

Battelle

The Business of Innovation

**Environmental Technology
Verification Program
Advanced Monitoring
Systems Center**

Test/QA Plan for Verification of
Ambient Hydrogen Sulfide Analyzers
at a Swine Finishing Farm

ET ✓ ET ✓ ET ✓

TEST/QA PLAN

for

Verification of Ambient Hydrogen Sulfide Analyzers at a Swine Finishing Farm

April 12, 2005

Prepared by

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A2 TABLE OF CONTENTS

<u>Section</u>		<u>Page</u>
A	PROJECT MANAGEMENT	
A1	Title Page	1
A2	Table of Contents	2
A3	Distribution List	5
A4	Verification Test Organization	6
A5	Background	13
A6	Verification Test Description and Schedule	14
A7	Quality Objectives	20
A8	Special Training/Certification	20
A9	Documentation and Records	21
B	MEASUREMENT AND DATA ACQUISITION	
B1	Experimental Design	22
B2	Reference Sample Collection	33
B3	Sample Handling and Custody Requirements	34
B4	Laboratory Reference Methods	34
B5	Quality Control	36
B6	Instrument/Equipment Testing, Inspection, and Maintenance	37
B7	Instrument Calibration and Frequency	37
B8	Inspection/Acceptance of Supplies and Consumables	38
B9	Non-Direct Measurements	38
B10	Data Management	38
C	ASSESSMENT AND OVERSIGHT	
C1	Assessments and Response Actions	41
C2	Reports to Management	44
D	DATA VALIDATION AND USABILITY	
D1	Data Review, Validation, and Verification Requirements	45
D2	Validation and Verification Methods	45
D3	Reconciliation with User Requirements	45
E	REFERENCES	46

List of Figures

Page

Figure 1	Organization Chart	7
Figure 2	Test Site	19

List of Tables

Table 1	Planned Verification Schedule	16
Table 2	Planned Weekly Test Activities During the Field Period	18
Table 3	Verification Test Performance Parameters	22
Table 4	Approximate H ₂ S Concentrations and Order for Multi-point Challenges	25
Table 5	Interferants and Approximate Concentrations for Interference Checks	26
Table 6	Reference Method Quality Control Requirements and Target Acceptance Criteria	37
Table 7	Summary of Data Recording Process	39

ETV Advanced Monitoring Systems Center

Test/QA Plan for Verification of
Ambient Hydrogen Sulfide Analyzers
at a Swine Finishing Farm

Version 1.0

April 12, 2005

VENDOR ACCEPTANCE:

Name _____

Company _____

Date _____

A3 DISTRIBUTION LIST

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SECTION A

PROJECT MANAGEMENT

A4 VERIFICATION TEST ORGANIZATION

The verification test will be conducted under the auspices of the U.S. Environmental Protection Agency (EPA) through the Environmental Technology Verification (ETV) Program. It will be performed by Battelle, which is managing the ETV Advanced Monitoring Systems (AMS) Center through a cooperative agreement with EPA. The scope of the AMS Center covers verification of monitoring technologies for contaminants and natural species in air, water, and soil.

The day to day operations of this verification test will be coordinated and supervised by Battelle personnel, with the participation of the vendors who will be having the performance of their hydrogen sulfide (H₂S) analyzers verified. The testing will be conducted at a large swine finishing farm near Ames, Iowa in collaboration with the U.S. Department of Agriculture National Soil Tilth Laboratory (USDA-NSTL) and Applied Measurement Science, which is a private consulting company located in Fair Oaks, California. Staff from the USDA will support this test by helping to install the analyzers to be tested, providing infrastructure at the test site, overseeing operation of the analyzers during periods of routine operation, and performing reference method sample collection and analysis. Applied Measurement Science, who will be operating with funding from the American Petroleum Institute, will provide reference method sampling and analysis. ASTM method D5504-01¹ will be used as the reference method with the following substitution: pulsed flame photometric detection (PFPD) will be used instead of sulfur chemiluminescence detection (SCD). Reference H₂S measurements in ambient air will be carried out by both USDA-NSTL and Applied Measurement Science using gas chromatography (GC) with PFPD, but will differ in the sample collection method. Each analyzer vendor will install their respective analyzer, operate the analyzer through portions of the test (unless they give written consent for Battelle staff to operate it), and repair or maintain their analyzer during the test. Quality Assurance (QA) oversight will be provided by the Battelle Quality Manager and

also by the EPA AMS Center Quality Manager, at her discretion. The organization chart in Figure 1 identifies the responsibilities of the organizations and individuals associated with the verification test. Roles and responsibilities are defined further below.

