Appendix B

EPA Hydrogen Sulfide Monitoring Quality Assurance Project Plan (QAPP)

Quality Assurance Project Plan for Georgia-Pacific CAA Investigations Monitoring Activities in EPA Region 6

Prepared for:

U.S. Environmental Protection Agency
Office of Civil Enforcement
1200 Pennsylvania Avenue

Washington, DC 20460
Prepared by:

Eastern Research Group, Inc.
14555 Avion Parkway
Suite 200
Chantilly, VA 20151-1102

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TITLE AND APPROVAL SHEET

Quality Assurance Project Plan for the
National CAA Investigations Enforcement Support Region 6

12/14/16

Paul Buellesbach, ERG Program Manager Date

12/14/16

Jill Lucy, ERG Project QA Coordinator Date

12/14/16

Jason Sese, ERG Work Assignment Manager Date

01/03/17

Sounjay Gairola, OCE Work Assignment Manager Date

12/15/16

Rich Satterfield, EPA HQ QA Manager Date

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1. INTRODUCTION

The U.S. EPA Office of Civil Enforcement, Air Enforcement Division (OCE/AED) is directing ERG to assist Region 6 of the United States Environmental Protection Agency (EPA) with monitoring efforts at the Georgia-Pacific facility in Crossett, Arkansas. In cooperation with EPA Region 6, the Arkansas Department of Environmental Quality (ADEQ), and the Arkansas Department of Health, Georgia-Pacific has been conducting ambient air monitoring for hydrogen sulfide through a community monitor located near their paper mill in Crossett, Arkansas. The air monitor is about a half mile north of the wastewater treatment (WWT) clarifier. The Agency for Toxic Substance and Disease Registry (ATSDR) has published minimum risk levels (MRLs) and reference concentrations (RfCs) in its *Toxicological Profile for Hydrogen Sulfide and Carbonyl Sulfide,* and the monitor has periodically showed readings above the acute MRL of 70 parts per billion volume (ppbV). Because of these elevated concentrations of hydrogen sulfide, ERG will assist EPA Region 6 with ambient air monitoring through network design and passive sample collection and analysis. The resulting data will be used to determine point sources of hydrogen sulfide in the WWT system and if ambient levels of hydrogen sulfide are detected at levels exceeding the ATSDR intermediate MRL of 20 ppbV or the EPA's chronic inhalation reference concentration (RfC) of 1 ppbV.

2. PROJECT MANAGEMENT ELEMENTS

This section addresses project management, including project objectives, roles and responsibilities, and project goals. In addition, this section discusses the mechanisms ERG will use to ensure that all participants understand the goals and the approach used in the sampling of hydrogen sulfide levels around the Georgia-Pacific Crossett paper mill.

In its *Requirements for Quality Assurance Project Plans QA/R-5* (1), EPA has identified nine elements to be discussed in this section. ERG provided element A1, Title and Approval Sheet, and Element A2, Table of Contents earlier in this document. Table 2-1 presents the remaining elements and corresponding document sections.

Table 2-1. Crosswalk Between Document Sections and EPA Quality Assurance Project Plan Elements

Quality Assurance Project Plan Element		Document Section
A1 and A2	Title and Approval Sheet	Title Page and Approval Sheet
A3 through A9	Distribution List, Project Organization, Problem Definition/Background, Project/Task Description, Quality Objectives and Criteria, Special Training/Certification, Documents and Records	2.0
B1 through B10	Sampling Process Design; Sampling Methods; Sample Handling and Custody; Analytical Methods; Quality Control; Instrument/Equipment Testing, Inspection, Maintenance, and Calibration; Inspection/Acceptance of Supplies and Consumables, Non-Direct Measurements (Not applicable to this project); Data Management	3.0
C1 and C2	Assessments and Response to Actions, Reports to Management	4.0
D1, D2, and D3	Data Review, Verification, and Validation; Verification and Validation Methods; Reconciliation with User Requirements	5.0

2.1 Element A.3: Distribution List

Table 2-2 presents the distribution list for this Quality Assurance Project Plan (QAPP). The ERG Work Assignment Manager or his designee will be responsible for ensuring that the QAPP and any QAPP revisions are distributed to everyone in Table 2-2.

Table 2-2. QAPP Distribution List

Name	Organization	Role
Sounjay Gairola	US EPA/OCE	OCE Work Assignment Manager
Rich Satterfield	US EPA/OCE	EPA HQ QA Manager
Sarah Frey	US EPA/OCE	OCE Technical Lead
Mary Willett	ERG	ERG Corporate QA Manager
Jill Lucy	ERG	ERG Project QA Coordinator
Paul Buellesbach	ERG	ERG Program Manager
Sarah Yates	ERG	ERG Technical Reviewer
Jason Sese	ERG	ERG Work Assignment Manager
Dave Dayton	ERG	ERG Team Leader
Leta Kent	ERG	ERG Team Member

2.2 Element A.4: Project Organization

Figure 2-1 depicts the project organization for ERG and EPA Region 6 to conduct the Georgia-Pacific hydrogen sulfide sampling event. Jason Sese will serve as ERG's Work Assignment Manager (WAM). He will be responsible for all management and administrative aspects of the work performed and for ensuring that the quality of work, schedule, and budget meet the requirements of EPA/OCE. He will provide technical direction to ERG staff and will be responsible for the daily activities on the project. Mr. Sese will be the principal contact for EPA on project issues and schedule. Mr. Sese will maintain the finalized QAPP. He will also keep the ERG Project QA Coordinator and the Program Manager advised of any quality problems that arise.

Jill Lucy will serve as ERG's Project QA Coordinator responsible for ensuring that the requirements of this QAPP are implemented and documented. She is independent from the day-to-day activities on the project. Mary Willett is ERG's Corporate QA Manager. The Corporate QA Manager will interact with the Project QA Coordinator to ensure that project-specific quality assurance/quality control (QA/QC) programs are commensurate with project objectives and with ERG's quality system.

Sarah Yates will provide ERG's technical review, including review of the this QAPP and the sampling plan. She will be available during the execution of the project to provide technical expertise to the project team.

Dave Dayton will lead and direct ERG's team while in the field. He will make decisions in the field that support the goals of the project and will ensure his team follows the health and safety guidelines in the Health & Safety Plan in Appendix B. Leta Kent will provide field support with sample device setup.

ALS Environmental (ALS) located in Cincinnati, OH will provide analytical support for this investigation. Additional details on ERG's project QA organization can be found in ERG's *Enforcement and Technical Support for the Office of Civil Enforcement Contract Quality Management Plan (QMP)* (2), Section 1.2 Project Organization and Staff Responsibilities.

