problem, a new standard prepared from a fresh calibration stock solution should be run. If this still fails, the instrument will need to be recalibrated.

9.4.3 Replicates - Replicates consist of running two or more separate aliquots of the sample through the entire analytical procedure. A duplicate must be performed for each batch of samples. The relative percent difference and the mean should be tabulated in a method precision log.

9.4.4 Matrix spike recovery - A matrix spike may be prepared for each batch of samples. Using the mean concentration determined by the replicate analyses or the level determined from a single measurement, determine the spiking level which will give at least three times the sample concentration. If the sample does not have detectable levels of analytes, spike the sample at approximately five times the lowest calibration level of the instrument. Spike the sample with the determined amount of the calibration standard/matrix spike solution (Section 7.4) and analyze the sample in the normal manner. Calculate the percent recovery using Equation 1.

Equation 1

$$R = \left(\frac{C_S - C_N}{C_T} \right) \times 100$$

Where:

R = percent recovery of matrix spike
C_S = measured concentration of spiked sample
C_N = measured concentration of native sample
C_T = theoretical concentration of spike

10.0 Calibration and Standardization

10.1 FID operating conditions

Assemble the GC/FID and establish the operating conditions outlined in Table 1 or 2. Once the GC/FID system is optimized for analytical separation and sensitivity, the same 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 a bakeout of the system be performed after approximately 50 injections. This should consist of heating the injector to 250°C, the oven to over 200°C but less than 260°C, and the detector to 350°C for several hours.

10.3 GC/FID analysis of calibration standards

10.3.1 Determine the retention times of the analytes by taking 2.0 mL of the mid-range calibration solution and adding 10 µL of the internal standard solution. This will result in concentrations of 150 mg/L or 200 mg/L of cyclohexanol or 2,2,2-trifluoroethanol, respectively, in the autosampler vial. Inject 1 µL of this solution and determine the relative retention times of the analytes to the internal standard using Equation 2.

10.3.2 Prepare a five-point calibration curve for the four analytes by taking 2.0 mL of each calibration solution and adding the internal standard solution as described above. The calibration range is defined in Section 7.4. Use of an internal standard for calibration is required.

10.3.3 Calculate the relative response factor (RRF_M) for each analyte using Equation 3. If the relative standard deviation (RSD) of the average RRF_M is less than 10% for methanol and 15% for acetaldehyde, propionaldehyde, and MEK, the calibration is acceptable. The average RRF_M can be used in all subsequent calculations. If the calibration does not pass the criteria the calibration curve solutions must be reanalyzed and reevaluated. It may be necessary to perform instrument maintenance prior to reanalysis. If reanalysis also fails to produce a linear curve, new calibration standards must be prepared and analyzed.

10.3.4 Analyze and calculate the concentration of the mid-range calibration standard daily, prior to each sample set, using Equation 4. Calculate the percent recovery of the standard using Equation 5 to verify the calibration. In-house percent recovery control limits must be determined, and are not to exceed ±10% for methanol and ±15% for the other three analytes. If the limits are exceeded, either prepare a new standard or perform instrument maintenance. If necessary, recalibrate the instrument.

Equation 2

$$RRT_A = \left[\frac{Rt_A}{Rt_{IS}} \right]$$

Where:

RRT_A = relative retention time of compound A
Rt_A = retention time of compound A
Rt_{IS} = retention time of internal standard (cyclohexanol or 2,2,2-triflouroethanol)

Equation 3

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

Where:

A_M = area of methanol peak
A_{IS} = area of internal standard peak
C_M = concentration of methanol injected
C_{IS} = concentration of internal standard injected

Equation 4

$$C_A = \left[\frac{A_A \times C_{IS}}{A_{IS} \times RRF_A} \right]$$

Where:

C_A = concentration of compound A in sample (mg/L)
A_A = area of the compound A peak in the sample
C_{IS} = concentration of the internal standard (mg/L)
A_{IS} = area of the internal standard peak
RRF_M = relative response factor of compound A (Section 10.3)

Equation 5

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

Where:

C_M = concentration of analyte measured
C_E = concentration of analyte expected

10.4 Analytical range and minimum calibration level

10.4.1 Demonstrate that the calibration curve is linear (relative response factors exhibit a RSD less than 10% for methanol or 15% for the other three analytes) throughout the range of the calibration curve described in Section 7.4.

10.4.2 Demonstrate that acetaldehyde, propionaldehyde and MEK are detectable at 1.0 mg/L with an RSD of less than 14% for acetaldehyde and less than 10% for the other two analytes as described in Section 9.3.3.

11.0 Procedure

11.1 Transfer an aliquot (2.0 mL) of the sample to an autosampler vial by gas-tight syringe. Add 10 µL of the internal standard primary spike solution (30,000 mg/L cyclohexanol or 40,000 mg/L 2,2,2-trifluoroethanol) to each of the autosampler vials. Perform the analysis by direct aqueous injection into the GC/FID. If the concentration of an analyte is more that 10% above the calibrated range, the sample should be diluted and reanalyzed to measure the analyte concentration.

11.2 If dilution is necessary, inject some fractional volume less than 2.0 mL using a gas-tight syringe into an autosample vial which is then brought to 2 mL with DI water and analyzed as described in Section 11.1. Calculate the dilution factor using Equation 6.

Equation 6

$$DF = \frac{2}{V}$$

Where:

DF = the dilution factor
V = the volume of sample (mL) injected into the autosample vial

12.0 Data Analysis and Calculations

12.1 GC/FID data analysis

12.1.1 The analytes are identified by comparison of the retention times relative to the internal standard established in the calibration to the relative retention times in the samples. The sample component relative retention time (RRT) should fall within ±0.01 RRT units of the RRT of the standard component.

12.1.2 Calculate the sample concentration, using the internal standard response factors established in Section 10.3.3, according to Equation 7. Use a dilution factor of 1 if no dilution is made and choose the proper correction factor based on the internal standard and hardware configuration used. Use a correction factor of 1 if no significant correction factor is found.

Equation 7

$$C_A = \left[\frac{A_A \times C_{IS} \times CF \times DF}{A_{IS} \times RRF_A} \right]$$

Where:

C_A = concentration of compound A in sample (mg/L)
A_A = area of the compound A peak in the sample
C_{IS} = concentration of the internal standard (mg/L)
A_{IS} = area of the internal standard peak
RRF_M = relative response factor of compound A (Section 10.3)
CF = correction factor from Method 301 validation (Table 3)
DF = dilution factor

12.1.3 If samples cannot be analyzed without dilution, the MML must be adjusted to reflect the lowest dilution factor used by multiplying the MML (1 mg/L) by the dilution factor calculated in Equation 6.

12.2 Data review requirements

12.2.1 The data are reviewed for accuracy of the identification, GC problems, interferences, and bias. Any problems should be corrected prior to reporting analytical results.

12.2.2 All the chromatograms are manually reviewed to confirm internal standard and analyte identification as well as the integration areas. As part of this

review, the analyst assesses whether or not the concentration is within the calibration range of the instrument. The analyst should determine whether dilution of the samples is required. Another tool that can be utilized to identify the analyte peaks is to overlay the sample chromatogram with the standard chromatogram.

12.2.3 The internal standard area counts must be reviewed and added to a control chart. The in-house determined control limits must not exceed ±20% of the mean.

12.2.3 Any inconsistencies between replicate analyses must be resolved (i.e., if an analyte is detected in one replicate and not the other), and attempts made to determine the reason for the inconsistencies.

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

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

12.2.6 Where analytes are not detected or are detected below the lowest calibration standard, report the Minimum Measurement Level. Report a revised Minimum Measurement Level in accordance with Section 12.1.3 for any dilute analyses where less dilute samples were not run and for any analyte that was not detected.

12.3 Data reporting requirements

12.3.1 Report results in mg/L to three significant figures.

12.3.2 Report all corresponding blanks, replicates, and matrix spike recoveries for each analytical batch of samples.

13.0 Method Performance

13.1 Single laboratory method validation studies were performed during the development of the method, and included evaluation based on the United States Environmental Protection Agency (EPA) Method 301, *Field Validation of Emission Concentrations from Stationary Sources* (Appendix A to CFR 63). A summary of the method performance data is presented in Section 17, Table 3.

14.0 Pollution Prevention

14.1 The laboratory should check state and local requirements to determine if pollution prevention equipmentis 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 of the Paper Industry for Air and Stream Improvement, Inc. (NCASI). 1994. *Volatile organic emissions from pulp and paper mill sources, Part X - Test methods, quality assurance/quality control procedures, and data analysis protocols*. Technical Bulletin No. 684. Research Triangle Park, NC: National Council of the Paper Industry for Air and Stream Improvement, Inc.

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

17.0 Tables, Diagrams, Flowcharts, and Validation Data

17.1 Through the use of the EPA Method 301 validation procedure, this method has been shown to be a valid method for measurement of methanol, acetaldehyde, methyl ethyl ketone, and propionaldehyde in condensates from kraft mill sources. A summary of these validation data is presented in Table 3.

Table 1. GC/FID Operating Conditions for Selected HAPs Analysis
Purged-Packed Injector

Injection:	Direct (Splitless)
Injector Temperature:	170°C
Injection Volume:	1 µL
Injection Liner Size:	2 mm id (no packing)
Syringe Rinse	10 rinses with VOC free DI water
FID Detector Temperature:	275°C
H_2 Flow Rate:	approx. 50 mL/min
Air Flow Rate:	approx. 500 mL/min
Makeup Gas:	Nitrogen or Helium
Makeup Gas Flow Rate:	approx. 25 mL/min
Carrier Gas:	Helium
Carrier Gas Flow Rate:	constant pressure mode to give 6 mL/min at room temperature, or use constant flow mode at 6 mL/min
Column:	J&W DB-624, 75 m x 0.53 mm id x 3 micron fused silica capillary column with 10 m deactivated fused silica guard column
Cryogenics:	On
Temperature Program °C:	
Initial:	5°C for 1 min
Ramp 1:	6°C/min to 90°C for 0 minutes
Ramp 2:	40°C/min to 150°C for 7 minutes
Ramp 3:	70°C/min to 250°C for 4 minutes
Retention Time Order:	Acetaldehyde, Methanol, Propionaldehyde, 2,2,2-Trifluoroethanol, Methyl Ethyl Ketone, Cyclohexanol
Cyclohexanol Retention Time:	22.081 min
Relative Retention Time:	Acetaldehyde - 0.336 Methyl Mercaptan - 0.356 Methanol - 0.367 Ethanol - 0.458 Propionaldehyde - 0.487 Acetone - 0.499 Dimethyl sulfide - 0.503 2,2,2-Trifluoroethanol - 0.608 MEK - 0.672

Table 2. GC/FID Operating Conditions for Selected HAPs Analysis
Split/Splitless Injector