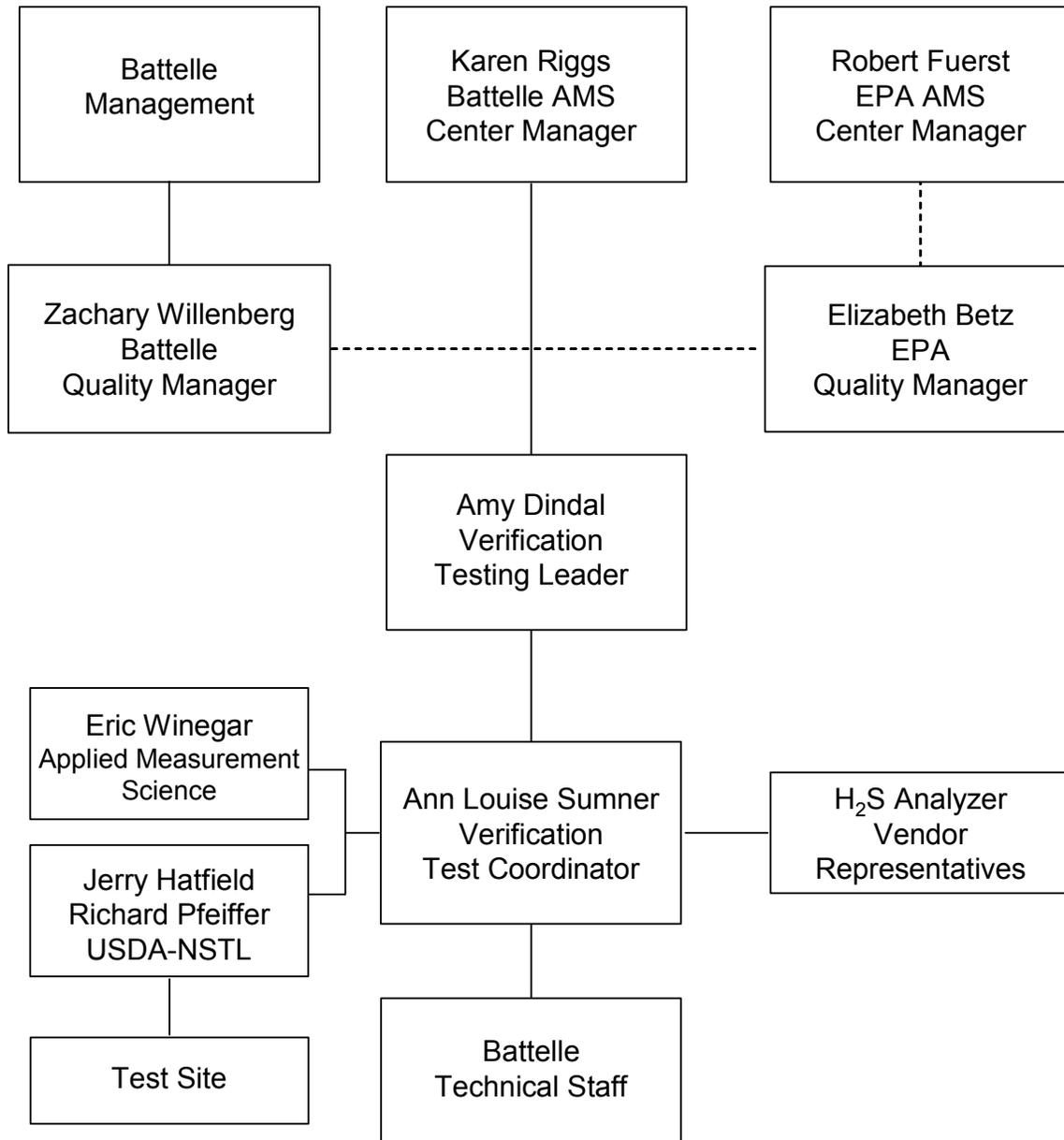


Figure 1. Organization Chart

A4.1 Battelle

Dr. Ann Louise Sumner is the AMS Center's Verification Test Coordinator for this test. In this role, Dr. Sumner will have overall responsibility for ensuring that the technical, schedule, and cost goals established for the verification test are met. Specifically, Dr. Sumner will:

- Prepare the draft test/QA plan, verification reports, and verification statements.
- Revise the draft test/QA plan, verification reports, and verification statements in response to reviewers' comments.
- C Assemble a team of qualified technical staff to conduct the verification test.
- C Establish a budget for the verification test and manage staff to ensure the budget is not exceeded.
- C Direct the team (Battelle, USDA, and Applied Measurement Science staff) in performing the verification test in accordance with this test/QA plan.
- C Ensure that all quality procedures specified in the test/QA plan and in the AMS Center Quality Management Plan² (QMP) are followed.
- Serve as the primary point of contact for vendor representatives.
- C Ensure that confidentiality of sensitive vendor information is maintained.
- C Assist vendors and USDA staff as needed during the analyzer installation and verification testing.
- C Become familiar with the operation and maintenance of the H₂S analyzers through instruction by the vendors, if needed.
- C Perform testing activities and data acquisition as specified in this test/QA plan.
- Respond to any issues raised in assessment reports and audits, including instituting corrective action as necessary.
- Coordinate distribution of the final test/QA plan, verification reports, and verification statements.

Ms. Amy Dindal is a Verification Testing Leader for the AMS Center. As such, Ms. Dindal will provide technical guidance and oversee the various stages of verification testing. She will:

- Support Dr. Sumner in preparing the test/QA plan and organizing the testing.

- Review the draft and final test/QA plan.
- Review the draft and final verification reports and verification statements.

Ms. Karen Riggs is Battelle's manager for the AMS Center. Ms. Riggs will

- C Review the draft and final test/QA plan.
- C Review the draft and final verification reports and verification statements.
- C Ensure that necessary Battelle resources, including staff and facilities, are committed to the verification test.
- C Ensure that confidentiality of sensitive vendor information is maintained.
- C Support Dr. Sumner in responding to any issues raised in assessment reports and audits.
- C Maintain communication with EPA's technical and quality managers.
- C Issue a stop work order if Battelle or EPA QA staff discovers adverse findings that will compromise test results.

Battelle Technical Staff will support Dr. Sumner in planning and conducting the verification test. The responsibilities of the technical staff will be to:

- C Assist in planning for the test, and making arrangements for the installation of the analyzers.
- C Perform statistical calculations specified in this test/QA plan on the H₂S analyzer data as needed.
- C Provide results of statistical calculations and associated discussion for the verification reports as needed.
- C Support Dr. Sumner in responding to any issues raised in assessment reports and audits related to statistics and data reduction as needed.

Mr. Zachary Willenberg is Battelle's Quality Manager for the AMS Center. Mr.

Willenberg will:

- C Review the draft and final test/QA plan.
- C Conduct a technical systems audit once during the verification test, or designate other QA staff to conduct the audit.
- C Audit at least 10% of the verification data.
- C Prepare and distribute an assessment report for each audit.
- C Verify implementation of any necessary corrective action.
- C Request that Battelle's AMS Center Manager issue a stop work order if audits indicate that data quality is being compromised.
- C Provide a summary of the QA/QC activities and results for the verification reports.
- C Review the draft and final verification reports and verification statements.
- C Assume overall responsibility for ensuring that the test/QA plan is followed.

A4.2 Hydrogen Sulfide Analyzer Vendors

The responsibilities of the H₂S analyzer vendors are as follows:

- C Review and provide comments on the draft test/QA plan.
- C Accept (by signature of a company representative) the final test/QA plan prior to test initiation (see page 4).
- C Provide an H₂S analyzer for evaluation during the verification test.
- C Provide all other equipment/supplies/reagents/consumables needed to operate their analyzer for the duration of the verification test.
- C Supply a representative to install and maintain their technology, and to operate it in portions of the test specified in this test/QA plan, or provide written consent and instructions for Battelle and USDA staff to carry out these activities.
- C Provide written instructions for routine operation of their analyzers, including a daily checklist of diagnostic and/or maintenance activities.
- C Provide maintenance and repair support for their analyzers, on-site if necessary, throughout the duration of the verification test.

- C Review and provide comments on the draft verification report and statement for their respective analyzers.

A4.3 EPA

EPA's responsibilities in the AMS Center are based on the requirements stated in the "Environmental Technology Verification Program Quality Management Plan" (EPA QMP).³ The roles of specific EPA staff are as follows:

Ms. Elizabeth Betz is EPA's AMS Center Quality Manager. For the verification test, Ms. Betz will:

- C Review the draft test/QA plan.
- C Perform at her option one external technical systems audit during the verification test.
- C Notify the EPA AMS Center Manager of the need for a stop work order if the external audit indicates that data quality is being compromised.
- C Prepare and distribute an assessment report summarizing results of the external audit.
- C Review draft verification reports and verification statements.

Mr. Robert Fuerst is EPA's manager for the AMS Center. Mr. Fuerst will:

- C Review the draft test/QA plan.
- C Approve the final test/QA plan.
- C Review the draft verification reports and verification statements.
- C Oversee the EPA review process for the test/QA plan, verification reports, and verification statements.
- C Coordinate the submission of verification reports and verification statements for final EPA approval.