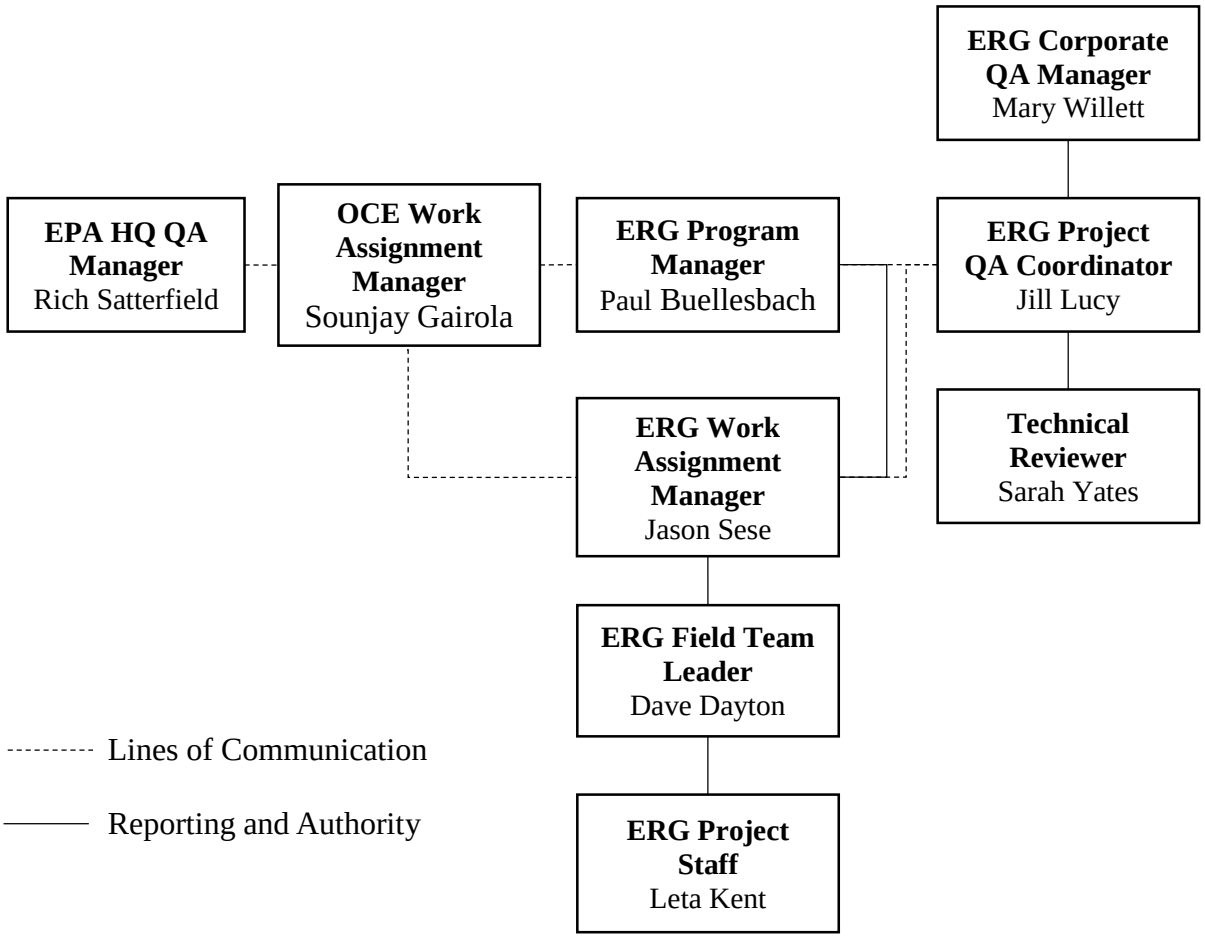


Figure 2-1. ERG Project Level QA Organization for the Georgia-Pacific Sampling Event

2.3 Element A.5: Problem Definition/Background

EPA Region 6 is tasked with determining point sources of hydrogen sulfide in the WWT system at the Georgia-Pacific paper mill in Crossett, Arkansas and if there is the potential for chronic exposure in the community. Georgia-Pacific has been conducting ambient air monitoring for hydrogen sulfide with a community monitor near their paper mill in Crossett, Arkansas. The monitoring results have periodically shown elevated hydrogen sulfide readings and EPA Region 6 has received complaints from the community related to strong smells coming from the direction of the plant. ERG will support EPA in evaluating hydrogen sulfide levels surrounding the WWT system by conducting passive sampling and determining if hydrogen sulfide levels are above the acute or intermediate ATSDR MRLs. Table 2-3 outlines relevant MRLs as well as RfC Values. ERG will assist in the initial set up of the monitors and training the EPA staff to collect and set up the sample tubes for the duration of the sampling event.

This QAPP specifically addresses set up of the monitoring stations, sample collection and delivery to the laboratory, analytical laboratory selection, and compilation of the results. For this facility, OCE will seek to answer the following questions:

- What are the sources of hydrogen sulfide in the WWT system at the mill?
- Is hydrogen sulfide leaving the facility property?
- Is there a risk of chronic exposure in the community?
- Should more monitors be placed in the community for long term monitoring?

Table 2-3. ATSDR MRL and EPA RfC Values

Substance	Acute Duration Inhalation MRL (ppmV)	Intermediate Duration Inhalation MRL (ppmV)	Chronic Inhalation RfC (ppm)
Hydrogen Sulfide	0.07	0.02	0.001

Values found in *Toxicological Profile for Hydrogen Sulfide and Carbonyl Sulfide*

2.4 Element A.6: Project/Task Description

ERG will support EPA in conducting passive sampling at the Georgia-Pacific Paper Mill in Crossett, Arkansas. The objectives of the investigation are to collect representative measurements of hydrogen sulfide from air samples at 20 locations on-and-around the Georgia-Pacific Paper Mill property once every two weeks for a duration of 24 weeks to determine point sources of hydrogen sulfide from the WWT system and the potential for chronic exposure in the community. In addition to samples collected at each of the 20 locations, two quality control samples will be collected every two weeks. The location of these two samples will change on a rotational basis. This results in 22 samples per each sampling episode, with a sampling episode being defined as one round of sample collection. The passive sampling tube technology being utilized is limited to a collection duration maximum of 15 days. EPA will replace the sampling tubes at each location every 14 days. EPA will use a courier service (i.e., FedEx) to deliver all samples to the designated laboratory for hydrogen sulfide analysis. EPA will also provide the laboratory with temperature data from an on-site station operated by TRC Environmental Corporation. EPA will pull the temperature data from www.TRCAir.com and calculate one average temperature for the sample duration. Table 3-1 summarizes the analytical methods that the laboratory will use. The laboratory will deliver analysis results to EPA within 14 days after receiving the samples and temperature data from EPA. The results from the analysis will be in the form of electronic spreadsheets and the field data sheets will be in PDF form.

To supplement this QAPP, ERG has developed site-specific planning documents to prepare for the sampling activities, including: (1) Investigation Sampling Plan and Shipping Procedures (see Appendix A); and (2) Investigation Health and Safety Plan (see Appendix B). These documents will be the primary sources of procedural information and a guide for the ERG team. Table 2-4 presents the project schedule.

Table 2-4. Project Schedule

Activity	Date(s)
Submit QAPP and Sampling Plan to EPA for Review and Approval	12/14/2016
Initial placement of passive monitors around G-P Crossett Mill	1/13/2017
EPA Replace Sampling Tubes and Submit Collected Tubes	1/27/2017, 2/10/2017, 2/24/2017, 3/10/2017, 3/24/2017, 4/7/2017, 4/21/2017, 5/5/2017, 5/19/2017, 6/2/2017, and 6/16/2017
EPA Send Average Temperature Data to Laboratory for Analysis	Within 2 Days After the Recovery of Samples from each Episode
Lab Provides Results of Bi-weekly Collections to EPA	Within 14 Days of Receipt of Samples and Temperature Data
EPA Final Collection of Sampling Tubes and Collection of Equipment	6/30/2017

2.5 Element A.7: Quality Objectives and Criteria

This section discusses how ERG and EPA determines that information collected for this project is "fit for use."

Sample Collection and Analysis. This project will involve collection and analysis of air samples. Results of these analyses will be used to quantitatively determine concentrations of hydrogen sulfide in the air. A meteorological station operated on-site by TRC Environmental Corporation will also measure ambient temperature. EPA and ERG will use these data along with the results of the air sample analyses to determine point sources of hydrogen sulfide in the WWT system.

ALS will use appropriate methods to analyze the hydrogen sulfide samples. Analytical methods are summarized in Table 3-1. Along with the sample analysis results, ALS will report the results of concurrent laboratory QC samples, which include blanks and co-located (duplicate) samples. Table 2-5 presents the data quality criteria identified in the test methods. If a sample result does not meet the control limits specified or the field blanks/duplicates do not meet control limits, ALS will notify EPA. In the event a sample result does not meet the quality specifications, the ERG WAM will consult with the EPA WAM and ERG Team Leader to determine the corrective action to be taken.

Table 3-2 identifies the type and frequency of field QC samples that will be prepared for analysis with collected samples. EPA Region 6 will collect duplicate co-located samples and field blanks to meet QC requirements. Requirements for duplicate sample collection will be satisfied by the sampling schedule (see the Sampling Plan in Appendix A). EPA will use the field QC results to determine how the analytical results may be used. In particular, the duplicate samples assess comparability and variability in the sampled air, in EPA's sampling methods, and in the laboratory's analytical techniques. The precision criteria set in Table 2-5 will assist EPA in understanding the variability of the data generated by this project. It is up to the discretion of EPA whether to use data that does not meet the precision criteria. Variability in the samples may be a result of heterogeneities in the material sampled.

ALS will conduct all sample analyses in accordance with the protocols of the SOP that they have provided. ALS will provide all supporting QA/QC information or persons capable of testifying to the authenticity and quality of the data. ALS will document deviations from the method in its laboratory reports. ALS will provide sufficient documentation to allow an independent validation and verification of the analytical results. ALS will provide electronic files for all data deliverables

Table 2-5. Data Quality Criteria for Field Investigations.