Injection:	Direct (Splitless)
Purge Flow Rate:	approx. 40 mL/min
Purge Time:	0.25 min
Injector Temperature:	110°C
Injection Volume:	1 µL
Injection Liner Size:	2 mm id with fused silica packing in the bottom (Restex #20713-200.5)
Syringe Rinse	10 rinses with VOC free DI water
FID Detector Temperature:	275°C
H_2 Flow Rate:	approx. 50 mL/min
Air Flow Rate:	approx. 500 mL/min
Makeup Gas:	Nitrogen or Helium
Makeup Gas Flow Rate:	approx. 25 mL/min
Carrier Gas:	Helium
Carrier Gas Flow Rate:	constant pressure mode to give 6 mL/min at room temperature, or use constant flow mode at 6 mL/min
Column:	J&W DB-624, 75 m x 0.53 mm id x 3 micron fused silica capillary column with 10 m deactivated fused silica guard column
Cryogenics:	On
Temperature Program °C:	
Initial:	5°C for 1 min
Ramp 1:	6°C/min to 90°C for 0 minutes
Ramp 2:	40°C/min to 150°C for 7 minutes
Ramp 3:	70°C/min to 250°C for 4 minutes
Retention Time Order:	Acetaldehyde, Methanol, Propionaldehyde, 2,2,2-Trifluoroethanol, Methyl Ethyl Ketone, Cyclohexanol
Cyclohexanol Retention Time:	22.081 min
Relative Retention Time:	Acetaldehyde - 0.336 Methyl Mercaptan - 0.356 Methanol - 0.367 Ethanol - 0.458 Propionaldehyde - 0.487 Acetone - 0.499 Dimethyl sulfide - 0.503 2,2,2-Trifluoroethanol - 0.608 MEK - 0.672

Table 3. Method 301 Validation Results

	Correction Factor (CF)			
Internal standard Injector	Acetaldehyde	Methanol	Propionaldehyde	Methyl ethyl ketone
Cyclohexanol Packed purge	1.12	NA[a]	1.12	0.97
Cyclohexanol Split/splitless	1.09	1.04	1.09	1.03
2,2,2-Trifluoroethanol Packed purge	1.14	NA[a]	1.14	1.07
2,2,2-Trifluoroethanol Split/splitless	1.06	NA[a]	1.06	NA[a]

[a] not applicable due to insignificant bias

Figure 1. VOA Sample Cooling Train

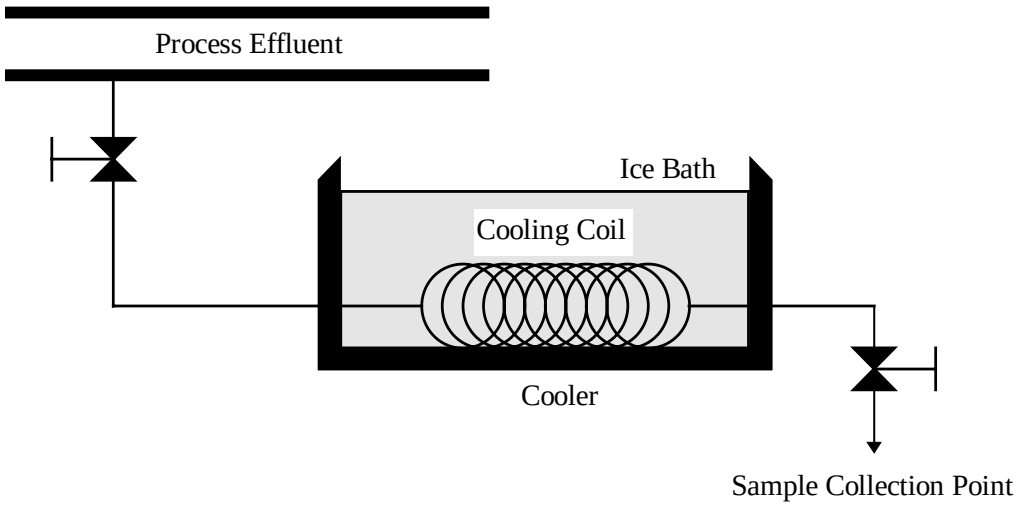


Figure 2: Entire Sample Chromatogram of Resolution Test Mixture

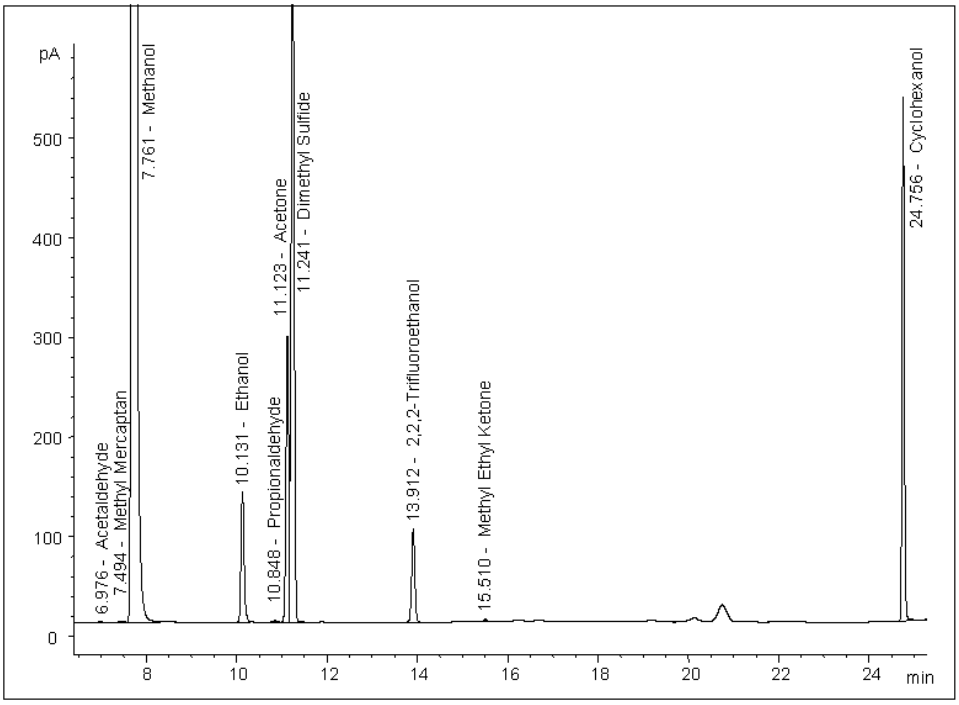


Figure 3: Partial Sample Chromatogram of Resolution Test Mixture

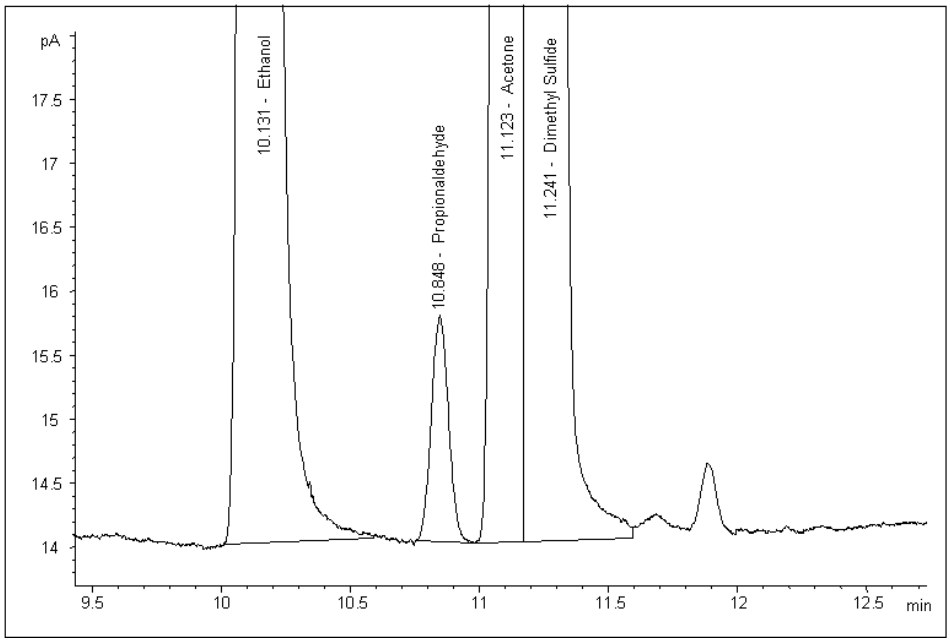


Figure 4. EPA Method 301 Validation Approval Letter – page 1

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

SEP 22 2000

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

OFFICE OF
AIR QUALITY PLANNING
AND STANDARDS

Dear Dr. Gunshefski:

We have reviewed your report entitled, "EPA Method 301 Validation Report of the NCASI Method 'Selected HAPS in Condensates By GC/FID.' " We agree with your conclusion that this method, in all of its variations, met Method 301 criteria for measuring acetaldehyde, methanol, propionaldehyde, and methyl ethyl ketone in samples from the pulp and paper mill condensate streams regulated under 40 CFR Part 63, Subpart S, Paragraph 446(b). I have summarized in the enclosed Tables 1-4 the correction factors for the individual HAP's for each of the four variations in the test method. 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.

For our records we would like to have an electronic file copy of the test method and the supporting report in Wordperfect 6.x format.

If you have any questions about our comments or you would like to meet to discuss them, please contact Gary McAlister of my staff at (919) 541-1062.

Sincerely,

J. David Mobley, Acting Director
Emissions, Monitoring and Analysis Division

cc: K. C. Hustvedt (MD-13)
Stephen A. Shedd (MD-13)
Jeffrey A. Telander (MD-13)

Enclosure

Internet Address (URL) • http://www.epa.gov
Recycled/Recyclable • Printed with Vegetable Oil Based Inks on Recycled Paper (Minimum 25% Postconsumer)

Figure 4. (cont.) EPA Method 301 Validation Approval Letter – page 2

2

Table 1. NCASI Method DI/HAPS-99.01 - Purged-Packed Injector and Cyclohexanol as the Internal Standard

Compound	Validated	Correction Factor
Acetaldehyde	Yes	1.12
Methanol	Yes	None
Propionaldehyde	Yes	1.12
Methyl Ethyl Ketone	Yes	0.97

Table 2. NCASI Method DI/HAPS-99.01 - Split/Splitless Injector and Cyclohexanol as the Internal Standard

Compound	Validated	Correction Factor
Acetaldehyde	Yes	1.09
Methanol	Yes	1.04
Propionaldehyde	Yes	1.09
Methyl Ethyl Ketone	Yes	1.03

Table 3. NCASI Method DI/HAPS-99.01 - Purged-Packed Injector and 2,2,2-Trifluoroethanol as the Internal Standard

Compound	Validated	Correction Factor
Acetaldehyde	Yes	1.14
Methanol	Yes	None
Propionaldehyde	Yes	1.14
Methyl Ethyl Ketone	Yes	1.07

Table 4. NCASI Method DI/HAPS-99.01 - Split/Splitless Injector and 2,2,2-Trifluoroethanol as the Internal Standard

Compound	Validated	Correction Factor
Acetaldehyde	Yes	1.06
Methanol	Yes	1.01
Propionaldehyde	Yes	1.06
Methyl Ethyl Ketone	Yes	None

NCASI METHOD RSC-02.02

REDUCED SULFUR COMPOUNDS BY DIRECT INJECTION GC/PFPD

NCASI
West Coast Regional Center
Organic Analytical Program
March 2007

Acknowledgements

This method was prepared by Diana Cook, Project Leader, and Dean Hoy, Research Associate, at the NCASI West Coast Regional Center.