A4.4 U.S. Department of Agriculture National Soil Tilth Laboratory

This test will be conducted in collaboration with the USDA-NSTL, who will provide in-kind support for this test. The responsibilities of personnel from the USDA-NSTL include the following:

- C Coordinate use of the test site for the purposes of ETV testing, assuring access to the test site for Battelle, USDA-NSTL, Applied Measurement Science, EPA, and vendor representatives.
- C Support the test by providing space and needed utilities (e.g., instrument trailer, electricity, compressed and cryogenic gases) for the H₂S analyzers and reference methods during testing.
- C Assist Battelle and vendor staff in the installation, operation, testing, and removal of the H₂S analyzers at the test site.
- C Plan and perform reference H₂S sampling and analysis.
- C Perform testing activities and data acquisition on the H₂S analyzers specified in this test/QA plan.
- C Collect basic meteorological data (e.g., wind speed, wind direction, temperature, and relative humidity) at the test site during the field period
- C Calculate the H₂S reference results in terms of ambient H₂S concentrations and provide a data package to Battelle that includes all sampling data sheets, analysis records, calibration data, and QA information, and that presents the H₂S sample analysis results, QA results, and calculated ambient H₂S concentrations as well as the recorded meteorological data.
- C Provide daily oversight of the H₂S analyzers during periods of routine operation, checking diagnostic indicators according to vendor directions and contacting Battelle if faults in analyzer operation are observed.
- C Record observations about the maintenance and operation of the H₂S analyzers during the field period.
- C Review the draft verification reports, and verification statements.

A4.5 Applied Measurement Science

Dr. Eric Winegar of Applied Measurement Science will be providing in-kind support on this test, with support from the American Petroleum Institute. The responsibilities of Dr. Winegar include the following:

- C Perform on-site reference H₂S measurements and conduct QA efforts as specified in this test/QA plan.
- C Calculate the H₂S reference results in terms of ambient H₂S concentrations and provide a data package to Battelle that includes all sampling data sheets, analysis records, calibration data, and QA information, and that presents the H₂S sample analysis results, QA results, and calculated ambient H₂S concentrations.
- C Review that portion of the verification reports that describes the in-situ reference method and analysis.

A5 BACKGROUND

The ETV Program's AMS Center conducts third-party performance testing of commercially available technologies that detect or monitor natural species or contaminants in air, water, and soil. Stakeholder committees of buyers and users of such technologies recommend technology categories, and technologies within those categories, as priorities for testing. Hydrogen sulfide analyzers were identified as a priority technology category through the AMS Center stakeholder process.

Hydrogen sulfide is formed at animal feeding operations (AFOs) during the bacterial decomposition of sulfur-containing organic compounds present in manure produced by livestock. Also known as sewer gas, H₂S has the characteristic odor of rotten eggs and, at high levels, can cause death from even brief exposure. Ambient H₂S concentrations at swine farms, for example, are expected to range from sub-part per billion (ppb) concentrations to 100 ppb or more.⁴ Ammonia and volatile organic compounds (VOCs) are also produced from bacterial processing of livestock waste and are likely to be present in significant concentrations at AFOs.^{5,6}

The National Academy of Sciences 2003 report, “Air Emissions from Animal Feeding Operations,”⁶ identified the need for need for improved methods for measuring and estimating air emissions from animal feeding operations (AFO), including emissions of H₂S. The analytical approach of the H₂S analyzers that will be evaluated in this verification test has been identified for use in the National Air Emissions Monitoring Study Protocol that will be used to conduct measurements of emissions from AFOs as directed by the U.S. EPA Animal Feeding Operations Consent Agreement.⁷ The data collected as a result of the monitoring study will be used to ensure compliance of AFOs with applicable provisions of the Clean Air Act, Comprehensive Environmental Response, Compensation and Liability Act (CERCLA), and Environmental Planning and Community Right-to-Know Act (EPCRA) and to promote a national consensus on methods for estimating AFO emissions. In addition to this federal effort, several states, including Iowa, California, and North Carolina, have developed or are developing standards for ambient H₂S.

A6 VERIFICATION TEST DESCRIPTION AND SCHEDULE

A6.1 Summary of Technology Category

The analyzers to be tested in this verification test are single point analyzers designed for quantifying gas phase H₂S in ambient air. The analyzers will be tested in the range of H₂S mixing ratios expected at a large AFO, in this case a swine finishing farm, and must be capable of H₂S quantification at low (5-20) ppb levels. A number of analytical techniques have been employed by vendors of H₂S analyzers, and include electrochemical detection, chromatography with sulfur chemiluminescence, oxidation of H₂S followed by ultra-violet (UV) sulfur dioxide (SO₂) fluorescence, and others.

The analyzers that will be evaluated in this verification test are stand-alone, automated instruments that continuously determine H₂S concentrations in ambient air by oxidizing H₂S in the air sample to SO₂, which is detected using UV fluorescence. The analyzers draw ambient air into the unit at flow rates less than one liter per minute, passing the air through a scrubber to remove SO₂ from the air. The H₂S remaining in the sample is oxidized to SO₂ in a catalytic converter maintained at approximately 300EC. The SO₂ produced from the conversion is then detected by UV fluorescence. Both analyzers can be configured to measure both H₂S and SO₂,

alternating between the two at user-specified intervals. Optional features include on-board H₂S or SO₂ permeation tubes and/or valves for zero air and span gases, which allow for automated zero and span checks. Results from multi-point H₂S calibrations are stored internally and used to determine the H₂S concentration in ambient air in units of ppb or parts per million (ppm), depending on the selected analyzer range. Although data are collected continuously, averages at specified intervals (e.g., 3 minutes) are calculated internally and relayed to analog and other data outputs (e.g., RS-232 or ethernet).

In performing the verification test, Battelle will follow the technical and QA procedures specified in this test/QA plan and will comply with the data quality requirements in the AMS Center QMP.²

A6.2 Verification Schedule

Table 1 shows the planned schedule of activities in field testing and data analysis/reporting in this verification test. As shown in Table 1, the field test of H₂S analyzers is planned to begin in April 2005 with installation of the analyzers at the swine finishing farm, and to extend into May 2005. The period of operation of the analyzers at the facility will be approximately 5 weeks, during which time the analyzers will monitor and record H₂S in the ambient air at the test site. Periodically over the duration of the field period, the analyzers will be challenged with H₂S and other compressed gas standards. Measurements will also be conducted using two H₂S reference methods during the field period. Subsequent to the field testing, a separate verification report will be drafted for each analyzer, reviewed, revised, and submitted to EPA for final signature.