Precision Objectives – Based on Field Co-located Samples	
Analyte	**Air**
Hydrogen Sulfide	±20% RPD [1]
Blank Objectives – Based on Field/Trip Blanks	
Analyte	**Air**
Hydrogen Sulfide	< Method Detection Limit
RPD (Relative Percent Difference), is calculated as follows: RPD (%) = Absolute Value of: [(x1 - x2) / (x1 + x2)/2] * 100% Where: x1 = Concentration Observed in Original Sample and x2 = Concentration Observed in Duplicate Sample	

Sampling Summary Quality Objectives. EPA will use the information and data collected during the Georgia-Pacific sampling to determine point sources of hydrogen sulfide in the WWT system, determine chronic exposures, and open discussions with Georgia-Pacific about hydrogen sulfide in their processes. EPA is responsible for reviewing the completeness and accuracy of field collection procedures and laboratory results.

2.6 Element A.8: Special Training/Certification

ERG staff assisting with the Georgia-Pacific sampling have received appropriate health and safety training per OSHA 29 CFR Part 1910.120. Yearly refresher trainings are held by the ERG Health and Safety Coordinator. ERG's Health and Safety Coordinators maintain the health and safety training records. The ERG WAM will ensure that all team members have received the necessary training and training certificates.

2.7 Element A.9: Documents and Records

ERG has developed and instituted document control methods for the review, revision, and distribution of QAPPs. Each QAPP has a signed approval form, title page, table of contents, and EPA-approved document control format that appears in the upper left-hand corner of each page. Table 2-2 presents the distribution list for this QAPP. The EPA QA Manager will maintain a copy of the approved QAPP. The ERG WAM will circulate any revision to the QAPP to everyone on the distribution list during the project and shall maintain the finalized QAPP.

ALS will provide EPA with analytical results of bi-weekly collections within 14 days of receipt of the samples and meteorological data. Section 3.6 of this plan provides further discussion of the management of project-related information.

[1] RPD is based on the average of all the 12 samples sets collected, not for each individual sample set.

3. DATA GENERATION AND ACQUISITION

This section discusses how ERG will ensure that sample collection methods appropriate for the Georgia-Pacific sampling are employed and documented. ERG will not use existing analytical data as a part of this investigation. Since all data collected will be direct observation and or/measurement, Element B.9 Non-direct Measurements does not apply.

3.1 Elements B.1 Sampling Process Design and B.2 Sampling Methods

Sampling collection will be done at designated sampling sites and will involve collection and analysis of air samples. EPA is currently planning on sampling at 20 sites in the community and the area around the WWT system at Georgia-Pacific. ERG will assist in setting up passive sampling monitors and training EPA team members in proper handling of the monitors. EPA will collect approximately 22 air samples every two weeks (20 primary samples, one co-located sample, and one field blank). Sampling will take place over 24 weeks for a total of 264 air samples. EPA will ensure the sampled material is representative of material from the area of concern. The number of sampling sites may change based on EPA observations after arrival. If the sampling site at the facility or the facility itself becomes inaccessible, EPA will work to gain access to the site or find an alternate sampling location. A meteorological station operated on-site by TRC Environmental Corporation will measure ambient temperature continuously across each collection episode. EPA will pull the temperature data from www.TRCAir.com and calculate one average temperature for the sample duration representing each complete 14-day collection period to provide to the laboratory for analysis within 2-days after each episode shipment. Refer to the Investigation Sampling Plan in Appendix A for further details on the sampling schedule.

The primary equipment to be used by EPA and ERG for this sampling event includes the following:

- Radiello Diffusive Samplers for Hydrogen Sulfide;
  - Blue diffusive body code 1201
  - Supporting plate code 121
  - Chemiadsorbing cartridge code 170
- Radiello shelters
- Support poles
- PVC support heads; and
- All required tools (hand/battery powered/Sledge hammer)

ERG will support EPA in setting up sampling devices at specified sites. Detailed information on the sampling Standard Operating Procedure (SOPs), sampling procedures, decontamination procedures, and sampling equipment and support facilities is in the Sampling Plan in Appendix A. The ERG team will follow the procedures described in Appendix M, Sampling Guidelines, of The EPA NEIC *Multi-Media Investigation Manual,* Revised March 1992 EPA-330/9-89-003-R, or other guidance specified by the ERG project leads and specific to the methods and objectives of the work detailed in this QAPP. The ERG field team leader will ensure that sampling device set up procedures follow the guidelines set forth in the SOPs.

3.2 Element B.3 Sampling Handling and Custody

ERG will provide EPA sampling personnel with the materials and guidance on how to follow standard chain-of-custody procedures to ensure analytical results or other information generated from samples collected on this program may be used in litigation. This includes maintaining the sample integrity at all times, from sample collection through analysis. This also includes an inspection notebook, sample identification labels, and chain-of-custody forms to provide documentation that sample integrity was maintained. ERG will use a consistent set of site names and sample numbers to track all samples for this project.

To maintain a record of sample collection, sample transfer between personnel, and sample receipt by laboratory, the team will complete a chain-of-custody form for each box that is transferred to the laboratory. These chain-of-custody forms will document sample custody transfer from the team to the laboratory and will contain the following information:

- Name and location;
- Sample number for each sample shipment;
- Collection date and time for each sample shipment;
- Number of containers of each sample;
- Sample description (environmental matrix);
- Analyses required for each sample;
- Sample conditions or comments for laboratory instructions; and
- The name of the courier transferring the samples to the laboratory.

EPA personnel collecting the sampling tube from the monitor are responsible for completing the chain-of-custody forms, signing the chain-of-custody forms, and noting the date and time of shipment. These individuals will also inspect the chain-of-custody forms for completeness and accuracy. The original chain-of-custody forms will accompany the sample shipment while EPA/ERG will retain a copy. Appendix C contains a copy of the field chain-of-custody form EPA and ERG will use during this investigation.

When the laboratory receives the samples, the laboratory sample custodian will check all bottles against the chain-of-custody forms, record the condition of the samples, and sign, date, and mark the time of receipt on the chain-of-custody forms. Table 3-1 lists the hold time and analytical method to be used. The laboratory sample custodian will immediately report any discrepancies or problems to the ERG team leader. The laboratory will provide completed chain-of-custody forms with the analytical results delivered to EPA. ERG will retain any paperwork generated in collecting and shipping samples (e.g., air bills) as part of the permanent documentation.

Table 3-1. Laboratory Analytical Methods

Analyte	Method	Maximum Number of Samples Analyzed	Hold Time
H_2S	Supelco Edition H1, H_2S	280	6 months

The laboratory will also follow a written SOP for sample custody. The laboratory will log all samples into a sample receipt logbook or computerized laboratory information system and will document the following information:

- Date and time of sample receipt;
- Project number and name;
- Field sample number;
- Laboratory sample number;
- Sample matrix;
- Analytical parameters;
- Storage location;
- Log-in person's initials; and
- Log-in sample temperature.

Laboratory personnel will secure all information relevant to the samples at the end of each business day. They will store all samples in a designated storage refrigerator with restricted access. The laboratory will properly dispose of the samples once the data quality review of the data is completed.

3.3 Elements B.4 Analytical Methods and B.5 Quality Control

To ensure that analyses of samples collected during the Georgia-Pacific sampling event are of known and documented quality, ERG will:

- Use laboratories that possess appropriate state certification, with appropriate capability and quality assurance performance;

- Specify turnaround times for the laboratory to process the samples and deliver the data package in the statement of work and in the Sampling Plan in Appendix A;

- Use method-specific performance criteria for the sampling in this episode as specified in Section A.7 (and Table 2-5).

- Specify the method, which is identified in Table 3-1

Table 3-2. QC Sample Requirements

MEDIUM	CO-LOCATED SAMPLES	FIELD BLANKS
Air	One per collection episode (12 Total)	One per collection episode (12 Total)

ERG discusses the quality control procedures and corrective actions for exceedances of control limits in Section 4.1. Details about how control actions will be determined and documented, and formulas for calculating applicable QC statistics (e.g., precision objectives for duplicate samples) are discussed in Section 2.5. The ERG team leader will ensure that all corrective actions are taken and the team leader will convey all information to the EPA WAM.