For more information about this method, contact:

Diana Cook
NCASI West Coast Regional Center
PO BOX 458
Corvallis, OR 97339
(541) 752-8801
FAX (541) 752-8806
DCook@ncasi.org

For information about NCASI publications, contact:

Publications Coordinator
NCASI
PO Box 13318
Research Triangle Park, NC 27709-3318
(919) 941-6411
publications@ncasi.org

National Council for Air and Stream Improvement, Inc. (NCASI). 2007. Reduced Sulfur Compounds by Direct Injection GC/PFPD. *NCASI Methods Manual*. Research Triangle Park, NC: National Council for Air and Stream Improvement, Inc.

© 2007 by the National Council for Air and Stream Improvement, Inc.

NCASI's Mission:
To serve the forest products industry as a center of excellence for providing technical information and scientific research needed to achieve the industry's environmental goals.

Disclaimer

The mention of trade names or commercial products does not constitute endorsement or recommendation for use.

NCASI METHOD RSC-02.02

REDUCED SULFUR COMPOUNDS BY DIRECT INJECTION GC/PFPD

1.0 SCOPE AND APPLICATION

1.1 This method is used for the determination of the reduced sulfur compounds (RSCs) total sulfide as hydrogen sulfide (H_2S) [7783-06-4], methyl mercaptan (MeSH) [74-93-1], dimethyl sulfide (DMS) [75-18-3], dimethyl disulfide (DMDS) [624-92-0], and dimethyl trisulfide (DMTS) [3658-80-8] in wastewaters from pulp and paper mills. The RSCs are measured by direct aqueous injection gas chromatography with pulsed flame photometric detection (GC/PFPD).

1.2 The concentration of sulfide (H_2S) measured using this method represents the total amount of sulfide in the sample volatile at pH 2.5. It is believed that this includes all freely dissolved sulfide plus sulfide weakly associated with either dissolved organic matter or certain transition metals. If native sample pH is greater than 2.5, the actual total sulfide concentration in solution might be less than the concentration measured by this method.

1.3 The method has been applied to influent to wastewater treatment, samples from within the wastewater treatment system, and effluent from wastewater treatment.

1.4 This method has been validated for a single laboratory.

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 aqueous process stream or wastewater basin using appropriate collection vessels. Samples require two different preservation techniques to preserve all analytes. Samples are kept refrigerated until analysis.

2.2 In the laboratory, an aliquot of the sample is transferred to a 2-mL sealed vial. An aliquot of an internal standard solution is added to each of the vials. The sample is acidified (total sulfide only) and injected into the GC with a split injection. The GC column is temperature programmed to separate the analytes from other compounds which may be present in the sample. The analytes are selectively detected with a PFPD.

2.3 Identification of the RSCs is determined by comparison of their relative retention times with the relative retention times of an internal standard. If the results are questionable, confirmation using a second column may be necessary.

2.4 The RSCs are quantified by comparison with liquid standards using the internal standard technique. Multiple standards are analyzed to cover a calibration range of 20 to 1000 µg S/L. Calibration to lower concentrations may be possible for some compounds. Dilution is required to analyze samples with concentrations above 1000 µg S/L.

2.5 The method detection limit was calculated using the USEPA procedure in 40 CFR Part 136 Appendix B (Federal Register 1984) in a final effluent collected from an unbleached kraft mill after allowing the sulfide level to drop to less than 50 µg S/L. The method detection limit determined for total sulfide was 32.0 µg S/L. The sensitivity of the method has not been determined for MeSH, DMS, DMDS, and DMTS, and the detection limits have not been established. MeSH, DMS, DMDS, and DMTS have been successfully calibrated down to concentrations of 20 µg S/L.

2.6 Data quality is assured with ongoing recovery assessments, duplicate analyses, surrogate recovery experiments, matrix spike experiments, and blank analyses. MeSH, DMS, and DMDS standards are checked by comparing the results with an independently prepared standard. The sulfide standard is verified by independent analysis using EPA Methods 376.1 and 376.2.

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 µg/L – micrograms of compound per liter

3.1.2 µg S/L – micrograms of sulfur per liter

3.1.3 May – this action, activity, or procedural step is neither required nor prohibited

3.1.4 Must not – this action, activity, or procedural step is prohibited

3.1.5 Must – this action, activity, or procedural step is required

3.1.6 Should – this action, activity, or procedural step is suggested, but not required

4.0 INTERFERENCES

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, injection port liners, 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, and glassware that comes in contact with concentrations less than 50 µg S/L may need to be deactivated. Glassware can be deactivated either by soaking in acid followed by silylation or by Siltek™ coating as described in Section 6.1.1. After use, clean all glassware by washing with mild

detergent in hot water and rinsing with tap water. The glassware should then be drained until completely dry.

4.3 It is required that all metal surfaces that come in contact with the sample be deactivated. This includes injection port liners, seals, and syringe needles. Deactivate the metal surfaces as described in Section 6.1.1.3.

4.4 The internal standard, thiophene, may be present in some pulp mill process streams. If the composition on a matrix is unknown, a sample analyzed without internal standard should be examined for the presence of thiophene. The surrogate, thioanisole, can be used as an internal standard if interference with thiophene is identified.

4.5 Some compounds can interfere with the chromatography if the separation is not efficient. Specific interference includes partial coelution of carbon disulfide with dimethyl disulfide. When performed properly, this method separates these compounds sufficiently. During the development of the method, carbon disulfide was not detected in any of the wastewater samples analyzed.

4.6 After a number of injections of samples, a sulfur dioxide artifact peak can interfere with methyl mercaptan. A clean, deactivated injection port liner should be installed after approximately 20 sample injections. The injection port gold seal should also be cleaned with deionized water, methanol, and acetone using a long cotton swab prior to inserting the clean injection port liner during liner changes.

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 be employed (NRC 1995).

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 The RSCs are either flammable gases or liquids that may be harmful if inhaled or ingested. These compounds can also cause a considerable nuisance odor. Use them 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 amber glass bottles with minimal headspace. It is recommended that 40-mL amber, borosilicate glass vials with Teflon™ faced silicone backed lids (VOA vials) be used. Although passivation of glassware for RSC compounds is common practice, passivation of sample containers during this study has not been found to be necessary in the standard operating range of this method. Some improvement of the lower level calibration response has been found when using passivated autosampler vials. If passivation of glassware is desired, one of the following techniques can be used.

6.1.1.1 Soak clean glassware in a 10% HCl solution for at least one hour. Rinse the glassware thoroughly with water, followed by an acetone rinse, air drying, and treatment with 5% dimethyldichlorosilane in toluene. Rinse the glassware with toluene, methanol, and water, then air dry it.

6.1.1.2 Treat clear VOA vials with the Siltek deactivation process (Restek Corporation, Bellefonte, PA). Caution: strong caustic detergents will remove the Siltek coating.

6.1.1.3 Treat syringe needles by slowly pumping a 15% solution of BSTFA in hexane three times followed by a rinse with acetone, methanol, and water.

6.1.2 The use of automatic sample collection equipment has not been validated for this method and should not be incorporated until its effectiveness has been proven.

6.2 Laboratory Glassware and Supplies

6.2.1 Amber 2-mL autosampler vials deactivated if desired by one of the methods described in Section 6.1.1

6.2.2 Volumetric flasks (10-mL, 50-mL)

6.2.3 Syringes (including gas-tight syringes) deactivated by methods described in Section 6.1.1.3.

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 and all required accessories including syringes, analytical columns, and gases

6.3.2 Injection port liner – 4-mm deactivated (silanized or Siltek) straight glass liner lightly packed with a plug of deactivated (silanized) quartz two-thirds the distance from the septum end of the liner (Section 17, Figure 1)

6.3.3 Column – 30 m x 0.25 mm x 1.4 μm, 6% cyanopropylphenyl 94% dimethylpolysiloxane bonded phase (624 phase) fused silica capillary column

6.3.4 GC detector – pulsed flame photometric detector (OI Analytical or equivalent) with appropriate data system

7.0 REAGENTS AND STANDARDS

7.1 Reagents

7.1.1 Deionized (DI) water should be tested immediately before use to verify the absence of any target analytes. If the water is 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).

7.1.2 Prepare phosphoric acid solution by combining one part of phosphoric acid (reagent grade) with three parts deionized water.

7.1.3 Prepare acidified DI water by adding phosphoric acid solution (Section 7.1.2) to DI water (Section 7.1.1) until the pH is between 2.3 and 2.7. It takes approximately 0.5 mL of acid in 1 L of water to reach this pH.

7.1.4 L-Ascorbic acid (ACS reagent grade)

7.1.5 Methanol (distilled in glass)

7.1.6 Prepare the zinc acetate solution (40 mmole/L) by adding 1.75 g of zinc acetate dehydrate (reagent grade) to 200 mL of DI water. Slowly adjust the pH drop wise by adding 1N NaOH while stirring the DI water containing the zinc acetate (this takes 20 to 30 minutes). Dropwise addition is important up to pH 8.0 in order to produce small crystals of the resulting salt which will homogenize upon shaking. Once pH 8.0 is achieved dropwise addition is not longer required. Finish adjusting the pH to between 12 and 12.5 using the 1N NaOH solution (total 1N NaOH required is approximately 20 mL). This solution should produce a fine, even suspension which does not settle rapidly. If you shake the container and then let it sit, it will usually remain in suspension for over 20 minutes.

7.1.7 Prepare dimethyldichlorosilane (DMDCS) 5% in toluene by adding 25 mL of DMDCS to 475 mL of toluene. It is also available as a mixture from Supelco as Sylon CT.

7.1.8 Prepare N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) 15% in hexane by adding 1.5 mL of BSTFA to 8.5 mL of hexane.

7.1.9 Toluene (distilled in glass)

7.1.10 Hexane (distilled in glass)

7.1.11 $CaCl_2$ desiccant, 96%+ ACS reagent grade

7.1.12 Prepare NaOH 1 N by dissolving 40 g of pellets (97+%) into 1 L of DI water.

7.2 Analytical Standards

Analytical standards are prepared from pure standards. Reported purity should be greater than 95% for all the neat material used.

7.2.1 Prepare the internal standard primary solution by weighing 26 mg (to the nearest 0.1 mg) of thiophene and diluting to 10 mL in volumetric flasks with methanol. Prepare the primary standard at a concentration of approximately 1 mg S/mL . Calculate the actual concentration using Equation 1.