Table 1. Planned Verification Schedule

Month (2005)	Test Activity	
	Analyzer Field Activities	Data Analysis and Reporting
April	Set up/install H ₂ S analyzers Analyzer training by vendors H ₂ S standard gas challenges H ₂ S reference sampling Routine operation	Begin preparation of report template Analyze H ₂ S reference samples Compile data from H ₂ S gas challenges
May	H ₂ S standard gas challenges Interferant challenges H ₂ S reference sampling Routine operation Remove analyzers from test site	Review and summarize operator observations Compile data from H ₂ S gas challenges Compile data from interferant challenges Analyze H ₂ S reference samples Compile data packages for reference methods
June		Complete summary of operator observations Finalize data from all gas challenges Finalize results for reference methods Complete common sections of reports Complete report sections on H ₂ S and other gas challenges and operator observations
July		Complete report sections on reference method comparisons Internal review of draft reports Vendor review of draft reports
August		Revision of draft reports Peer review of draft reports
September		Revision of draft reports Submission of final reports for EPA approval

Table 2 shows the activities to be conducted in each week of the test during the field period in April and May, 2005. The test procedures are described in Section B of this test/QA plan. Repeated challenges with zero air and H₂S gas standards will be conducted early in the field period to obtain the analyzer “baseline” responses and the analyzer response time. The same challenges with zero air and H₂S gas standards will be conducted twice each week to address analyzer span and zero drift. Multi-point challenges with H₂S gas standards will be conducted once early in the field period and again late in the field period to address analyzer measurement accuracy, bias, precision, and linearity. Once during the field period, the analyzers

will be challenged with gas standards of sulfur-containing species to evaluate analyzer interference effects. Reference method sampling will be conducted throughout the field period for comparison to the analyzer response to ambient air. In substantial portions of the field period, the analyzers will routinely monitor ambient H₂S to allow assessment of operational factors and data completeness under continuous operation.

Table 2. Planned Weekly Test Activities During the Field Period

Week of (Planned Month and Day, 2005)	Test Activities
April 11	<ul style="list-style-type: none"> C Install H₂S analyzers C Establish inlet connections C Training of USDA and Battelle staff by vendor representatives C Conduct trial operations
April 18	<ul style="list-style-type: none"> C Zero air/H₂S standard challenge for analyzer response (baseline) and analyzer response time C H₂S standard challenges for linearity, accuracy, bias, precision C One zero/span check C Two USDA reference samples collected and analyzed C Routine operation
April 25	<ul style="list-style-type: none"> C Two zero/span checks C Two USDA reference samples collected and analyzed C Install Applied Measurement Science reference method at test site C Begin Applied Measurement Science reference method measurements C Routine operation
May 2	<ul style="list-style-type: none"> C Continue/complete Applied Measurement Science reference method measurements C Two zero/span checks C Two USDA reference samples collected and analyzed C Routine operation
May 9	<ul style="list-style-type: none"> C Demobilize Applied Measurement Science reference method analyzer C Two zero/span checks C Two USDA reference samples collected and analyzed C Gas standard challenges for interference check C Routine operation
May 16	<ul style="list-style-type: none"> C Two zero/span checks C Two USDA reference samples collected and analyzed C H₂S standard challenges for linearity, accuracy, bias, precision C Routine operation
May 23	<ul style="list-style-type: none"> C Remove analyzers from test site

A6.3 Test Site

This verification test will take place at a large swine finishing farm near Ames, Iowa. The layout of the farm is shown in Figure 2. The farm has ten animal barns arranged in two parallel rows of five, with each barn housing up to 2,000 swine. The overall test schedule shown in Table

1 (Section A6.2) begins approximately six weeks after the farm will be populated by feeder pigs. The urine and feces from the swine exit the barns through metal gratings in the floor and are deposited in two nutrient lagoons located on the southern end of the farm; the primary H₂S source is expected to be the lagoons. The perimeter of the farm is lined with trees and agricultural fields surround the perimeter. A temperature-regulated instrument trailer will be placed on-site during the test to house the monitoring equipment and to provide a sheltered work space. The H₂S analyzers will be installed inside the instrument trailer and a Teflon inlet line or manifold will be used to sample ambient air. Sample tubing lengths will be minimized both for ambient air sampling and for delivery of gas standards.

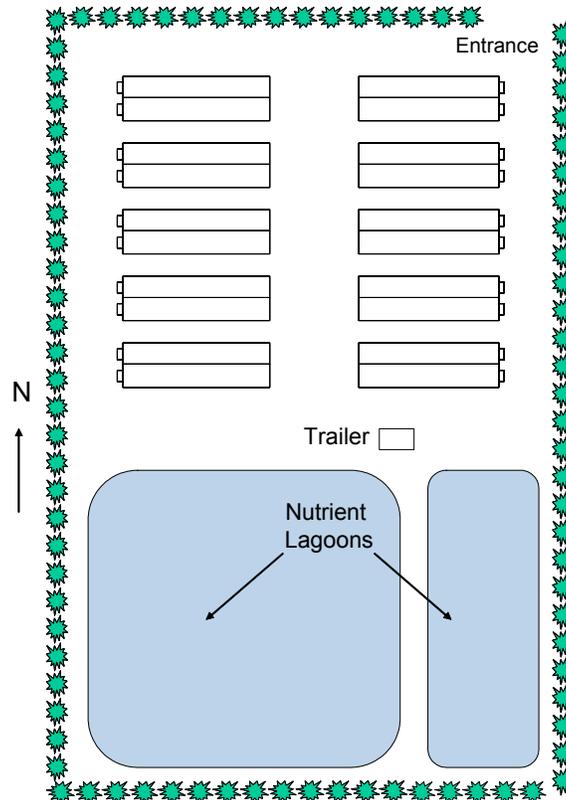


Figure 2. Test site

A7 QUALITY OBJECTIVES

This verification test will evaluate the performance of analyzers for determining H₂S in ambient air at a swine finishing farm. This evaluation will include a comparison of the analyzer results to the results of two reference methods for H₂S. The quality of the reference measurements will be monitored by inclusion of blank samples, performance evaluation (PE) audit samples, and duplicate samples, when applicable. The PE audit samples will be prepared using H₂S compressed gas cylinders or permeation devices that are independent of those used for reference method calibration. These samples are meant to independently confirm that the reference measurements are being performed correctly and are producing accurate results. Control limits on the duplicate and PE samples are given in Section C1. All H₂S standards to be used to challenge the H₂S analyzers and to prepare PE audit samples must meet National Institute of Standards and Technology (NIST) traceability. Commercially available compressed gas standards or permeation devices may be used in this test.

The Battelle Quality Manager or his designate will perform a technical systems audit (TSA) at least once during this verification test. The EPA Quality Manager also may conduct an independent TSA, at her discretion.

A8 SPECIAL TRAINING/CERTIFICATION

Documentation of training related to technology testing, field testing, data analysis, and reporting is maintained for all Battelle technical staff in training files. Documentation of the expertise and experience of USDA-NSTL and Applied Measurement Science staff in H₂S reference method sampling and analysis is similarly available. The Battelle Quality Manager may verify the presence of appropriate training records prior to the start of testing. If Battelle or USDA staff operate and/or maintain an analyzer during the verification test, the analyzer vendor will be required to train those staff prior to the start of testing. Battelle will document this training with a consent form, signed by the vendor, that states which specific Battelle/USDA staff have been trained on their analyzer. Battelle technical staff will have a minimum of a bachelor's degree in science/engineering or have equivalent work experience.