3.4 Elements B.6 and B.7 Instrument/Equipment Testing, Inspection, Maintenance, and Calibration

No instruments will be used during the monitoring. Equipment that the ERG and EPA teams will use during set up of sample sites include nitrile gloves, zip lock bags, and all the materials associated with the passive sampling technology. The Sampling Plan in Appendix B lists the analytical equipment inspection and maintenance requirements. All equipment is inspected before going out into the field. To ensure that the team knows that the passive sampling devices will work properly, the team will read the users manuals and follow any instructions for assembly and setup.

3.5 Element B.8 Inspection/Acceptance of Supplies and Consumables

Section 4 of the ERG QMP (2) details ERG's standard procurement procedures for project-related supplies and consumables, including inspection and acceptance criteria and procedures for tracking, storage, and receiving supplies. Sampling diffusors and tubes and sheltering for the tubes will be purchased by ERG from Supelco. The ERG team leader is responsible for ensuring all materials meet project requirements.

3.6 Element B.10 Data Management

ERG's standard controls for project-related data, documents, and records are presented in Section 5 of the QMP (2). Section 2.7 discusses the document storage, archive, and retrieval process as it relates to the ERG-Chantilly network.

Because EPA is collecting the samples, ERG will coordinate with EPA sampling personnel to ensure that EPA records data acquired in the field, including site and visual information into bound field notebooks. Each sample collection team member will sign their notebook and pertinent information from the team member notebooks will be included in the final report.

4. ASSESSMENT AND OVERSIGHT ELEMENTS

This section describes the methods ERG will use to assess the effectiveness of the air sampling activities implemented at Georgia-Pacific and the associated QA and QC activities.

4.1 Element C.1: Assessments and Response Actions

No final reports or summaries have been requested, so ERG is not generating any work products during the Georgia-Pacific monitoring that require review. Instead, ERG will forward the data provided by the laboratory directly to EPA without review. EPA will conduct all assessments on the data.

Ms. Jill Lucy will serve as the Project QA Coordinator for this project. She is independent from the data generation for this project and the day-to-day activities. Ms. Lucy has the authority to issue a stop work order at any point during her assessment process. She will use the following tools to assess the implementation of QA/QC procedures on this project:

- Review of the QAPP (this document) for completeness and applicability; and
- Audit of project files to ensure project staff are using appropriate checklists and SOPs.

At any time or at the end of the project or work assignment, Ms. Lucy or her designee may inspect the project QA files.

4.2 Element C.2: Reports to Management

ERG is not responsible for data quality review, so no QA reports have been requested.

5. DATA VERIFICATION/VALIDATION AND USABILITY ELEMENTS

This section describes the data validation and usability elements. EPA is responsible for assessing the usability of information collected under the Georgia-Pacific hydrogen sulfide sampling event.

5.1 Element D.1: Data Review

Data review is an in-house data examination, performed to ensure that data have been calculated, recorded, and transmitted correctly; for example, by checking for transcription and calculations errors. Because ERG is transmitting the data from the lab directly to EPA without review, ERG will not be performing data review for this effort.

5.2 Element D.2: Data Verification and Validation

Data verification is the confirmation by examination and review of objective evidence that the data are complete, correct, consistent, and in compliance with technical requirements, established standards, and contractual requirements. Data verification criteria are based upon the measurement quality objectives developed in the project QAPP. Data quality criteria are listed in Table 2-5. EPA is responsible for data verification and validation.

An EPA team member will review laboratory quality control checks, including

- Chain-of-custody;
- Sample Receipt logs and checklists;
- Equipment and instrument calibration;
- Sensitivity (detection limits achieved);
- Laboratory blank contamination; and
- Field blank contamination.

Data validation is an analyte- and sample-specific process that extends the evaluation of data beyond method, procedural, or contractual compliance (i.e. data verification) to determine the analytical quality of a specific data set.[2] An EPA team member will review laboratory data using engineering judgment to verify that the data appear reasonable based on knowledge of the facility's processes and pollutants with the potential to be present in the samples collected. If necessary, ERG will consult with EPA on data validation.

To evaluate the variability in the lab's results, an EPA team member will use the equations listed at the bottom of Table 2-5 to calculate relative percent difference (RPD) for each analyte in each set of duplicate samples, and compare the calculated RPD to control limits.

[2] EPA Guidance for Quality Assurance Project Plans EPA QA/G-5

5.3 Element D.3: Reconciliation with User Requirements

EPA will determine if data generated for this project are of known and documented quality and if they are fit for their intended use.

6. REFERENCES

1. U.S. Department of Health and Human Services, October 2014. *Toxicological Profile for Hydrogen Sulfide and Carbonyl Sulfide*. Agency for Toxic Substances and Disease Registry.

2. U.S. Environmental Protection Agency, 2001 (Reissued 2006). *EPA Requirements for Quality Assurance Project Plans QA/R-5*. EPA/240/B-01/003, Office of Environmental Information.

3. Eastern Research Group, July 2014. Enforcement and Technical Support for the Office of Civil Enforcement Contract Quality Management Plan.

Appendix A Investigation Sampling Plan and Shipping Procedures

The U.S. EPA Office of Civil Enforcement, Air Enforcement Division (OCE/AED) is directing ERG to assist Region 6 of the United States Environmental Protection Agency (EPA) with monitoring efforts at the Georgia-Pacific facility in Crossett, Arkansas. The objectives of the investigation are to collect representative measurements of hydrogen sulfide from air samples at 20 locations on-and-around the Georgia-Pacific Paper Mill property once every two weeks for a duration of 24 weeks to determine point sources of hydrogen sulfide from the WWT system and the potential for chronic exposure in the community. In addition to samples collected at each of the 20 locations, two quality control samples will be collected every two weeks. This plan presents the procedures for collecting Primary, Co-located, and Field/Trip Blank samples, and then shipping the samples to the analytical laboratory, on a collection episode basis. During sample setup, ERG will work to minimize the duration between site efforts and while at each site itself. The same is true during sample recovery. Also, the sites should be visited in the same order for both setup and recovery, within a given collection episode. This will help ensure that, to the largest extent, the same collection duration is accomplished across the network as a whole.

Primary Sample Setup

A primary sample will be collected at every site for every collection episode.

1. Inspect the site area to ensure that nothing has changed that could bias the sample collection. Inspect the shelter and ancillary equipment to ensure that it functional and in good working condition.

2. Don nitrile gloves.

3. Remove the storage/transport container from its zip lock bag. Remove the cap from the storage/transport container.

4. Have a new or clean diffuser body ready. (Note: the diffuser bodies will be cleaned after each 2-week collection duration).

5. Position the opening on the storage/transport container so that it is aligned with the inlet on the diffuser body.

6. Load the passive sampling tube into the body of the diffuser (without touching the tube) by having it slide out of the storage/transport container directly into the diffuser body.

7. Screw the diffuser body (now loaded with the passive sampling tube) onto the triangular support plate. (At this time, sample collection has been initiated, so note the time.)

8. Position the support plate inside of the site shelter and secure it in place by 1) fastening the pinch clip to the rail running along the inside top of the shelter, and 2) pressing the Velcro pad located on the back of the support plate to its corresponding pad located on the wall of the shelter. Predetermined positions for the support plate will be evident by where the Velcro pad(s) is located on the side wall(s) of the shelter. The position for a primary sample is located on the left inside wall, and the position for co-located sample is located on the right inside wall.

9. Complete all required documentation in the "Field Setup" section of the "Field Data Sheet/COC". Retain the Field Data Sheet/COC for use during sample recovery.

10. Retain the storage/transport container with cap and zip lock bag for use during sample recovery.

11. Repeat this procedure at each monitoring site.

Co-located Sample Setup

A co-located sample will be collected at one site during each collection episode on a rotating basis.

1. Refer to the Sample Collection Schedule to determine which site is slated to collect a co-located sample for a given collection episode.

2. Don nitrile gloves.

3. Remove the storage/transport container from its zip lock bag. Remove the cap from the storage/transport container.

4. Have a new or clean diffuser body ready. (Note: the diffuser bodies will be cleaned after each 2-week collection duration).

5. Position the opening on the storage/transport container so that it is aligned with the inlet on the diffuser body.

6. Load the passive sampling tube into the body of the diffuser (without touching the tube) by having it slide out of the storage/transport container directly into the diffuser body.