Equation 1

$$C_S = \frac{(m * FS)}{V_S}$$

where: C_S *is the concentration of sulfur in the standard (mg S/mL)*
m is the mass of the compound added to the standard (mg)
FS is the fraction of sulfur in the compound (Section 17, Table 6 except for $NaS_2 \bullet 9H_2O$*, which is 0.1335)*
V_S *is the total volume of the standard (mL)*

7.2.2 Prepare the surrogate standard primary solution by weighing, to the nearest 0.1 mg, 40 mg of thioanisole and diluting to 10 mL in volumetric flasks with methanol. Prepare the primary standard at a concentration of approximately 1 mg S/mL. Calculate the actual concentration using Equation 1.

7.2.3 Prepare a combined internal standard and surrogate working solution by adding 400 µL of each primary stock (Sections 7.2.1 and 7.2.2) to a 10-mL volumetric flask and diluting to the mark with methanol. The concentration in the solution is approximately 40 µg S/mL for each compound.

7.2.4 Prepare a primary and working standard of sulfide from sodium sulfide nonahydrate (Na_2S). The $Na_2S \bullet 9H_2O$ should be either opaque or white crystals. This material is hydroscopic and will turn into a slurry if not stored in a dry environment such as a desiccator containing anhydrous $CaCl_2$ and wrapped with tape to seal the bottle. It will also turn yellow or green (elemental sulfur) in storage. Prepare the working solution by adding 340 mg of zinc acetate dihydrate to 40 mL of purged DI water. Slowly adjust the pH drop wise by adding 1N NaOH while stirring the water containing the zinc acetate (this takes 10 to 20 minutes). Dropwise addition is important up to pH 8.0 in order to produce small crystals of the resulting salt which will homogenize upon shaking. Once pH 8.0 is achieved dropwise addition is not longer required. Finish adjusting to between 10.5 and 11 using the 1 N NaOH solution. Add 38 mg of $Na_2S \bullet 9H_2O$, weighed to the nearest 0.1 mg, while continuing to stir for 5 minutes. This solution should be a well dispersed suspension with no visible clumping of the solids. Transfer the solution quantitatively into a 50-mL volumetric flask and dilute to the mark with purged DI water. The concentration in the solution will be approximately 100 µg S/mL, with an equivalent total sulfide concentration of 106 µg/mL.

Calculate the actual concentration using Equation 1. The fraction of sulfur (FS) in $Na_2S \bullet 9H_2O$ is 0.1335.

7.2.5 Prepare a primary solution of MeSH by slowly bubbling MeSH gas into a tared 10-mL volumetric flask containing methanol. Allow the MeSH to dissolve into the methanol until approximately 15 mg (weighed to the nearest 0.1 mg) has been added. This corresponds to approximately 7.5 mL of pure gas at room temperature. Use a thin (1/16 inch) Teflon line to transfer the MeSH into the methanol and be sure that any methanol clinging to the line is knocked back into the volumetric flask before measuring the final weight. Dilute to the mark with methanol for a concentration of approximately 1 mg S/mL or 1.6 mg/mL as MeSH. Calculate the actual concentration using Equation 1.

7.2.6 Prepare a primary solution of DMS by weighing 19 mg (to the nearest 0.1 mg) of DMS into a 10-mL volumetric flask containing methanol. Dilute to the mark with methanol for a concentration of approximately 1 mg S/mL or 1.9 mg/mL as DMS. Calculate the actual concentration using Equation 1.

7.2.7 Prepare a primary solution of DMDS by weighing 15 mg (to the nearest 0.1 mg) of DMDS into a 10-mL volumetric flask containing methanol. Dilute to the mark with methanol for a concentration of approximately 1 mg S/mL or 1.5 mg/mL as DMDS. Calculate the actual concentration using Equation 1.

7.2.8 Prepare a primary solution of DMTS by weighing 13 mg (to the nearest 0.1 mg) of DMTS into a 10-mL volumetric flask containing methanol. Dilute to the mark with methanol for a concentration of approximately 1 mg S/mL or 1.3 mg/mL as DMTS. Calculate the actual concentration using Equation 1.

7.2.9 Prepare a working solution of MeSH by adding 1.0 mL of the primary solution (Section 7.2.4) to a 10-mL volumetric flask and diluting with methanol. MeSH is not stable when mixed with the other standards.

7.2.10 Prepare a primary solution of carbon disulfide (CS_2) by weighing 12 mg (to the nearest 0.1 mg) of CS_2 into a 10-mL volumetric flask containing methanol. Dilute to the mark with methanol for a concentration of approximately 1 mg S/mL or 1.2 mg/mL as CS_2. Calculate the actual concentration using Equation 1.

7.2.11 Prepare a working solution of mixed RSCs and CS_2 by adding 1.0 mL of the primary solutions of DMS (Section 7.2.6), DMDS (Section 7.2.7), DMTS (Section 7.2.8), and CS_2 (Section 7.2.10) to a 10-mL volumetric flask and diluting with methanol.

7.3 Calibration Standards

7.3.1 Prepare a multilevel calibration working solution by adding 500 µL of each of the individual working solutions of sulfide (Section 7.2.4), MeSH (Section 7.2.9), and mixed RSCs (Section 7.2.11) to a 5-mL volumetric flask. Dilute to the mark with purged DI water and adjust the pH to around 2.5 with

phosphoric acid solution. The calibration working solution has limited stability and should be prepared the day it is used.

7.3.2 Prepare a nominal 20 µg S/L calibration standard by adding 4.0 µL of the multipoint calibration solution (Section 7.3.1) to 1.8 mL of pH 2.5 adjusted DI water (Section 7.1.3) in a 2-mL autosample vial. Add 9 µL of the internal standard working solution (Section 7.2.3) for a nominal internal standard concentration of 200 µg S/L. Calculate the concentration of each of the analytes and the internal standard using Equation 2.

Equation 2

$$C_{cal} = \frac{C_{WS} * V_{WS}}{V_{cal}}$$

where: C_{cal} *is the concentration of the analyte/internal standard in the calibration standard (µg S/L)*
C_{WS} *is the concentration of the analyte in the working solution (µg S/mL)*
V_{WS} *is the volume of working solution added to the calibration standard (mL)*
V_{cal} *is the volume of the calibration standard (0.002 L)*

7.3.3 Prepare a nominal 50 µg S/L calibration standard by adding 10 µL of the multipoint calibration solution (Section 7.3.1) to 1.8 mL of pH 2.5 adjusted DI water (Section 7.1.3) in a 2-mL autosample vial. Add 9 µL of the internal standard working solution (Section 7.2.3) for a nominal internal standard concentration of 200 µg S/L. Calculate the concentration of each of the analytes and the internal standard using Equation 2.

7.3.4 Prepare a nominal 200 µg S/L calibration standard by adding 40 µL of the multipoint calibration solution (Section 7.3.1) to 1.8 mL of pH 2.5 adjusted DI water in a 2-mL autosampler vial. Add 9 µL of the internal standard working solution (Section 7.2.3) for a nominal internal standard concentration of 200 µg S/L. Calculate the concentration of each of the analytes and the internal standard using Equation 2.

7.3.5 Prepare a nominal 500 µg S/L calibration standard by adding 100 µL of the multipoint calibration solution (Section 7.3.1) to 1.7 mL of pH 2.5 adjusted DI water in a 2-mL autosample vial. Add 9 µL of the internal standard working solution (Section 7.2.3) for a nominal internal standard concentration of 200 µg S/L. Calculate the concentration of each of the analytes and the internal standard using Equation 2.

7.3.6 Prepare a nominal 1000 µg S/L calibration standard by adding 200 µL of the multipoint calibration solution (Section 7.3.1) to 1.6 mL of pH 2.5 adjusted DI water in a 2-mL autosample vial. Add 9 µL of the internal standard working solution (Section 7.2.1) for a nominal internal standard concentration of

200 µg S/L. Calculate the concentration of each of the analytes and the internal standard using Equation 2.

7.3.7 Prepare a daily calibration check standard (200 µg S/L) by adding 4.0 µL of the working standards of sulfide (Section 7.2.4), MeSH (Section 7.2.9), and mixed RSCs (Section 7.2.11) to 1.8 mL of pH 2.5 adjusted DI water (Section 7.1.3) in a 2-mL autosample vial. Add 9 µL of the internal standard working solution (Section 7.2.1) for a nominal internal standard concentration of 200 µg S/L. Calculate the concentration of each of the analytes and the internal standard using Equation 2.

7.3.8 When preparing standards or samples, the autosampler vial has an air bubble after being sealed. This is important so that the analyte and internal standard spikes can be mixed well before analyzing the sample or standard. At least three good inverted shakes should be performed before injecting the standard or sample.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Collection

Collect grab samples directly from the process liquid stream using appropriate collection vessels, typically 40-mL VOA amber vials. Fill each vial with the sample, leaving minimum headspace. Collect a separate sample for analyzing total sulfide because of the preservation technique. A substantial quantity of preservative is required, so a dilution factor is needed to correct for dilution due to preservation. This can be accomplished by measuring the volume of preservative added and the final volume of the sample including preservative.

8.2 Preservation

8.2.1 Preservation for the analysis of MeSH, DMS, DMDS, and DMTS requires the addition of 120 mg of ascorbic acid to a 40-mL VOA vial (3 g/L) and pH adjustment to <2.5 with phosphoric acid solution. To adjust the pH, add a representative sample to an extra vial containing ascorbic acid. Measure the volume of phosphoric acid required to reach the target pH and discard that sample. Use that volume of acid to adjust the samples to be analyzed. If the volume of acid needed is less than 2 mL, no correction for dilution is required.

8.2.2 Preservation for the analysis of total sulfide requires the addition of 5 mL of zinc acetate solution (Section 7.1.6) to a 40-mL VOA vial. The final pH of the sample should be greater than 10. Adjust the pH with 1 N NaOH solution if necessary. A correction for the dilution of the sample by the preservative must be made. For example, if 35 mL of sample is diluted to 40 mL, the measured concentration should be multiplied by a dilution factor of 1.14. Sample volumes can be measured gravimetrically or using calibrated glassware (graduated cylinder).

8.3 Storage

All samples must be stored in a refrigerator (4°C) until analysis. Storage stability has been found to be matrix dependent. Using the prescribed preservation techniques, greater than 80% recovery was found for all compounds in both a bleached kraft mill effluent and an unbleached kraft mill effluent after 14 days of storage. Storage of zinc acetate preserved samples with native concentrations of <0.1 mg S/L collected in highly aerated portions of WWTP have yielded increasing concentrations of total sulfide over time.

9.0 QUALITY CONTROL

To control the quality of the data generated using this method, an initial calibration check, independent standard check, daily blank checks, daily calibration checks, surrogate recovery experiments, periodic duplicates, and periodic matrix spikes should be performed.

9.1 Initial Calibration Check

A multipoint internal standard calibration should be performed covering the operating range of the method (20 to 1000 µg S/L). A wider or narrower range is acceptable if all sample concentrations fall within that range. The criterion for acceptable linearity is a mean absolute percent error (MAPE) for the curve of less than or equal to 20% (Section 10.2.3).