A9 DOCUMENTATION AND RECORDS

The records for this verification test will include the test/QA plan, chain-of-custody (COC) forms, laboratory record books (LRB), data collection forms, electronic files (both raw data and spreadsheets), and the final verification report and verification statement. All of these records will be maintained in the Verification Test Coordinator's office or the test site during the test and will be transferred to permanent storage at Battelle's Records Management Office at the conclusion of the verification test. The location (e.g., specific personal computer, server, or media type and storage location) of final versions of the electronic files will be noted in the test records. All Battelle LRBs are stored indefinitely, either by the Verification Test Coordinator or Battelle's Records Management Office. EPA will be notified before disposal of any files. The documentation and results of the H₂S reference measurements made by USDA and Applied Measurement Science will be submitted to Battelle immediately upon completion of all sample analyses, review of the H₂S data, and calculation of ambient H₂S concentrations, preferably on a daily basis. Section B10 further details the data recording practices and responsibilities.

All written records must be in ink. Any corrections to notebook entries, or changes in recorded data, must be made with a single line through the original entry. The correction is then to be entered, initialed, and dated by the person making the correction. In all cases, strict confidentiality of data from each vendor's analyzer, and strict separation of data from different analyzers, will be maintained. Separate files (including manual records, printouts, and/or electronic data files) will be kept for each analyzer.

SECTION B
MEASUREMENT AND DATA ACQUISITION

B1 EXPERIMENTAL DESIGN

This test will specifically address verification of analyzers for ambient H₂S under the conditions of a swine finishing farm by evaluating the accuracy, bias, linearity, and selectivity of H₂S measurements made by each analyzer in ambient air and/or synthetic gas mixtures, their response to rapid changes in H₂S concentration, the extent of baseline and calibration drift, and the ability of the analyzers to perform continuous monitoring with minimal intervention. The precision of the analyzer measurement data while sampling synthetic H₂S gas mixtures will also be determined. Specifically, the H₂S analyzers will be evaluated for the performance parameters summarized in Table 3 and discussed in detail in the following section.

Table 3. Verification Test Performance Parameters

Performance Parameter	Method of Evaluation
Accuracy	Analyzer response to H ₂ S standards compared to nominal concentrations
Bias	Analyzer response to H ₂ S standards compared to nominal concentrations
Precision	Percent relative standard deviation (%RSD) of repeated analysis H ₂ S standards with the same concentration
Linearity	Analyzer response to H ₂ S standards compared to nominal concentrations
Span and Zero Drift	Stability of analyzer response to zero air and H ₂ S gas standard over time
Response Time	Time required to reach 95% of response to H ₂ S gas standards
Interference Effects	Analyzer response to non-H ₂ S sulfur-containing compounds, butyric acid, and ammonia compared to nominal concentrations
Comparability	Analyzer response to ambient air compared to results of two reference methods
Data Completeness	Percentage of maximum data return over field period
Operational Factors	Operator observations, records of needed and performed maintenance, vendor activities, use of expendable supplies

In addition to the testing activities specified in this test/QA plan, Battelle and/or USDA staff will perform regular maintenance and other routine procedures requested by the vendor for their analyzer. This information will be summarized by the vendor in a “daily checklist” that will include specific instructions and frequency for each regular maintenance activity or routine procedure, any diagnostic values that should be recorded and typical or acceptable ranges for those values, vendor contact information, and a space for Battelle and/or USDA staff to sign and date the form daily upon completion of the items on the checklist.

B1.1 Test Procedures

The following sections describe the test procedures that will be used to evaluate each of the H₂S analyzer performance parameters listed in Table 3. Procedures will be conducted on each analyzer separately unless a common manifold is used to deliver challenge gases and sample ambient air. If a manifold is used, testing activities will be performed on the H₂S analyzers simultaneously. The manifold will be constructed of a bored-out 2.5 inch (in) inner-diameter Teflon cylinder that is 10 inches length. The manifold has 3/8 in inlet and outlet fittings, and four 1/4 in male connectors (at the same position along the length) to which the H₂S analyzers can be connected. A pump will be installed at the outlet port and configured to draw a flow through the manifold that is in excess of that required by the H₂S analyzers [approximately 3 liters per minute (Lpm)].

The electronic analyzer responses will be recorded continuously throughout the verification test and used for all analyses. Each gas standard will be delivered for a minimum of 20 minutes to allow for stabilization of the analyzer response. Gas standards will be prepared from the dilution of higher concentration (i.e., 2-500 part per million) standard cylinders in zero air using a calibrated dilution system with heated internal components. Gas standards will be supplied in excess of the analyzer sample flow rate; the excess flow will be vented outside the trailer to ambient pressure.

B1.1.1 Accuracy, Bias, Precision, and Linearity

Twice during the verification test, the analyzers will be challenged with compressed H₂S gas standards diluted in zero air to achieve measurements over a range of concentrations from approximately 0 to 100 ppb (or the upper range of measurement of the analyzer being tested, whichever is lower). If the ambient H₂S concentrations are found to be significantly larger than 100 ppb, additional H₂S gas dilutions may be tested to reflect the actual range, if possible.

Three non-consecutive measurements will be recorded at each of five different nominal concentration levels. Each concentration will be supplied to the analyzer(s) for at least twenty minutes. A programmable dilution system may be used to automatically supply the diluted gas standards to the H₂S analyzer(s) at fixed time intervals. Table 4 shows the nominal H₂S concentration values to be supplied to the analyzers being tested, and the order in which the concentrations will be supplied, for conditions where the maximum H₂S level encountered at the site is ~100 ppb. If H₂S concentrations greater than 200 ppb are encountered, the H₂S challenge gas concentrations may be modified upwards (e.g., to 0, 20, 60, 100, and 200 ppb) to more accurately reflect the range of ambient H₂S levels. As Table 4 indicates, the H₂S concentrations will first be supplied to the analyzers in increasing order, then in random order, and finally in decreasing order. After the last measurement has been recorded, the analyzer will be returned to sampling of ambient air.

The analyzer response to the series of H₂S gas standards will be used to evaluate accuracy, bias, precision, and linearity. Section B1.2 presents the statistical procedures that will be used. Accuracy will be calculated at each concentration and for each replicate relative to the nominal H₂S concentration. Bias will be calculated for each series of multi-point H₂S challenges. The analyzer precision will be demonstrated by the reproducibility of the analyzer response at each nominal H₂S concentration after a stable reading is achieved. Linearity will be assessed by establishing a multi-point calibration curve from the analyzer response.