7. Screw the diffuser body (now loaded with the passive sampling tube) onto the triangular support plate. (At this time, sample collection has been initiated, so note the time.)

8. Position the support plate inside of the site shelter and secure it in place by 1) fastening the pinch clip to the rail running along the inside top of the shelter, and 2) pressing the Velcro pad located on the back of the support plate to its corresponding pad located on the wall of the shelter. Predetermined positions for the support plate will be evident by

where the Velcro pad(s) is located on the side wall(s) of the shelter. The position for a co-located sample is located on the left inside wall, and the position for primary sample is located on the right inside wall. Set up the co-located sample before the primary sample as it will be located further back in the shelter.

9. Complete all required documentation in the "Field Setup" section of the "Field Data Sheet/COC". Retain the Field Data Sheet/COC for use during sample recovery.

10. Retain the storage/transport container with cap and zip lock bag for use during sample recovery.

Field/Trip Blank Sample Setup

A field/trip blank sample will be collected at the same site during each collection episode. Collections will occur at Site 1 (the Community Site) only. The shelter at Site 1 will be outfitted with a specialized tube, mounted to the inside center of the top of the shelter.

1. Remove the storage/transport container from its zip lock bag. Do not open/remove the cap from the storage/transport container.

2. With the passive sampling tube still inside, slide the storage/transport container into the specialized tube (mounted to the inside center of the top of the shelter) until it stops. The cap end of the container should be visible.

3. Complete all required documentation in the "Field Setup" section of the "Field Data Sheet/COC". Retain the Field Data Sheet/COC for use during sample recovery.

4. Retain the zip lock bag for use during sample recovery.

Primary Sample Recovery

1. Inspect the site area to ensure that nothing has changed that could bias the sample collection. Inspect the shelter and ancillary equipment to ensure that it functional and in good working condition.

2. Don nitrile gloves.

3. Remove the cap from the storage/transport container. Attach the adhesive backed Barcode ID tag (with the number corresponding to the Sample ID presented on the Field Data Sheet/COC) to the storage/transport container. The Barcode ID should be in the center of the container with the number running parallel to the length of the container. Place cap and container on top of the shelter.

4. Remove the support plate from the shelter. It is recommended that the primary sample be recovered before the co-located sample as it will be located further forward in the shelter.

5. Unscrew the diffuser body (loaded with the passive sampling tube) from the triangular support plate.

6. Position the opening on the storage/transport container so that it is aligned with the inlet on the diffuser body.

7. Load the passive sampling tube into the storage/transport container (without touching the tube) by having it slide out of the diffuser body directly into the storage/transport container and cap the container. (At this time, sample collection has been terminated, so note the time.)

8. Place the storage/transport container in its zip lock bag.

9. Complete all required documentation in the "Field Recovery" section of the "Field Data Sheet/COC".

10. Repeat this procedure at each monitoring site.

Co-located Sample Recovery

1. Don nitrile gloves.

2. Remove the cap from the storage/transport container. Attach the adhesive backed Barcode ID tag (with the number corresponding to the Sample ID presented on the Field Data Sheet/COC) to the storage/transport container. The Barcode ID should be in the center of the container with the number running parallel to the length of the container. Place cap and container on top of the shelter.

3. Remove the support plate from the shelter.

4. Unscrew the diffuser body (loaded with the passive sampling tube) from the triangular support plate.

5. Position the opening on the storage/transport container so that it is aligned with the inlet on the diffuser body.

6. Load the passive sampling tube into the storage/transport container (without touching the tube) by having it slide out of the diffuser body directly into the storage/transport container and cap the container. (At this time, sample collection has been terminated, so note the time.)

7. Place the storage/transport container in its zip lock bag.

8. Complete all required documentation in the "Field Recovery" section of the "Field Data Sheet/COC".

Field/Trip Blank Sample Recovery

1. Don nitrile gloves.

2. Slide the storage/transport container out of the specialized tube (mounted to the inside center of the top of the shelter).

3. Place the storage/transport container in its zip lock bag.

4. Complete all required documentation in the "Field Recovery" section of the "Field Data Sheet/COC".

Sample Shipping

Each collection episode will result in 22 samples (if all the scheduled collections are determined to be valid).

1. Ensure that the correct total number of samples to be shipped to the analytical laboratory is correct.

2. Ensure that each storage/transport container has a Barcode ID attached to it, and that there is a corresponding field data sheet/COC (with the same Barcode ID as part of the sample ID).

3. Check over the field data sheet/COC to ensure that all the required information is present and correct.

4. Remove the "Pink" copy of the field data sheet/COC and retain it as the field copy.

5. Place the samples (i.e., the exposed passive tubes, inside of their barcode labeled containers, inside of their zip lock bags) and the corresponding field data sheet/COCs into a shipping container. The tubes must be secured within bubble wrap to prevent them from moving inside the shipping container. Also, place the corresponding field data sheet/COCs inside the container.

6. Ship the samples to the analytical laboratory using FedEx "Overnight" service. Be sure to arrange for "Signature Required Upon Receipt" and set up to receive the email alerts for, package pick up, package delivery, and receipt signature obtained. The ship to address is:

ALS Environmental
4388 Glendale Milford Road
"Sample Receiving"
Cincinnati, OH 45242
Attn: Chris Amidon / (513)733-5336

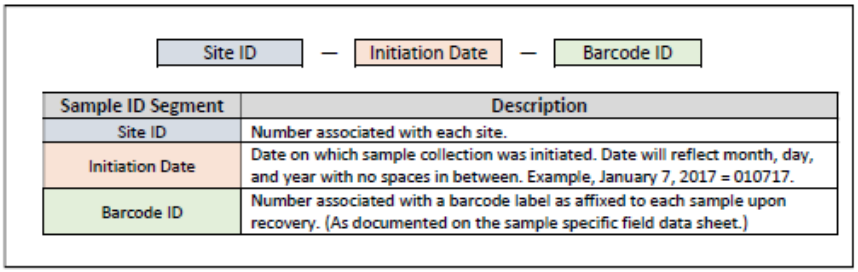
ALS Environmental will complete the all information pertaining to receipt of the samples at the laboratory, and will send the "White" copy each COC to EPA as a PDF along with the corresponding H_2S concentration data. The laboratory will retain the "Canary" copy for their records.

Table A-1. Sampling Schedule

Site Name	Site #	Sample Episode Number and Start Date[a]											
		1 01/13/17	2 01/27/17	3 02/10/17	4 02/24/17	5 03/10/17	6 03/24/17	7 04/07/17	8 04/21/17	9 05/05/17	10 05/19/17	11 06/02/17	12 06/16/17
COM1	1	P, F, C	P, F	P, F	P, F	P, F	P, F	P, F	P, F	P, F	P, F	P, F	P, F
COM2	2	P	P, C	P	P	P	P	P	P	P	P	P	P
COM3	3	P	P	P	P	P	P	P	P	P	P	P	P
COM4	4	P	P	P	P	P	P	P	P	P	P	P	P
COM5	5	P	P	P, C	P	P	P	P	P	P	P	P	P
COM6	6	P	P	P	P, C	P	P	P	P	P	P	P	P
COM7	7	P	P	P	P	P	P	P	P	P	P	P	P
COM8	8	P	P	P	P	P, C	P	P	P	P	P	P	P
THUR	9	P	P	P	P	P	P, C	P	P	P	P	P	P
MILL	10	P	P	P	P	P	P	P, C	P	P	P	P	P
PCLR	11	P	P	P	P	P	P	P	P, C	P	P	P	P
CONV	12	P	P	P	P	P	P	P	P	P, C	P	P	P
WABI	13	P	P	P	P	P	P	P	P	P	P, C	P	P
EABI	14	P	P	P	P	P	P	P	P	P	P	P, C	P
WABO	15	P	P	P	P	P	P	P	P	P	P	P	P, C
EABO	16	P	P	P	P	P	P	P	P	P	P	P	P
SBO	17	P	P	P	P	P	P	P	P	P	P	P	P
ASB1	18	P	P	P	P	P	P	P	P	P	P	P	P
ASB2	19	P	P	P	P	P	P	P	P	P	P	P	P
OUT	20	P	P	P	P	P	P	P	P	P	P	P	P
Samples Per Episode		22	22	22	22	22	22	22	22	22	22	22	22
Overall Total Samples		264											

P = Primary Sample Collection
F = Field/Trip Blank Sample Collection
C = Co-located Sample Collection
[a] Sampling tubes for each episode will be collected 14 days after the start date.