9.2 Independent Standard Check

When a primary standard is prepared for calibration and matrix spike experiments, it should be compared with an independent standard either prepared from another source of compound or obtained from a certified standard vendor. Only methyl mercaptan, dimethyl sulfide, and dimethyl disulfide are commercially available as solutions in methanol at this time (Crescent Chemicals). The independent standard should match the primary standard used for calibration and matrix spikes within 30%. This check will minimize bias due to errors in standard preparation.

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 1.8 mL of purged DI water with internal standard and surrogate as described in Section 11.1. The RSC level in the blank should not exceed 20% of the lowest calibration point (4 µg S/L for MeSH, DMS, DMDS, and DMTS; 6 µg S/L for total sulfide).

9.4 Daily Calibration Checks

Prepare and analyze a mid-level calibration point every day that samples are analyzed. The percent recovery of each compound in the standard should be within 20% of the percent recovery of the same calibration level in the multipoint calibration. If the daily calibration check fails, it should be repeated. If it fails a second time, the standards (working, primary, internal standard) should be

reprepared. If it continues to fail, the multipoint calibration should be repeated. A summary of single laboratory daily calibration checks for this method is provided in Section 17, Table 1.

9.5 Surrogate Recovery Check

In this method thioanisole is utilized as a surrogate for the reduced sulfur compounds. All samples are spiked with 9 μL of the thioanisole spiking solution (Section 7.2.1) to monitor surrogate recovery. The percent recovery of the surrogate should be determined and the results charted to document the surrogate recovery of the method. Performance criteria for acceptable surrogate recovery, as determined during a single-laboratory validation of this method, are presented in Section 17, Table 2.

9.6 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 sample. The relative percent difference between the two samples should be calculated and charted to estimate the method's precision. Section 17, Table 3 lists the relative percent differences found during a single laboratory validation of the method.

9.7 Matrix Spike Analyses

A matrix spike analysis should be performed with each set of samples (batch of samples no greater than 20). A known amount of the RSC working solutions should be added to a sample so that the native plus the spike level of each RSC is at least one times the native level. The percent recovery of the matrix spike should be determined and the results charted to document the recovery of the method. Section 17, Table 3 lists the recovery found during single laboratory validation studies.

9.8 Field Replicates and Field Spikes

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

9.9 Resolution Checks

The resolution of the separation should be checked periodically (ideally on a daily basis) by measuring the valley between the DMS and CS_2 peaks. The valley should be less than 10% of the average peak heights of the two peaks. If the valley is 10% or greater, maintenance of the injection port and/or column is necessary.

10.0 CALIBRATION AND STANDARDIZATION

10.1 GC/PFPD Operating Conditions

Assemble the GC/PFPD and establish the operating conditions outlined in Section 17, Table 4. Use the conditions specified by the PFPD manufacturer to optimize for the detection of sulfur compounds. Once the GC/PFPD system is optimized for

analytical separation and sensitivity, the same operating conditions must be used to analyze all samples, blanks, calibration checks, and quality assurance samples.

If excessive peak broadening is observed for sulfide and MeSH, a pressure pulse during the injection might keep the injection focused on the column. This has been necessary when using autoinjectors with a rapid injection stroke. An initial pressure of 30 psi for 0.2 min followed by a rapid drop back to a constant flow of 1.2 mL/min sharpened the early eluting peaks. Keep the pressure pulse time to a minimum because the PFPD loses its sulfur response at high carrier gas flow rates.

10.2 Initial Multipoint Calibration

The square root of the PFPD response for sulfur is approximately linear with respect to concentration over the operating range of the method. To demonstrate this and establish a calibration function for the method, prepare and analyze calibration standards to cover this range. The internal standard calibration approach should be used for this method. Calibrate the RSCs using concentrations normalized to the sulfur content of the standard. The use of sulfur concentrations ensures that the concentrations prepared cover the operating range of the detector. It also allows the relative response factors to be checked, because, theoretically, they should all be 1.

10.2.1 Determine the retention times of the analytes by analyzing a daily calibration solution (Section 7.3.7). A chromatogram similar to that shown in Section 17, Figure 2 should be obtained. Identify the peaks and determine their relative retention times using Equation 3. Section 17, Table 6 lists the relative retention times for the RSCs using this method.

Equation 3

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

where: RRT_i *is the relative retention time for compound i*
RT_i *is the retention time for compound i*
RT_{IS} *is the retention time for the internal standard*

10.2.2 Prepare a five point calibration curve to determine the relationship between instrument response and concentration over the operating range for each analyte. Analyze each of the calibration standards prepared as described in Sections 7.3.2 through 7.3.7.

10.2.3 The results of the calibration standard analyses for each compound are either fitted to a quadratic equation or described by an average relative response factor using internal standard calibration techniques. To find the best quadratic fit for the data, plot the response ratio of each compound as calculated in Equation 4 versus the ratio of the standard concentration versus the internal standard concentration. Curve fitting software either in the data system (e.g., Agilent Chemstation) or external to the data system (e.g., Excel) can be used to fit the best quadratic equation in the form of Equation 5.

Equation 4

$$RR = \frac{A_i}{A_{IS}}$$

where: RR is the response ratio
A_i is the area of the peak for compound i
A_{IS} is the area of the internal standard peak

Equation 5

$$RR_i = a + b * C_R + c * C_R^2$$

where: RR is the response ratio
a is the y-intercept from the quadratic regression
b is the linear constant from the quadratic regression
C_R is the ratio of the compound concentration versus the internal standard concentration
c is the quadratic constant from the quadratic regression

If the calibration criteria cannot be met using a quadratic fit, the average response factor can be used. Calculate the average response factor by finding the mean of the relative response factors calculated for each concentration of standard, as shown in Equation 6.

Equation 6

$$RRF_i = \left(\frac{A_i \times C_{IS}}{A_{IS} \times C_{cal}} \right)$$

where: RRF_i is the relative response factor for compound i
A_i is the area of the peak for compound i
A_{IS} is the area of the internal standard peak
C_{cal} is the concentration as sulfur in the calibration standard (µg S/L)
C_{IS} is the concentration of internal standard as sulfur (µg S/L)

To evaluate the closeness of the fit for the calibration, use the calibration model chosen (quadratic curve or average response factor) to calculate the concentration for each calibration level. Use Equation 7 to calculate the concentration using the quadratic model or Equation 8 to calculate the average response factor model. Determine the error for each level and calculate the mean absolute percent error (MAPE) as shown in Equation 9. The MAPE is used by software packages such as SAS and Statgraphics to evaluate the fit between a model prediction and the measured values.

Equation 7

$$C_i = \frac{\left(-b + \sqrt{b^2 - 4c(a - RR)}\right)}{2c} * C_{IS}$$

where: C_i *is the measured concentration of compound i (µg S/L)*
a is the y-intercept from the quadratic regression
b is the linear constant from the quadratic regression
c is the quadratic constant from the quadratic regression
RR is the response ratio
C_{IS} *is the concentration of internal standard as sulfur (µg S/L)*

Equation 8

$$C_i = \frac{RR}{RRF} * C_{IS}$$

where: C_i *is the measured concentration of compound i (µg S/L)*
RR is the response ratio
RRF is the relative response factor
C_{IS} *is the concentration of internal standard as sulfur (µg S/L)*

Equation 9

$$MAPE = \frac{\sum \left| \frac{C_{cal} - C}{C_{cal}} \right| * 100}{n}$$

where: MAPE is the mean absolute percent error
C_{cal} *is the concentration in the calibration standard*
C is the concentration measured for the calibration level
n is the number of calibration levels

The MAPE should be below 20% for each compound. Section 17, Table 5 lists the MAPE found for several calibrations using both an average and a quadratic calibration model. Section 17, Figure 3 shows a typical calibration curve for the PFPD response with a quadratic fit.

If a 20% MAPE cannot be achieved, one or more of the following actions should be taken.

10.2.3.1 Standards should be reanalyzed if the analysis appears to be suspect due to large variation from predicted response.

10.2.3.2 Standards should be reprepared if they appear to be suspect after reanalysis.

10.2.3.3 System maintenance should be performed, including replacing the injection port liner, replacing the septum, clipping the column, checking the split ratio, and checking the detector parameters.

10.2.3.4 The calibration range may be reduced by eliminating the low level or high level calibration standard. If the calibration range is changed, do not report values that are measured outside this range. This is especially true for the quadratic model, where large errors can occur.

10.3 Daily Calibration Check

Prior to analyzing samples each day, a daily calibration check should be prepared (Section 7.3.7) and analyzed. Calculate the percent recovery of the standard using Equation 10 to verify the calibration. In-house percent recovery control limits should be determined, and should not exceed ±20%. If the calibration check does not pass, the action items in Section 10.2.3 should be repeated. If these fail, the initial multipoint calibration should be repeated. Section 17, Table 1 summarizes the results for daily calibration checks during the method evaluation and subsequent single laboratory analyses.

Equation 10

$$R = \left(\frac{C_i}{C_{IC}} \right) \times 100$$

where: R is the recovery in percent
C_i is the measured concentration for compound i (µg S/L)
C_{IC} is the concentration measured during the initial calibration (µg S/L)

10.4 Blank Analysis

A method blank should be prepared and analyzed with the initial calibration and every day on which samples are analyzed. Prepare the blank the same as the calibration standards, but only add the internal standard solution (Section 7.3). The blank concentration should be less than 20% of the lowest calibration point. High blank levels can be caused by contaminated reagent water/acid, contaminated internal standard, contaminated glassware or syringes, and dirty injection ports. Resolution of sulfur dioxide, a common contaminate, from methyl mercaptan is critical for meeting the blank criteria. Section 17, Figure 4 shows a typical sample with MeSH resolved from the artifact peak.

11.0 PROCEDURE

11.1 Sample Analysis

Transfer a known volume (1.8 mL) of the sample to a autosample vial using a deactivated gas-tight syringe. If the sample is preserved at pH 2.5 no pH adjustment is required. If the sample is preserved at pH 10, phosphoric acid solution should be added to bring the pH to between 1.5 and 2.5. Determine the amount of acid needed using a trial sample, then add the determined amount to the sample to be analyzed (typically 15 to 20 µL). Add 9 µL (assuming a sample volume of 1.8 mL) of the internal standard solution (40 mg S/L thiophene and thioanisole) to the vial. Be sure that the spike goes into the sample liquid and that it is well mixed (Section 7.3.8). Inject the sample using the exact instrumental conditions used for the analysis of the calibration standards (Section 10.1). Calculate the concentration of each RSC using Equation 7 or 8, depending on the calibration model. If the concentration is above the calibration range, the sample must be diluted and reanalyzed.