Table 4. Approximate H₂S Concentrations and Order for Multi-point Challenges

Concentration	0 ppb	10 ppb	30 ppb	50 ppb	100 ppb
Measurement Number	1	2	3	4	5
	7	10	6	9	8
	15	14	13	12	11

B1.1.2 Span and Zero Drift

The “baseline” response of each analyzer to zero air and a 30 ppb dilution of a compressed H₂S gas standard will be determined during the first week of testing. Each analyzer will be alternately challenged with the diluted H₂S gas standard and zero air, for a total of five replicates of both the gas standard and zero air. Each gas will be supplied sequentially to the analyzer for at least twenty minutes. The switch between zero air and the H₂S standard will be made as quickly as possible if conducted manually; a programmable dilution system will be used if available. The mean and standard deviation of the analyzer response to zero air and to the 30 ppb H₂S standard will be calculated from the five replicates.

Twice each week (preferably Monday and Friday) during the verification test, zero air and a 30 ppb H₂S standard will again be supplied to each of the analyzers being tested for twenty minutes each for a total of nine zero/span checks. Each response will be compared to baseline response to determine whether or not drift has occurred in the analyzer response to zero air or the 30 ppb H₂S standard.

B1.1.3 Response Time

The data collected for the zero/span check (Section B1.1.2) will also be used to determine the analyzer response time. The 95% rise time will be calculated for changes from zero air to the 30 ppb H₂S standard and the fall time will be calculated for changes from the 30 ppb standard to zero air. A minimum of three individual measurements will be used to determine the average rise and fall times.

B1.1.4 Interference effects

The analyzers being tested will be challenged with a series of gases (interferants, see Table 5) that may be present at an AFO and could interfere with the analyzer response to H₂S. Each interferant will be supplied at approximately 100 ppb in the presence and absence of 100 ppb H₂S. A 100 ppb H₂S standard will be supplied to the analyzers for at least twenty minutes and the responses will be recorded. The analyzer will then be flushed with zero air for at least two minutes. The first interferant will be diluted with zero air and delivered to the analyzers for at least twenty minutes. The analyzer responses will be recorded and each analyzer flushed for at least two minutes with zero air. A mixture of the first interferant with 100 ppb H₂S in zero air will then be supplied to each analyzer for at least twenty minutes. The analyzer responses will be recorded, and zero air will be supplied to each analyzer for approximately two minutes. This process will be repeated for each of the interferants. The interferant challenges need not all be completed in a single day.

Table 5. Interferants and Approximate Concentrations for Interference Checks

Interferant	Approximate Concentration (ppb)
Sulfur dioxide	100
Carbonyl sulfide	100
Carbon disulfide	100
Methyl mercaptan	100
Dimethyl sulfide	100
Hydrocarbon blend	500
Ammonia	500

B1.1.5 Comparability

The comparability of the H₂S analyzer response to ambient air will be evaluated by comparing the analyzer response to two H₂S reference methods, which will be carried out by

USDA and Applied Measurement Science. Both methods follow ASTM International Method D5504-01¹ for the determination of sulfur compounds using GC, but will use PFPD instead of SCD. Although the analytical approach of both methods is the same, the two methods differ in sample handling. The two reference methods will be compared to one another by calculating the relative percent difference (RPD) (the difference between the two reference method values divided by the average). This comparison will assess whether the different sample collection techniques produce differences in the measured H₂S concentrations. Details of the reference sample collection procedure and laboratory method are provided in sections B2 and B4, respectively. The QA procedures for the reference methods are described in section B5.

B1.1.1.5a Time-integrated Comparability

The USDA reference method will utilize time-integrated air samples that will be collected in Silonite canisters and taken to the USDA laboratory for analysis. Samples will be collected over two eight-hour intervals on each sampling day. Sampling is expected to be conducted on approximately the following schedule: 10:00 p.m. to 6:00 a.m. and 6:00 a.m. to 2:00 p.m. The sampling times have been selected to accommodate the schedule of the USDA analysis laboratory. Time-integrated reference measurements will be conducted on a total of ten days during the field period. The samples may be collected twice per week or some samples may be rescheduled to collect more frequently during the in-situ H₂S reference method measurement period. The results of a minimum of 15 time-integrated reference method measurements will be compared to the time-averaged analyzer responses over the same time periods to give the time-integrated comparability of H₂S analyzers.

B1.1.1.5b In-situ Comparability

The in-situ H₂S reference method will be conducted by Applied Measurement Science. The instrumentation for the in-situ method will be installed in the instrument trailer at the test site. Discrete air samples will be drawn from the same location outside of the trailer, or preferably from the common sampling manifold, over a relatively short time period. Volatile compounds in the samples will be cryotrapped, thermally desorbed, and injected directly onto

the GC-PFPD system. To the extent possible, the duration of sample collection will be coordinated with the sampling frequency of the H₂S analyzers being tested (approximately two to 30 minutes). In-situ reference measurements will be conducted for approximately 8 hours per day for ten days during the second and third weeks of the verification test. This in-situ system decreases the chance for H₂S loss due to sample handling, but does require a more complex air handling system to automate the sample collection and injection. The results of a minimum of 60 in-situ H₂S reference method measurements will be compared to the analyzer responses to ambient air recorded at the same time. If the measurement frequency of the in-situ H₂S reference method and the H₂S analyzer being tested do not match in time within \pm two minutes, each data set will be averaged to common time intervals (e.g., hourly averages).

B1.1.6 Data Completeness

No additional test procedures will be carried out specifically to address data completeness. This parameter will be assessed based on the overall data return achieved by each analyzer.

B1.1.7 Operational Factors

Operational factors such as maintenance needs, data output, consumables used, ease of use, repair requirements, etc., will be evaluated based on observations recorded by Battelle and USDA staff. A separate LRB will be maintained at the test site for each analyzer undergoing testing, and will be used to enter daily observations on these factors. Examples of information to be recorded in the record books include the daily status of diagnostic indicators for the analyzer; use or replacement of any consumables; the effort or cost associated with maintenance or repair; vendor effort (e.g., time on site) for repair or maintenance; the duration and causes of any analyzer down time or data acquisition failure; and operator observations about ease of use of the analyzer. These observations will be summarized to aid in describing analyzer performance in the verification report on each analyzer.

B1.2 Statistical Analysis

The statistical methods and calculations used for evaluation of the quantitative performance parameters are described in the following sections.

B1.2.1 Accuracy

Accuracy of the H₂S analyzers with respect to the individual H₂S gas standards will be assessed as the percent recovery (%R), using Equation 1:

$$\%R = \left[1 + \left(\frac{Y - X}{X} \right) \right] \times 100 \quad (1)$$

where Y is the average measured H₂S analyzer value and X is the nominal H₂S gas standard concentration. The average, minimum, and maximum %R values will be reported for each series of multi-level H₂S challenges.

B1.2.2 Bias

Bias of the H₂S analyzers is defined as a systematic error in measurement that results in measured error that is consistently positive or negative compared to the true value. The bias will be calculated as the average percent difference (%D) of the H₂S analyzer compared to the nominal H₂S gas standard concentration and will be calculated for each series of multi-point H₂S challenges, using Equation 2:

$$\%D = \frac{1}{k} \sum_{j=1}^k \left(\frac{Y - X}{X} \right)_j \times 100 \quad (2)$$

where *k* is the number of valid comparisons, and Y and X are the same as stated in B1.2.1.