Figure A-1. Sample Barcode ID



Sample ID Segment	Description
Site ID	Number associated with each site.
Initiation Date	Date on which sample collection was initiated. Date will reflect month, day, and year with no spaces in between. Example, January 7, 2017 = 010717.
Barcode ID	Number associated with a barcode label as affixed to each sample upon recovery. (As documented on the sample specific field data sheet.)

Figure A-2. Sample ID Convention

Appendix B Investigation Health and Safety Plan (HASP)

B.1 Purpose

The purpose of this Health and Safety Plan (HASP) is to inform ERG and EPA personnel of known or potential health and safety hazards that may be encountered during ambient air monitoring activities planned in Crossett, Arkansas. Accordingly, this HASP describes the possible hazards and the procedures required to minimize the potential for exposure, accidents, and/or injuries during the scheduled work activities. This HASP has been reviewed by the ERG Laboratory Health and Safety Coordinator.

B.2 Scope

EPA will conduct a sampling investigation to better assess potential human exposure to hydrogen sulfide in the community around the Georgia-Pacific Crossett paper mill. During this sampling investigation, passive sampling monitors will be placed throughout the area surrounding the mill to obtain H_2S concentration data over a 24-week period.

B.3 Physical Hazards Assessment

Possible dangers associated with project activities include physical hazards related to slips, trips, or falls; lifting; and animals, poisonous plants, and poisonous insects. Brief descriptions of these potential physical hazards and measures for preventing, or mitigating the consequences of, the hazards follow:

- Slips, Trips, or Falls - Testing at the site is expected to occur primarily at ground level. ERG personnel will use good safety sense in evaluating walking and working surfaces. It is expected that EPA will select monitoring sites such that neither testing personnel nor the general public will be injured by tripping or falling over test equipment

- Lifting Hazards – When carrying and lifting equipment, ERG field staff should practice good lifting techniques and avoid carrying heavy loads.

- Animals, poisonous plants, and poisonous insects – ERG field staff should be alert for and stay clear of wild and unsupervised animals, poisonous insects, and poisonous plants (e.g. poison ivy). Team members should also be aware of multiple poisonous spiders (e.g. brown recluse, brown widow, and black widow), coyotes, and skunks that are known to live in such areas. Snakes (e.g. rattlesnakes, copperheads, and water moccasins) could particularly be a problem for this area.

    — ERG field staff will wear thick gloves, leather boots, long pants, and long sleeve shirt. ERG field staff will also bring a first aid kit. Be aware of your surroundings; do not just blindly wander in the monitoring locations.

Observation is critical for avoidance. Check around with a sweeping glance for anything that seems out of place, your subconscious may notice a camouflaged animal.

— Tap the monitoring housing before reaching inside for the sample. Snakes and other animals have many sensing devices to warn them of your presence.

— If an ERG field staff is bitten by a snake, rodent, or spider, they should be taken to a medical facility immediately for treatment. Give the medical staff as much detailed information about the animal as possible. Describe the size, shape, and color of the animal.

B.4 Chemical Hazards Assessment

The sites have the potential for high concentrations of H_2S at selected sites. ERG and EPA field staff may be exposed to levels of hydrogen sulfide upwards of 5 ppm, depending on outdoor conditions and proximity to wastewater treatment system. Thus, ERG field staff will use a personal H_2S monitoring system (if provided by EPA) while approaching these sites and during work on these sites. If monitors are not provided, ERG field staff will stay close to EPA field staff, who will be wearing personal monitors. Monitors will be set to alarm at a concentration of 5 ppm. If a monitoring device alarms indicating unsafe levels of H_2S all personnel will leave the site immediately.

While hydrogen sulfide is highly flammable and explosive, risks of flash or explosion are low. Concentrations may be high enough to possibly affect health, but they will not likely be high enough to cause fire or explosion.

B.5 Contacts for Local Emergency Services

Prior to the first field activity, ERG will provide each of its field staff with the pertinent emergency contact information for the study area. This information will include phone numbers and addresses for the following:

Ashley County Medical Center
1015 Unity Road
Crossett, AR 71635
(870) 364-4111

Crossett Police Department
307 Main Street
Crossett, AR 71635
(870) 364-4131

Drew Memorial Hospital
778 Scogin Drive
Monticello, AR 71655
(870) 367-2411

B.6 Staff Concurrences

Prior to working on this air monitoring program, ERG will require all its associated field staff to read and understand this HASP.

ERG STAFF CONCURRENCE SHEET

I have read, understood, and agree to comply with this Project Health and Safety Plan.

_____	_____	_____
Signature	Printed Name	Date
_____	_____	_____
Signature	Printed Name	Date

Appendix C Chain of Custody Form

ERG

Lab ID #

H2S Passive Monitoring Field Data Sheet and Chain of Custody

Field Setup

Site ID: _____ *(Sample ID = Site ID-Initiation Date - Barcode ID)*

Initiation Date: _____ Sample ID = _____ - _____ - _____

Sampling Start Time: _____

Barcode ID: _____

Field Operator: _____

Notes:

Field Recovery

Recovery Date: _____

Sampling End Time: _____

Field Operator: _____

Total Elapsed Sampling Duration (minutes): _____

Notes:

Laboratory Receipt

Sample Received in proper condition (Y/N): _____ by: _____

Sample ID Verified (Y/N): _____ by: _____

Sample Logged In (Y/N): _____ by: _____

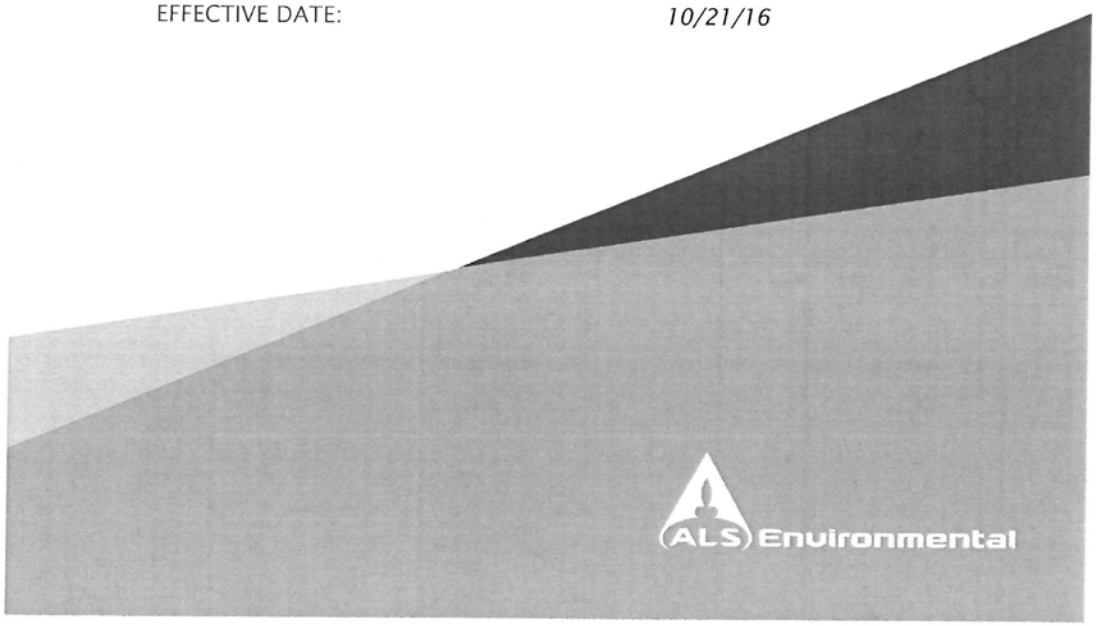
Notes:

Comments: _____

White: Sample Traveler Canary: Lab Copy Pink: Field Copy

ALS Standard Operating Procedure

DOCUMENT TITLE:	*COLORIMETRIC DETERMINATION OF HYDROGEN SULFIDE (H_2S) IN AIR*
REFERENCED METHOD:	*N/A*
SOP ID:	*IH-007*
REV. NUMBER:	*0*
EFFECTIVE DATE:	*10/21/16*



Appendix D
ALS Standard Operating Procedure

STANDARD OPERATING PROCEDURE APPROVAL SHEET

SOP TITLE: Colorimetric Determination of Hydrogen Sulfide (H2S) in Air

DOCUMENT CONTROL NUMBER: IH-007

EFFECTIVE DATE: 10/21/16

LAB DIRECTOR _____ Date 10/21/16

SECTION MANAGER _____ Date 10/21/2016

QUALITY ASSURANCE MANAGER Tracey Earle Date 10-21-16

RECORD OF MINOR REVISIONS:

DATE	LOCATION OF REVISION	QA APPROVAL

RECORD OF MAJOR REVISIONS:

NEW	1	2	3	4	5	6
0						

IH-007
Revision No.: 0
Date: October 21, 2016
Page: 1 of 9

STANDARD OPERATING PROCEDURE

COLORIMETRIC DETERMINATION OF HYDROGEN SULFIDE (H_2S) IN AIR

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the analysis of Hydrogen Sulfide (H_2S) in air collected on Radiello samplers (passive) which contain a cartridge made of microporous polyethylene impregnated with Zinc Acetate. This SOP follows the Supelco Edition H1 method.