11.2 Dilution

If dilution is necessary, inject some fractional volume less than 1.8 mL into the vial using a deactivated gas-tight syringe, bring it to 1.8 mL with DI water pH adjusted to 2.5, and analyze it as described in Section 11.1. Calculate the dilution factor by dividing 1.8 mL by the volume of sample used. For samples preserved for total sulfide analysis, dilution by the preservative must also be accounted for by multiplying the two dilution factors together.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Identification of Compounds

An analyte is identified by comparison of the relative retention time of the sample with the relative retention time of an authentic standard of the target compound analyzed using the same analytical conditions. Section 17, Table 6 lists the relative retention time windows for the RSCs and the absolute retention time windows for the internal standards.

12.2 Quantification of Compounds

Measure the concentration of each analyte as sulfur using Equation 7 or 8, then adjust for dilution and percent sulfur using Equation 11 to report the concentration as mass of compound instead of sulfur. The fraction of sulfur in each compound can be found in Section 17, Table 6.

Equation 11

$$C = \frac{C_i * DF}{FS}$$

where: C is the concentration of compound in the sample (µg/L)
C_i is the measured concentration for compound i (µg S/L)
DF is the dilution factor
FS is the fraction of sulfur in the compound

12.3 Duplicate Precision Estimate

Duplicate samples should be analyzed with each set of samples. Calculate the relative percent difference (RPD) for each duplicate pair as shown in Equation 12.

Equation 12

$$RPD = \frac{2 * |C_1 - C_2|}{(C_1 + C_2)} \times 100$$

where: RPD is the relative percent difference in the two determinations
C_1 is the first concentration measured (µg/L)
C_2 is the second concentration measured (µg/L)

12.4 Matrix Spike Calculation

A matrix spike experiment should be performed with each set of samples analyzed. Calculate the percent recovery using Equation 13.

Equation 13

$$R = \frac{(C_{MS} - C)}{C_S} \times 100$$

where: R is the percent recovery
C_{MS} is the concentration measured in the matrix spiked sample (µg/L)
C is the concentration measured in the unspiked sample (µg/L)
C_S is the theoretical concentration of the spiked compound (µg/L)

13.0 METHOD PERFORMANCE

13.1 Single laboratory performance of this method is detailed in Section 17, Tables 2 and 3. Single laboratory precision is estimated to be 12.3% MeSH and 10% or less for the other RSCs. The average matrix spike recoveries ranged from 93 to 112% for all target analytes. The average surrogate spike recovery was 106%.

13.2 Interlaboratory 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 Research Council (NRC) 1995. *Prudent Practices in the Laboratory*. National Academy Press. Washington, DC

16.2 Taylor, J.K. 1987. *Quality Assurance of Chemical Measurements.* Lewis Publishers. Chelsea, Michigan

17.0 TABLES AND DIAGRAMS

Table 1. Results of Daily Calibration Checks

Compound	Mean Recovery	RSD (%)	n
Total sulfide	106	11.2	94
Methyl mercaptan	95.0	10.6	42
Dimethyl sulfide	100	10.5	42
Dimethyl disulfide	111	8.3	42
Dimethyl trisulfide	102	11.5	42

Table 2. Surrogate Recovery

Compound	Mean Recovery	RSD (%)	n
Thioanisole	106	6.7	1077

Table 3. Duplicate Results and Matrix Spike Recovery

	Duplicate Precision		Matrix Spike Recovery		
Compound	Pooled RSD[a] (%)	n	Mean Recovery (%)	RSD (%)	n
Total sulfide	9.4	87	93	20.7	70
Methyl mercaptan	12.3	33	106	20.0	33
Dimethyl sulfide	5.6	34	102	11.7	34
Dimethyl disulfide	7.0	33	112	16.5	34
Dimethyl trisulfide	4.7	25	96	24.1	34

[a] equation for pooled relative standard deviation can be found in Taylor 1987

Table 4. GC/PFPD Operating Conditions for Measuring Reduced Sulfur Compounds

Injection port	split (15:1 ratio)
Injection volume	2 µL
Split vent flow rate	16 mL/min helium
Injector temperature	110°C
Injection liner	4 mm id with fused silica wool packing (deactivated, either Siltek or Silanized)
Carrier gas	helium
Carrier gas flow rate	constant flow mode at 1.2 mL/min (pressure pulse at injection might be necessary see Section 10.1)
Column	J&W DB-624, 30 m x 0.25 mm id with 1.4 µm film fused silica capillary column or equivalent
Oven temperature program	
Initial	10°C
Ramp 1	6°C/min to 35°C for 2 minutes
Ramp 2	8°C/min to 170°C
Ramp 3	40°C/min to 250°C for 3 minutes
Detector	PFPD (OI model 5380 or equivalent)
Temperature	250°C
Combustion tube	2 mm
Optical filter	BG-12 (purple)
Hydrogen flow	11 mL/min
Air flows	optimized as described by manufacturer
Pulse rate	3.1 Hz
Signal	square root of PMT signal

Table 5. Summary of Initial Calibration Results

	Average Response Factor		Quadratic Fit			
Compound	Mean RRF[a]	Mean MAPE[b]	Mean a[c]	Mean b[d]	Mean c[e]	Mean MAPE[b]
Total sulfide	0.641	30.2	-0.073	0.838	-0.006	20.7
Methyl mercaptan	0.673	21.5	-0.074	0.906	-0.025	14.8
Dimethyl sulfide	0.887	18.0	-0.062	1.094	-0.013	14.8
Dimethyl disulfide	0.983	16.8	-0.092	1.385	-0.083	13.0
Dimethyl trisulfide	0.989	16.3	-0.092	1.401	-0.089	12.1

[a] average of eight calibration sets' mean relative response factors
[b] average of fifteen calibration sets' mean absolute percent errors
[c] average of eight calibration sets' y-intercepts from a quadratic regression
[d] average of eight calibration sets' linear constants from a quadratic regression
[e] average of eight calibration sets' quadratic constants from a quadratic regression

Table 6. Retention Time Statistics for RSCs and Sulfur Fraction

Compound	Mean[a] RRT	RSD[b] (%)	Relative Retention Time Window[c]	Fraction Sulfur
Total sulfide	0.192	1.12	0.186 – 0.198	0.9408
Methyl mercaptan	0.318	0.84	0.310 – 0.326	0.6665
Dimethyl sulfide	0.527	0.57	0.518 – 0.536	0.5160
Dimethyl disulfide	1.217	0.11	1.213 – 1.221	0.6808
Dimethyl trisulfide	1.748	0.19	1.738 – 1.758	0.7618
Internal standards	Mean RT[d] (min)	RSD[b] (%)	Retention Time Window	Fraction Sulfur
Thiophene	11.37	0.37	11.24 – 11.49	0.3810
Thioanisole	22.41	0.17	22.52 – 22.29	0.2581

[a] mean relative retention time (relative to thiophene) for 30 calibration standard analyses
[b] relative standard deviation for 30 calibration standard analyses
[c] windows are calculate from the mean value ± three times the standard deviation
[d] mean retention time for 30 calibration standard analyses

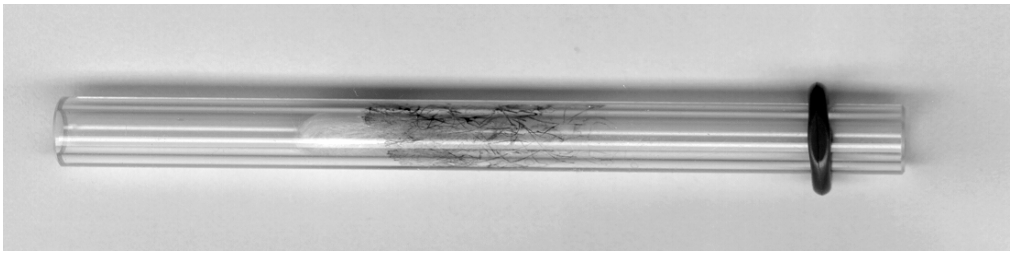


Figure 1. Injection Port Liner with Glass Wool Plug and Deposits from Approximately 20 injections Containing 3 g/L Ascorbic Acid

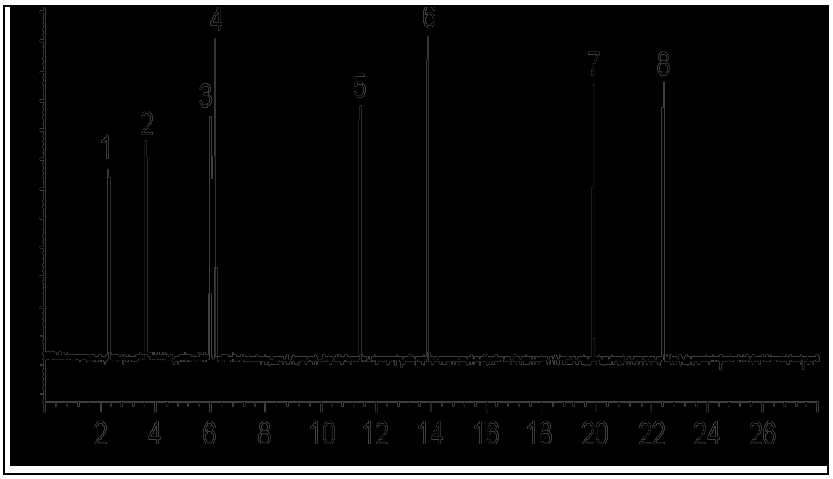


Figure 2. Chromatogram of 200 µg S/L Standard Containing (1) Total Sulfide; (2) MeSH; (3) DMS; (4) CS_2 (resolution check compound); (5) Thiophene (internal standard); (6) DMDS; (7) DMTS; (8) Thioanisole (internal standard)