B1.2.3 Precision

The precision of the H₂S analyzers will be evaluated from the triplicate responses to each H₂S gas standard supplied during the multi-point challenges (outlined in Table 4). The precision

will be defined as the percent relative standard deviation (%RSD) of the triplicate measurements and calculated for each H₂S concentration listed in Table 4, using Equation 3:

$$\%RSD_i = \frac{s}{\bar{Y}_i} \times 100 \quad (3)$$

where \bar{Y}_i is the average analyzer response at H₂S concentration i , and s the standard deviation of the analyzer responses at that concentration. The overall average %RSD will also be calculated for each series of multi-point H₂S challenges and will include the %RSD for all H₂S concentrations tested.

B1.2.4 Linearity

Linearity will be assessed by a linear regression analysis using the diluted H₂S standard gas concentrations as the independent variable and results from the H₂S analyzers being tested as the dependent variable. Linearity will be expressed in terms of slope, intercept, and coefficient of determination (r^2).

B1.2.5 Span and Zero Drift

The “baseline” response of the H₂S analyzers to zero air and the 30 ppb H₂S standard will be established on the first day of testing, as outlined in Section B1.1.2. The mean (\bar{Y}) and standard deviation (s) of the analyzer response to zero air and 30 ppb H₂S will each be calculated from the five replicate measurements conducted on the first day of testing. From these values, a control chart will be constructed and the $\bar{Y} \pm 2s$ “warning limit” and the $\bar{Y} \pm 3s$ “action limit” calculated. Span drift will be defined as having occurred if three consecutive span checks all fall either above or below the warning limit. Zero drift will also be defined as having occurred if three consecutive zero checks all fall either above or below the warning limit. However, if the mean and/or standard deviation from the baseline zero check are equal to zero, the warning limits may not be meaningful. In this case, the absolute differences to the zero air baseline mean will be reported for each zero check.

B1.2.6 Response Time

Response time will be assessed in terms of both the rise and fall times of each H₂S analyzer when sampling the 30 ppb H₂S gas standard and zero air on the first day of testing (Section B1.1.2). Rise time (i.e., 0% - 95% response time for the change in H₂S concentration) will be determined from the analyzer response to a rapid increase in the delivered H₂S concentration. Once a stable response is achieved with the H₂S standard, the fall time (i.e., the 100% to 5% response time) will be determined in a similar way, switching from the H₂S standard back to zero air.

B1.2.7 Interference Effects

The interference effects of the H₂S analyzers will be calculated in terms of the ratio of the response of the analyzer to the interferant relative to the actual concentration of the interfering species. For example, if 100 ppb of an interfering species results in a 1 ppb change in the response of the analyzer, the interference effect will be reported as 1% (i.e., 1 ppb/100 ppb). Interference effects will be reported separately for each interferant both in the absence and in the presence of H₂S in zero air.

B1.2.8 Comparability

Comparability between the H₂S analyzer results and the reference method results will be assessed by linear regression using the reference method H₂S concentrations as the independent variable and results from the H₂S analyzers being tested as the dependent variable. Linearity will be expressed in terms of slope, intercept, and r^2 , and will be calculated independently for the time-integrated H₂S reference method and the in-situ H₂S reference method. It is expected that the measured concentration of H₂S will vary by at least a factor of five during each phase of testing. However, if this magnitude of variation is not achieved for one or both of the reference methods, comparability for that method will be calculated using Equation 1 and Equation 2 and reported as a percent recovery and bias, rather than in terms of the linear regression results.

B1.2.9 Data Completeness

Data completeness will be calculated as the percentage of the total possible data return over the entire field period that is achieved by each analyzer. This calculation will use the total hours of data recorded from each analyzer, divided by the total hours of data in the entire field period. The field period is defined to begin at 8:00 a.m. on the first day of testing and to end at the completion of the last testing activity or 5:00 p.m. on the final day of the field period, whichever is later. No distinction will be made in this calculation between data recorded during a specific test activity (e.g., data recorded for comparison to H₂S reference method data) and that recorded during routine ambient air monitoring. The causes of any substantial incompleteness of data return will be established from operator observations or vendor records, and noted in the discussion of data completeness results.

B1.3 Reporting

The statistical comparisons described above will be conducted separately for each of the analyzers being tested, and information on the operational parameters will be compiled and reported. The data for each analyzer will be kept separate from data for all other analyzers, and no intercomparison of the analyzer data will be performed at any time. A separate verification report will be prepared for each analyzer tested, presenting the test procedures and test data, as well as the results of the statistical evaluation of those data.

Operational aspects of the analyzers will be recorded by testing staff at the time of observation during the field test, and summarized in the verification report. For example, descriptions of the data-acquisition procedures, use of vendor-supplied proprietary software, consumables used, repairs and maintenance needed, and the nature of any problems will be presented in the report. Each verification report will briefly describe the ETV program, the AMS Center, and the procedures used in verification testing. The results of the verification test will be stated quantitatively, without comparison to any other analyzer tested, or comment on the acceptability of the analyzer's performance. Each draft verification report will first be subjected to review by the respective analyzer vendor, then revised and subjected to a review by EPA and other peer reviewers. The peer review comments will be addressed in further revisions of the

report, and the peer review comments and responses will be tabulated to document the peer review process. The reporting and review process will be conducted according to the requirements of the AMS Center QMP.²

B2 REFERENCE SAMPLE COLLECTION

B2.1 Time-integrated H₂S Reference Method

The time-integrated reference method will utilize air samples that will be collected in evacuated 1.4 L Silonite Canisters (Entech Instruments, Inc.), which will be transported from the field site to the USDA laboratory for analysis. A restrictive sampler will be used to control the fill rate over 8 hours and maintain sub-ambient pressure in the canister at the completion of sampling (i.e., fill to ~80% capacity). Under sub-ambient pressure, H₂S scavenging by water vapor has been shown to be negligible in canisters with Silcosteel®-treated surfaces at 50% relative humidity for at least 48 hours.⁸ All components that contact ambient air samples will be Teflon or passivated metal (e.g., Silcosteel® or Silonite) to minimize scavenging of H₂S by bare metal or other surfaces. In accordance with ASTM Method D5504-01¹, canister samples will be analyzed by GC-PFPD within 24 hours.

As indicated in ASTM Method D5504-01,¹ it has been demonstrated that H₂S in passivated canisters does not degrade over 24 hours; therefore, detailed holding time tests are not necessary. However, the acceptability of this holding time will be verified by analyzing an ambient air sample several times over the period (at least 24 hours) following sample collection. The H₂S concentration at 24 hours following sample collection should be within 15% of the initial measured value. Holding time verifications will be performed at least once before the start of the verification test and again mid-way through the test.

B2.2 In-situ H₂S Reference Method

Reference samples need not be collected for the in-situ H₂S reference method, since this approach relies on direct cryotrapping of volatile components from a small sample air flow over

a relatively short time period, followed immediately by thermal desorption and GC-PFPD analysis.