2.0 SAFETY PRECAUTIONS

2.1 The toxicity or carcinogenicity of each compound or reagent used with this method is not precisely known. Each compound, mixture of standards, as well as the samples, should be treated as a potential health hazard. Exposure to each should be reduced to the lowest level possible through the use of gloves and a hood. Reference files of Material Safety Data Sheets (MSDS) are available to all personnel. Current OSHA regulations regarding the safe handling of the compounds specified in this method may be found on the internet (www.OSHA.gov).

2.2 Refer to the Laboratory's Environmental, Health and Safety Manual for safety guidelines. The analyst should employ the safety measures described in the manual. All applicable safety and compliance guidelines set forth by ALS, and by federal, state, and local regulations must be followed during performance of this procedure. All work must be stopped in the event of known or potential compromise to the health or safety of any ALS employee, and must be reported immediately to a laboratory supervisor.

2.3 Sodium Hydroxide (NaOH) is strong, caustic and a severe health and contact hazard. Use nitrile or latex gloves while handling pellets or preparing solutions.

2.4 Sulfuric Acid is extremely corrosive and care must be taken while handling it. At a minimum a lab coat, safety glasses and gloves should always be worn while working with these solutions. A face shield and apron should be used while pouring acids. Secondary containment should be used when dispensing significant quantities of acids (e.g., greater than 500 mL).

2.5 N,N-Dimethyl-p-phenylendiammonium oxalate (p-aminodimethylaniline) is toxic by inhalation, highly toxic by ingestion and toxic by skin absorption. Use all PPE when weighing and handling being careful to avoid formation of dust.

2.6 Pollution Prevention and Waste Management: The smallest quantities of sample and reagents will be prepared and used to minimize the amount of waste solutions. Hazardous materials is prepared and identified for disposal by the appropriate removal companies. Refer to the SOP for Waste Disposal for additional information. Wherever it is technically sound, feasible, and within method requirement, it is the practice of this laboratory to minimize the amount of solvents and reagents used to perform this method.

Standards are prepared in volumes consistent with laboratory use, and solvents are ordered in small quantities to minimize the volume of disposal for expired standards and solvents.

2.7 ALS Environmental, Cincinnati has a current Radiological License through the Ohio Department of Health. In order to limit exposure to personnel, radiological and/or beryllium containing samples are segregated from non-regulated material at the time of login. All radiological samples are stored in a locked, controlled storage cabinet. Only trained personnel may receive, handle, prepare, store, and dispose of regulated samples as stated in SOPs RAD-003, RAD-004, and RAD-005. Any questions on the handling of radiological samples should be directed to the current RSO.

3.0 SAMPLE HANDLING AND PRESERVATION

3.1 The unaltered Radiello cartridges are stable for 12 months (plastic over wrap will note expiration). The recommended exposure is 1 hour to 15 days making sure to protect the Radiello media from rain.

3.2 The holding time is 6 months after exposure.

3.3 At least 4 unexposed cartridges should be submitted per batch to use for Quality Control samples.

4.0 REPORTING LIMITS

4.1 Refer to LIMS for current routine reporting limits for this analysis.

5.0 INTERFERENCES

5.1 Strong reducing agents may prevent the formation of the blue color in the Methylene blue test.

5.2 Reduced sulfur compounds, such as Sulfite, Thiosulfate and Hydrosulfite, which decompose in acid may yield erratic results. Also, volatile iodine-consuming substances will give high results.

6.0 APPARATUS

6.1 Spectrophotometer capable of reading 665nm

6.2 Vortex Stirrer

6.3 Test Tubes

6.4 Volumetric Pipettes of various volumes

6.5 Class A volumetric flasks with ground-glass stoppers

6.6 Class A graduated cylinders

6.7 Radiello Components (client to use for passive sampling) Ready-to use code 123-6 or White diffusive body code 120, Supporting plate code 121, Vertical adapter code 122 (optional) & Chemiadsorbing cartridge code 170

6.8 Disposable, plastic cuvettes

7.0 REAGENTS

7.1 Deionized (DI) Water

7.2 RAD171 Solution: Purchased Methylene Blue Calibration Standard for H_2S

7.3 Amine Solution: Slowly add 12.5mL of concentrated Sulfuric Acid to 5mL of DI water and allow to cool. Add 3.375g of N,N-dimethyl-p-phenylendiammonium oxalate and dilute to a final volume of 500mL with cooled 1:1 v/v (Sulfuric Acid:DI Water). Store the solution in an airtight amber glass bottle. This solution is stable for 4 weeks.

7.4 Ferric Chloride Solution: Dissolve 100g FeCl3·6H2O in 40mL of DI water. This solution is stable for 1 year.

7.5 Ferric Chloride – Amine Solution: Mix 10mL of the Ferric Chloride solution with 50mL of the Amine solution. More or less can be prepared as long as the solution is 1:5 Ferric Chloride Solution:Amine Solution. Prepare fresh just prior to coloring samples.

7.6 Sulfuric Acid for dilution: Slowly and carefully add 40mL of concentrated Sulfuric Acid to 900mL of DI water in a 1L volumetric flash. Let the solution cool and then bring to volume.

8.0 CALIBRATIONS

8.1 A minimum of 5 Calibration Standards are prepared by setting up a series of labeled volumetric flasks. Add the RAD171 solution as shown below and dilute to volume with DI water. Please note that these concentration ranges may change.

Calibration Standard	Concentration (ug/L)	RAD 171 Volume (mL)	Final Volume (mL)
1	57.3	0.05	50
2	115	0.10	50
3	229	0.20	50
4	573	0.50	50
5	859	0.75	50
6	1145	1.0	50

8.2 Prepare an Initial Calibration Verification (ICV) by pipetting an appropriate aliquot of the RAD171 solution to yield a concentration near the middle of the curve.

8.2.1 To prepare a 573ug/L ICV solution, dilute 0.5mL of the RAD171 solution to 50mL with DI water.

8.2.2 The ICV, whenever possible, is prepared using a RAD171 solution that contains a different lot number than the RAD171 used to prepare the Calibration Standards.

8.3 Prepare a Continuing Calibration Verification (CCV) by pipetting an appropriate aliquot of the RAD171 solution to yield a concentration near the middle of the calibration curve.

8.3.1 To prepare a 573ug/L CCV solution, dilute 0.5mL of the RAD171 solution to 50mL with DI water.

8.3.2 The CCV, whenever possible, is prepared using the same lot # of RAD171 solution that was used to prepare the Calibration Standards.

8.4 Prepare an Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB) by filling a 50mL volumetric flask with DI water.

8.5 Calibration linearity is most easily achieved by performing a regression of the instrument response versus the concentration in the standards.

8.5.1 Linear regression will produce the slope and intercept terms for a linear equation in the form: y=mx+b where, y is the instrument response (absorbance), m is the slope of the line (also called the coefficient of x), x is the concentration of the calibration standard and b is the y-intercept.

8.5.2 The regression calculation will generate a correlation coefficient (r) that is a measure of the "goodness of fit" of the regression line to the data. A value of 1.00 indicates a perfect fit. In order to be used for quantitative purposes, r must be greater than or equal to 0.99.