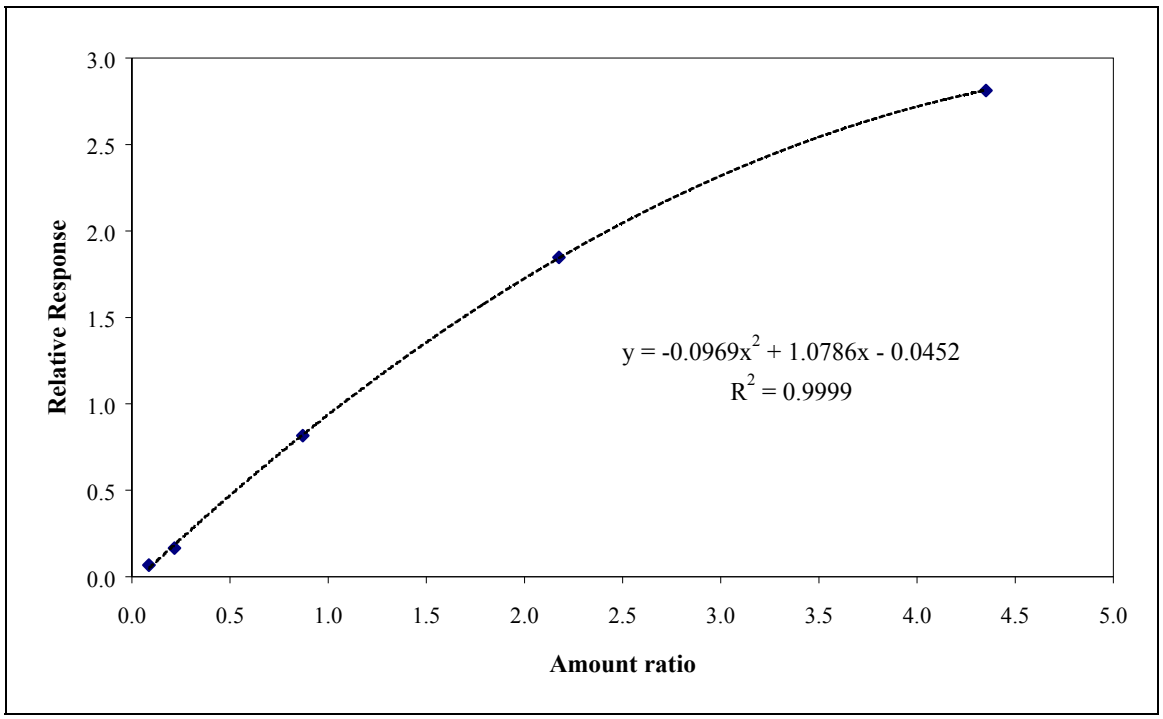


Figure 3. Typical Calibration Curve for Total Sulfide with Quadratic Equation

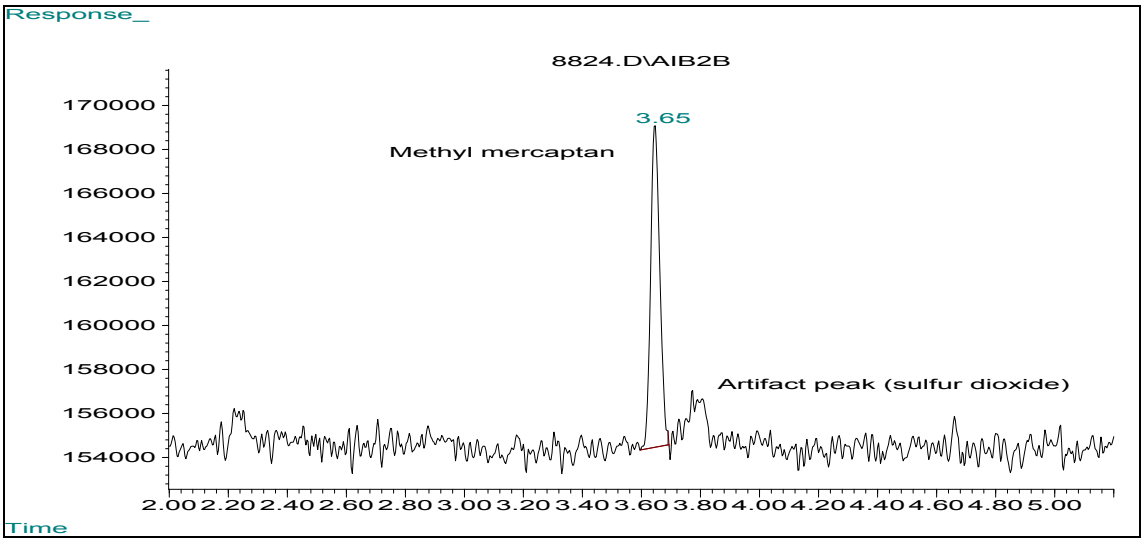


Figure 4. Separation of Methyl Mercaptan (100 µg S/L) from Artifact Peak in Pulp Mill Effluent

Sulfide

DOC316.53.01136

USEPA[1] Methylene Blue Method[2]

Method 8131

5 to 800 µg/L S^{2-} (spectrophotometers)

Reagent Solution

0.01 to 0.70 mg/L S^{2-} (colorimeters)

Scope and application: For testing total sulfides, H_2S, HS^-, and certain metal sulfides in groundwater, wastewater, brines and seawater.

[1] USEPA accepted for reporting wastewater analysis. Procedure is equivalent to Standard Method 4500-S^{2-} D.
[2] Adapted from Standard Methods for the Examination of Water and Wastewater.

Test preparation

Instrument-specific information

Table 1 shows all of the instruments that have the program for this test. The table also shows sample cell and orientation requirements for reagent addition tests, such as powder pillow or bulk reagent tests.

To use the table, select an instrument, then read across to find the applicable information for this test.

Table 1 Instrument-specific information

Instrument	Sample cell orientation	Sample cell
DR 6000 DR 3800 DR 2800 DR 2700 DR 1900	The fill line is to the right.	2495402 
DR 5000 DR 3900	The fill line is toward the user.	
DR 900	The orientation mark is toward the user.	2401906 

Before starting

Samples must be analyzed immediately after collection and cannot be preserved for later analysis.
Install the instrument cap on the DR 900 cell holder before ZERO or READ is pushed.
Some sulfide loss can occur if dilution is necessary.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.

Items to collect

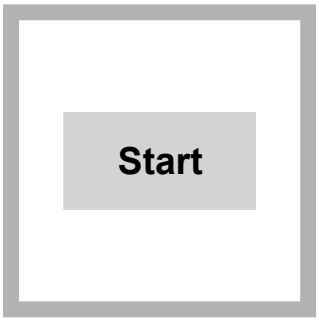
Description	Quantity
Sulfide 1 Reagent	1–2 mL
Sulfide 2 Reagent	1–2 mL
Water, deionized	10–25 mL
Pipet, serological, 10-mL	1
Pipet Filler, safety bulb	1
Sample cells (For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.)	2
Stoppers	2

Refer to Consumables and replacement items on page 5 for order information.

Sample collection

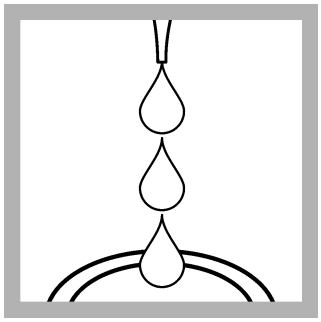
- Analyze the samples immediately. The samples cannot be preserved for later analysis.
- Collect samples in clean glass or plastic bottles with tight-fitting caps. Completely fill the bottle and immediately tighten the cap.
- Prevent agitation of the sample and exposure to air.

Reagent solution procedure

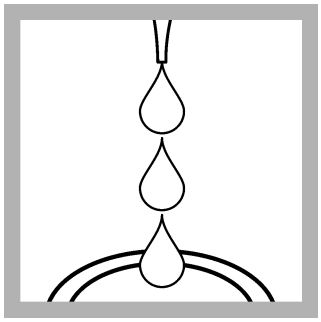


1. Start program **690 Sulfide**. For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.

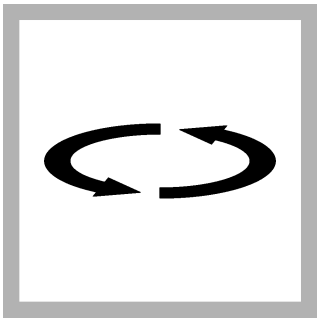
2. Prepare the blank: Fill a sample cell with deionized water. Use 10 mL for spectrophotometers and 25 mL for colorimeters.



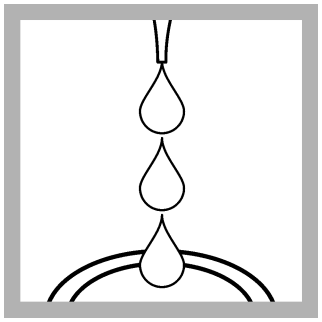
3. Prepare the sample: Use a pipet to add sample to a second sample cell. Use 10 mL for spectrophotometers and 25 mL for colorimeters. Do not mix the sample more than necessary to prevent sulfide loss.



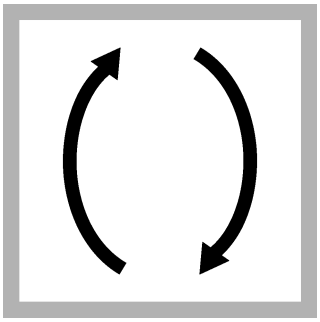
4. Add Sulfide 1 Reagent to each sample cell. Use 0.5 mL for spectrophotometers and 1.0 mL for colorimeters.



5. Swirl to mix.

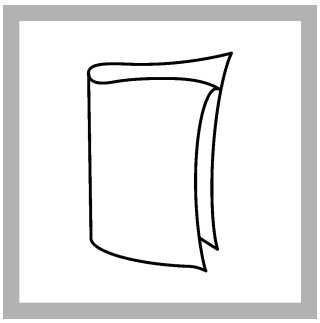


6. Add Sulfide 2 Reagent to each sample cell. Use 0.5 mL for spectrophotometers and 1.0 mL for colorimeters.

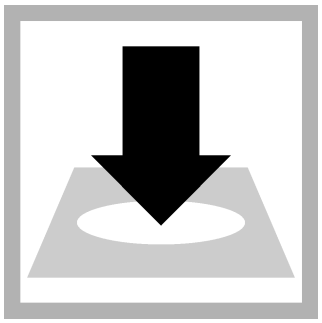


7. Close the sample cell. Invert the sample cell to mix. A pink color will develop initially. If sulfide is present, the solution becomes blue.

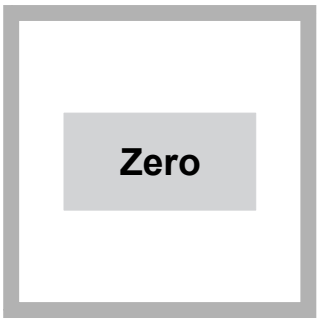
8. Start the instrument timer. A five-minute reaction time starts.



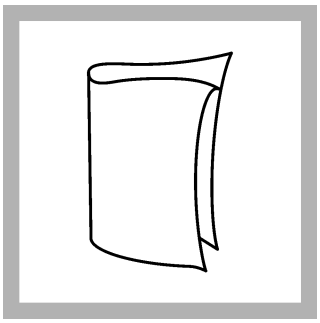
9. When the timer expires, clean the blank sample cell.



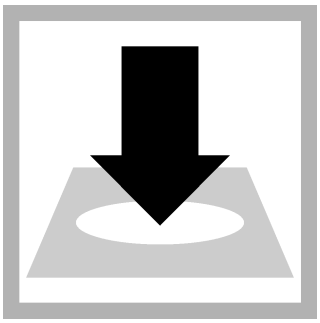
10. Insert the blank into the cell holder.



11. Push **ZERO**. The display shows 0 µg/L or 0.00 mg/L S^{2-}.



12. Clean the prepared sample cell.



13. Insert the prepared sample into the cell holder.

14. Push **READ**. Results show in µg/L or mg/L S^{2-}.

Soluble sulfides

To measure soluble sulfides, use a centrifuge to separate the solids. To make an estimate of the amount of insoluble sulfides in the sample, subtract the soluble sulfide concentration from the total (with solids) sulfide concentration.