9.0 SAMPLE PREPARATION

9.1. A Media Blank (MBLK), whenever possible, must be prepared for each analytical batch of 20 or fewer field samples. The MBLK must be matrix matched when possible, and it must be carried through the entire preparation procedure at the same time that the field samples are prepared. The MBLK must be an unexposed cartridge and it is recommended that the client supplies 3 MBLKs per batch of samples. Blanks will be prepared and their results will be averaged. This average result will be used to blank correct all QC and field samples.

9.2 A Laboratory Control Sample and Duplicate (LCS/LCSD) pair must be prepare for each analytical batch of 20 or fewer field samples. The LCS/LCSD must be matrix matched when possible, and they must be carried through the entire preparation procedure at the same time that the field samples are prepared.

9.2.1 Add the proper aliquot of the RAD171 solution prior to the addition of any other reagents to two unexposed cartridges. The target for the spike should be near 573ug/L.

9.2.1.1 The RAD171 solution used to spike the LCS/LCSD pair must come from a different lot than the RAD171 that was used to prepare the calibration standards.

9.2.2 Target spikes for the LCS/LCSD samples may change to better suit client's needs, element recovery, or project requirements.

9.3 Add 10mL of DI water to each of the QC and field sample Radiello tubes.

9.4 Cap each vial and vortex to mix.

9.5 Add 0.5mL of the Ferric Chloride – Amine solution, IMMEDIATELY recap, and vortex to mix. The tube must be capped immediately in order to avoid releasing any Hydrogen Sulfide.

9.6 Wait for a minimum of 30 minutes to allow the color to develop.

10.0 DIAGRAMS OR TABLES

10.1 None.

11.0 PROCEDURE

11.1 Turn on the Spectrometer and allow it to warm up for a minimum of 15 minutes.

11.2 Once the color for each sample has fully developed, add a sufficient amount of sample to a clean cuvette and place the cuvette in the Spectrometer.

11.3 Read each sample's absorbance at 665nm.

11.4 If provided, the average of the three MBLK samples will be averaged and subtracted from the sample absorbance readings for the field samples.

11.5 If a dilution of a field sample is necessary (the absorbance is higher than the calibration curve), the samples MUST be diluted with the Sulfuric Acid for dilution solution. NEVER USE WATER TO DILUTE THE SAMPLES.

11.6 Record all sample information and absorbances in a data logbook.

12.0 CALCULATIONS

12.1 Concentrations are calculated from the standard curve. Unknown sample concentrations are calculated by comparison of the background corrected absorbance to known standards using a linear regression fit. The resulting concentration is then multiplied by any dilution

factors to calculate the final result. All standards for QC are referenced where applicable. Any comments involving sample anomalies are noted in the data logbook.

12.2 Percent recovery calculation:

$$\text{Percent Recovery} = 100 * \frac{\text{Measured Value}}{\text{Target Value}}$$

12.3 Precision calculation:

$$\text{Relative Percent difference (RPD)} = 100 * \frac{|V_1 - V_2|}{(V_1 + V_2)/2}$$

where:
V1, V2 = found concentrations

12.4 ng/sample = ug/L (determined from curve) x 0.010L (extraction volume) x 1000 ng/ug

12.5 ppbV H_2S = $\frac{\text{ng}}{[(0.096\text{ng/ppb} \cdot \text{mins}) \times \text{time collected in minutes}]}$.

Note: The sampling rate is 0.096 + 0.005 ng.ppb-1.min-1 at 298 K (25°C) and 1013 hPa

12.6 ug/m3 = $\frac{(\text{ppbV } H_2S) \times 34.09 \text{ (MW of } H_2S)}{24.46 \text{ (gas constant)}}$

12.7 Temperature Conversion: QK= 0.096(K/298)3.8

Where QK = Sampling rate at temperature K ranging from 268 – 313K (from -5 to 40°C)

Where K = temperature at collection

Note: Sampling is invariant with humidity in the range of 10 – 90% wand wind speed between 0.1 and 10m·s^{-1}.

13.0 QUALITY ASSURANCE PROVISIONS

13.1 All quality control data must be maintained and readily available for reference and for auditing purposes.

13.2 The correlation coefficient (r) obtained from a least squares fit of the calibration must be ≥0.995. If this criterion is not satisfied, the error must be identified and corrected then the instrument must be recalibrated. If an instrument or calculation error is not found to be the source of the error, all of the applicable batch standards and samples must be reanalyzed.

Control Limits: ≥ 0.99

Corrective Action:

(1) Check for calculation errors, instrument performance
(2) Reanalyze all batch applicable standards, check standards, blanks, and samples.
(3) Flag data

13.3 Following successful calibration, check the instrument standardization and stability by analyzing appropriate check standards as follows:

13.3.1 Verify the calibration using the ICV standard. The result obtained from the analysis of the ICV must be within ± 30% of the true value. If this criterion is not met, terminate the analysis, correct the problem, and recalibrate the instrument. An acceptable ICV must occur prior to the analysis of any field samples.

Control Limits: 70-130% recovery

Corrective Action:

(1) Check for calculation errors, instrument performance
(2) Reanalyze all batch applicable standards, check standards, blanks, and samples.
(3) Flag data

13.3.2 Verify the stability of the initial calibration following every 10 samples and at the end of the sequence, using the CCV standard. The result obtained for the CCV analysis must be within ± 15% of the true value. If this criterion is not met, terminate the analysis, correct the problem, and recalibrate the instrument. Sample results must be bracketed by acceptable initial calibration and/or CCV standard results. If the samples are not bracketed by acceptable standard results, reanalyze all samples following the last passing CCV.

13.3.2.1 If the CCV result is high (beyond the + 15% acceptance limit) and H_2S is not detected in all the corresponding samples, re-analysis is not necessary due to the apparent high bias of the check standard. It may be inferred that all samples reported would also exhibit a high bias, but if H_2S is not detected within the samples, the high bias may be ignored, requiring not further analyses.

Control Limits: 85-115% recovery

Corrective Action:

(1) Check for calculation errors, instrument performance

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(2) Reanalyze all batch applicable standards, check standards, blanks, and samples.
(3) Flag data

13.3.3 One Method Blank (MBLK) must be prepared and analyzed for every analytical batch when applicable. The Initial Calibration Blank (ICB) must be analyzed immediately following the ICV. The ICB must pass prior to the analysis of any field samples. The Continuing Calibration Blank (CCB) must be analyzed immediately following the CCV. Sample results must be bracketed by acceptable CCB results. If the samples are not bracketed by acceptable results, reanalyze all samples following the last passing CCB.

Control limits: Less than the reporting limit

Corrective Action:

(1) Check for calculation errors, instrument performance.
(2) Reanalyze all applicable batch standards, check standards, blanks and samples.
(3) Flag data

13.4 Analyze one LCS/LCSD pair per analytical batch. Recoveries are within the established control limits. If there is insufficient data to generate control limits (minimum 20 analyses), advisory limits of +/- 30% will be used.

13.4.1 If the LCS/LCSD result is high (beyond the + 30% acceptance limit) and H_2S is not detected in all the corresponding samples, re-analysis is not necessary due to the apparent high bias of the check standard. It may be inferred that all samples reported would also exhibit a high bias, but if H_2S is not detected within the samples, the high bias may be ignored, requiring not further analyses.

13.4.2 The relative percent difference (RPD) of the duplicate analyses, when both the sample and duplicate results are greater than or equal to 10 times the MDL, is less than the laboratory established control limits. If there is insufficient data to generate control limits (minimum 20 analyses), advisory limits of <20% will be used.

Control Limits: 80-120% recovery or established control limits

Corrective Action:

(1) Check for calculation errors, instrument performance
(2) Reanalyze all batch applicable standards, check standards, blanks, and samples.
(3) Flag data

13.5 All positive results must be bracketed by the concentrations within the calibration range. Dilute and reanalyze any sample results that exceed the highest calibration standard.

13.6 A method detection limit (MDL) study must be performed annually as per the current version of the laboratory procedure "Method Detection Limits". The MDL study verifies the capability of the entire analytical procedure at or near the level of detection. Higher levels may be assumed to respond more consistently than values at or near the detection level.

14.0 REPORTING RESULTS

14.1 Report results in the units and format specified by the client or contract.

15.0 PREVENTIVE MAINTENANCE

15.1 Perform preventative maintenance in accordance with the instrument manufacturer's recommendations.

16.0 REFERENCES

16.1 Hydrogen Sulfide (H_2S, Supelco Edition H1)

17.0 APPENDICES

17.1 None