1. Fill a centrifuge tube completely with sample and immediately cap the tube.
2. Put the tube in a centrifuge and run the centrifuge to separate the solids.
3. Use the supernatant as the sample in the test procedure.

Interferences

Interfering substance	Interference level
Barium	Concentrations more than 20 mg/L barium react with the sulfuric acid in Sulfide 1 Reagent and form a $BaSO_4$ (barite) precipitate. To correct for this interference: **1.** Dilute the sample in the test procedure as follows: • Spectrophotometers: use a 0.1-mL or 1.0-mL sample volume and add deionized water to the 10-mL mark. • Colorimeters: use a 0.25-mL or 2.5-mL sample volume and add deionized water to the 25-mL mark. **2.** Add both Sulfide 1 and Sulfide 2 reagents per the procedure steps. **3.** After the 5-minute reaction period, pour the sample into a 50-mL beaker. **4.** Pull the sample into a Luer-Lock syringe (10 cc for spectrophotometers or 60 cc for colorimeters). **5.** Put a 0.45-µm filter disc on the Luer-Lock tip and filter the sample into a clean sample cell for measurement. Use deionized water to prepare the blank. **6.** Set the instrument zero and read the result, per the procedure steps. **7.** Multiply by the appropriate dilution factor for the dilution used (10 or 100).
Strong reducing substances such as sulfite, thiosulfate and hydrosulfite	Prevent the full color development or reduce the blue color
Sulfide, high levels	High concentrations of sulfide can inhibit the full color development. Use a diluted sample in the test procedure. Some sulfide loss can occur when the sample is diluted.
Turbidity	Pre-treat the sample to remove sulfide, then use the pre-treated sample as the blank in the test procedure. Prepare a sulfide-free blank as follows: **1.** Measure 25 mL of sample into a 50-mL Erlenmeyer flask. **2.** Add 30-g/L Bromine Water by drops with constant swirling until a yellow color remains. **3.** Add 30-g/L Phenol Solution by drops with constant swirling until the yellow color is removed. **4.** Use this solution to replace the deionized water blank in the test procedure.

Method performance

The method performance data that follows was derived from laboratory tests that were measured on a spectrophotometer during ideal test conditions. Users can get different results under different test conditions.

Program	Standard	Precision (95% confidence interval)	Sensitivity Concentration change per 0.010 Abs change
690	520 µg/L S^{2-}	504–536 µg/L S^{2-}	5 µg/L S^{2-}

Summary of method

Hydrogen sulfide and acid-soluble metal sulfides react with N,N-dimethyl-p-phenylenediamine sulfate to form methylene blue. The intensity of the blue color is proportional to the sulfide concentration. High sulfide levels in oil field waters may be determined after proper dilution. The measurement wavelength is 665 nm for spectrophotometers or 610 nm for colorimeters.

Pollution prevention and waste management

Reacted samples contain hexavalent chromium and must be disposed of as a hazardous waste. Dispose of reacted solutions according to local, state and federal regulations.

Consumables and replacement items

Required reagents

Description	Quantity/test	Unit	Item no.
Water, deionized	varies	4 L	27256
Sulfide Reagent Set	—	—	2244500
Includes:			
Sulfide 1 Reagent	1–2 mL	100 mL MDB	181632
Sulfide 2 Reagent	1–2 mL	100 mL MDB	181732

Required apparatus

Description	Quantity/test	Unit	Item no.
Pipet, serological, graduated, 10 mL	1	each	53238
Pipet filler, safety bulb	1	each	1465100
Stoppers for 18-mm tubes and AccuVac Ampuls	2	6/pkg	173106

Optional reagents and apparatus

Description	Unit	Item no.
Bromine Water, 30-g/L	29 mL	221120
Phenol Solution, 30-g/L	29 mL	211220
Stoppers for 18-mm tube	25/pkg	173125
Flask, Erlenmeyer, 50 mL	each	50541

FOR TECHNICAL ASSISTANCE, PRICE INFORMATION AND ORDERING:
In the U.S.A. – **Call toll-free 800-227-4224**
Outside the U.S.A. – **Contact the HACH office or distributor serving you.**
On the Worldwide Web – **www.hach.com**; E-mail – **techhelp@hach.com**

HACH COMPANY
WORLD HEADQUARTERS
Telephone: (970) 669-3050
FAX: (970) 669-2932

© Hach Company/Hach Lange GmbH, 1989–2015, 2018. All rights reserved.

09/2018, Edition 11

APPENDIX C – CMS MATRIX

Table C-1
Proposed Condensate Collection and Treatment CMS
New-Indy Catawba, SC Mill

Location of Measurement	Measurement Taken	Measurement Device	Calculation Method	Monitoring Period	CMS Downtime	Definition of Good Data Quality	CMS Verification/Calibration
Foul Condensate Hardpipe	Flow	Continuous flow meter	Gallons per day (gpd) = Average gallons per minute (gpm) x Operating minutes per day	24 hour total	Failure to obtain good data quality for 80% of the daily operating time, without backup measurement.	Instrument reading within range or the standard deviation of the raw instrument tag for the past three hours is greater than zero.	Per manufacturer recommendations, calibration/verification of flow meter and transmitter
Foul Condensate to Steam Stripper	Flow	Continuous flow meter	Gallons per hour (gph) = Average gallons per minute (gpm) x Operating minutes per hour	1-hour average	Failure to obtain good data quality for 80% of the daily operating time, without backup measurement.	Instrument reading within range or the standard deviation of the raw instrument tag for the past three hours is greater than zero.	Per manufacturer recommendations, calibration/verification of flow meter and transmitter
Steam Stripper Steam Feed Rate	Flow	Continuous flow meter	Average steam feed rate in pounds per hour (lb/hr)	1-hour average	Failure to obtain good data quality for 80% of the daily operating time, without backup measurement.	Instrument reading within range or the standard deviation of the raw instrument tag for the past three hours is greater than zero.	Per manufacturer recommendations, calibration/verification of meter and transmitter
Foul Condensate Steam Stripper Feed Temperature	Temperature	Continuous temperature probe	Average temperature in degrees Farenheit (°F)	1-hour average	Failure to obtain good data quality for 80% of the daily operating time, without backup measurement.	Instrument reading within range or the standard deviation of the raw instrument tag for the past three hours is greater than zero.	Per manufacturer recommendations, calibration/verification of meter and transmitter
Stripped Condensate Temperature	Temperature	Continuous temperature probe	Average temperature in degrees Farenheit (°F)	1-hour average	Failure to obtain good data quality for 80% of the daily operating time, without backup measurement.	Instrument reading within range or the standard deviation of the raw instrument tag for the past three hours is greater than zero.	Per manufacturer recommendations, calibration/verification of meter and transmitter
Stripped Condensate Flow	Flow	Continuous flow meter	Gallons per hour (gph) = Average gallons per minute (gpm) x Operating minutes per hour	1-hour average	Failure to obtain good data quality for 80% of the daily operating time, without backup measurement.	Instrument reading within range or the standard deviation of the raw instrument tag for the past three hours is greater than zero.	Per manufacturer recommendations, calibration/verification of meter and transmitter
Pulp Flow and Consistency meter	Digester production oven dried tons of pulp (ODTP)	Continuous pulp flow and consistency meters	ODTP = ADTUBP/d [(Daily average pulp slurry flow, gpm) x Daily average pulp consistency, %)/100 * gpm)*(pulp consistency, %/100)[8.17 + (0.0333 * pulp consistency, %)] * 1440 / 1800] * 0.9 ODTUBP/ADTUBP	24 hour total	Failure to obtain good data quality for 80% of the daily operating time, without backup measurement.	Instrument reading within range or the standard deviation of the raw instrument tag for the past three hours is greater than zero.	Per manufacturer recommendations, calibration/verification of pulp slurry flow meter and calibration of pulp consistency measurement devices per TAPPI method
Fresh Water Intake Flow (used for calculation of ASB Wastewater Inlet Flow)	Flow	Continuous flow meter	Wastewater inlet flow rate to ASB, gpd = Average gpm Fresh Water Intake flow x (1 - Evaporation Rate) x Flow Meter Operational Minutes per Day	24 hour total	Failure to obtain good data quality for 80% of the daily operating time, without backup measurement.	Instrument reading within range or the standard deviation of the raw instrument tag for the past three hours is greater than zero.	Per manufacturer recommendations, calibration/verification of flow meter and transmitter
Number of Aerators Operating per Zone	Count	Readout in Pi	Sum of aerators operating per zone	Instantaneous	Failure to obtain data for an operating day	Measurement is consistent with regular in-field verification	Per manufacturer recommendations for instrumentation, as applicable
ASB Total Aerator hp-hrs	Hp-hrs	Readout in Pi or calculated value	Total daily hp-hrs = Sum for all aerators (75 hp x daily runtime, hrs)	24 hour total	Failure to obtain good data quality for 80% of the daily operating time, without backup measurement.	Measurement is consistent with regular in-field verification	Per manufacturer recommendations for instrumentation, as applicable

APPENDIX D – SULFUR COMPOUND CHAIN OF CUSTODY

Chain of Custody Record & Analytical Service Request

2655 Park Center Drive, Suite A
Simi Valley, California 93065
Phone (805) 526-7161
Fax (805) 526-7270

Requested Turnaround Time in Business Days
10 Day-Standard

ALS Contact: **Kelly Horiuchi**

Company Name & Address (Reporting Information)	Project Name
	Project Number
Project Manager	P.O. # / Billing Information
Phone / Fax	Sampler (Print & Sign)
Email Address for Result Reporting	

NCASI Method RSC-02.02

Comments, Notes Specific Instructions

Client Sample ID	Laboratory ID Number	Date Collected	Time Collected	Initial Sample pH	NaOH if needed (µL)	Phos. Acid Added (µL)	Final pH	pH Criteria per method	Comments
								total Sulfide >9	
								total Sulfide >9	
								RSC <2.5	
								RSC <2.5	
								total Sulfide >9	
								total Sulfide >9	
								RSC <2.5	
								RSC <2.5	
								total Sulfide >9	
								total Sulfide >9	
								RSC <2.5	
								RSC <2.5	
								total Sulfide >9	
								total Sulfide >9	
								RSC <2.5	
								RSC <2.5	
								total Sulfide >9	
								total Sulfide >9	
								RSC <2.5	
								RSC <2.5	

Field Spike Sample ID	Spike standard # on vial	Initial Reading	Volume Spiked	Comments

Report Tier Levels - please select

Tier I - Results (Default if not specified) _____
Tier II (Results + QC Summaries) _____
Tier III (Results + QC & Calibration Summaries) _____
Tier IV (Data Validation Package) 10% Surcharge _____

EDD required Yes / No
Type: ________________

Relinquished by: (Signature)	Date:	Time:	Received by: (Signature)	Date:	Time:
Relinquished by: (Signature)	Date:	Time:	Received by: (Signature)	Date:	Time:

Cooler / Blank
Temperature
_______oC