B3 SAMPLE HANDLING AND CUSTODY REQUIREMENTS

All reference samples will be entirely in the custody of USDA or Battelle from sample collection through sample recovery, transport, and analysis. Samples will be carried by USDA or Battelle staff to the USDA laboratory for analysis. Sample custody will be documented throughout installation of the canisters at the field site, ambient air collection, recovery of the sample canisters, transport, and analysis of the reference samples, using standard forms used by USDA for this purpose or forms provided by Battelle. Each COC form will be signed by the person relinquishing samples once that person has verified that the COC form is accurate. Upon receipt at the laboratory, COC forms will be signed by the person receiving the samples once that person has verified that all samples identified on the COC forms are present. Any discrepancies will be noted on the form and the sample receiver will immediately contact the USDA sampling leader to report missing or compromised samples. Copies of all COC forms will be delivered to the Verification Test Coordinator upon request, and maintained with the test records.

B4 LABORATORY REFERENCE METHODS

Although the ASTM H₂S reference method¹ is primarily for determination of sulfur compounds in natural gas and gaseous fuels, it has successfully been applied to H₂S detection in ambient air. Both of the reference methods described in this test/QA plan follow the ASTM method¹ and adhere to the general measurement principle of H₂S determination by GC with sulfur chemiluminescence or other detection technique. In both methods, a cryofocus interface and thermal desorption will be utilized to deliver the ambient air sample to the GC for separation. Instead of SCD, PFPD will be used to detect H₂S. QA procedures for both reference methods are described in section B5.

B4.1 Time-integrated H₂S Reference Method

The time-integrated H₂S reference method will use an Agilent 5890 GC equipped with a PFPD from OI Analytical. The inlet device will be a Model 7100A Preconcentrator (Entech) that utilizes cryofocusing and thermal desorption to transfer the sample to the head of the column. The column is a GS-Gaspro, 60 meter (m) × 0.32 millimeter (mm) inner diameter (i.d.) capillary column (J & W).

A multi-point calibration curve for H₂S will be constructed before reference analyses are conducted using dilute standards prepared from NIST-traceable certified H₂S compressed gas standards (Scott Specialty Gases). Several gas concentrations will be prepared using a dynamic dilution system (EnviroNics), transferred into Silonite canisters, and analyzed in the same manner as the reference samples. In addition to H₂S, chromatograms will include retention time data for sulfur dioxide, methyl mercaptan, dimethyl sulfide, carbonyl sulfide, and carbon disulfide, if present at sufficient concentration.

All analyses of reference and QA/QC samples will be conducted by USDA staff. USDA is responsible for providing the analytical instrumentation, calibrating that instrumentation, performing method QA/QC (see Section B5), and maintaining calibration records for any instrumentation used. USDA will be required to provide Battelle with documentation on calibration and quality control of the reference analyses.

B4.2 In-situ H₂S Reference Method

The in-situ H₂S reference method will use a Varian 3800 GC with PFPD. The inlet system contains an internal valving system that allows for automated operation. The column is a GS-Gaspro, 30 m × 0.32 mm i.d. capillary column (J & W).

A multi-point calibration curve for H₂S will be constructed at the test site before reference method measurements will be conducted, using dilute standards prepared from NIST-traceable certified H₂S compressed gas standards or certified permeation tubes and sampled in the same way as ambient air. In addition to H₂S, several sulfur-containing species, including,

sulfur dioxide, methyl mercaptan, dimethyl sulfide, carbonyl sulfide, and carbon disulfide, will also be quantified if present at sufficient concentration.

All analyses of reference and QA/QC samples for the in-situ reference method will be conducted by Applied Measurement Science staff. Applied Measurement Science is responsible for providing the analytical instrumentation, calibrating that instrumentation, performing method QA/QC (see Section B5), and maintaining calibration records for any instrumentation used. Applied Measurement Science will be required to provide Battelle with documentation on calibration and quality control of the reference analyses.

B5 QUALITY CONTROL

Steps will be taken to maintain the quality of the data collected during this verification test. Table 6 summarizes the quality control requirements for the reference methods during this test. Although these requirements differ from the suggested QA procedures outlined in ASTM method D5504-01,¹ they are more appropriate for the detection of ambient H₂S at ppb levels (versus ppm levels) in an ambient air matrix. Both reference methods will be required to analyze continuing calibration verifications (CCV), quality control samples (QCS), and field blanks. The time-integrated H₂S reference method will also be required to repeat analyses of 10% of the samples to verify the method precision. The reference analytical procedure will be maintained to meet these requirements. If the analytical performance is outside of the required tolerances, the relevant QC samples will be prepared again and reanalyzed. If performance problems persist, the reference instrument(s) will be recalibrated, and/or affected samples will be reanalyzed. Reference sample results not meeting these requirements will be excluded from comparison to the H₂S analyzer results. A minimum of 15 time-integrated reference measurements and 60 in-situ reference measurements that meet these QC requirements must be collected for use in the comparability comparisons, as stated in sections B1.1.1.5a and B1.1.1.5b, respectively.

Table 6. Reference Method Quality Control Requirements and Target Acceptance Criteria

QC Parameter	Addressed By	Required Performance
CCV	CCV run before analysis of reference samples each day	%D of CCV result within 30% compared to expected value
QCS	QCS run every 4 hours and after analysis of reference samples each day	%D of QCS result within 30% compared to expected value
Replicate H ₂ S precision	Analyze 10% of all samples twice ^(a)	Results within 30% of one another
Measurement accuracy	Analyze H ₂ S standard from independent source ^(b)	Results within 30% of expected value
Field blanks	Analyze canisters filled with zero air recovered from the field site (weekly) ^(a) Analyze zero air passed through sample manifold (weekly) ^(c)	If blank >30% of sample H ₂ S, data must be flagged

^(a) Time-integrated H₂S reference method only.

^(b) This standard will be provided as part of the Performance Evaluation audit (Section C.1.1).

^(c) In-situ H₂S reference method only.

B6 INSTRUMENT/EQUIPMENT TESTING, INSPECTION, AND MAINTENANCE

The equipment used for the reference sampling and analysis will be tested, inspected, and maintained as per the standard operating procedures of USDA and Applied Measurement Science, so as to meet the performance requirements established in this document. When Battelle or USDA staff operate and maintain the H₂S analyzers undergoing testing, those activities will be done as directed by the vendor. Otherwise, operation and maintenance of the analyzers will be the responsibility of the analyzer vendors.

B7 INSTRUMENT CALIBRATION AND FREQUENCY

The instrumentation used for the reference H₂S analyses will be calibrated daily on days when reference samples will be analyzed. The calibration of other instrumentation used in this verification test, such as dilution systems and flow readers, will be verified immediately prior to use in this verification test. A minimum of three flow rates for each flow controller or flow reader will be verified with an independent factory-calibrated flow meter.

The H₂S analyzers undergoing testing will be calibrated initially by the respective analyzer vendors at the time of installation at the test site using H₂S gas standards independent of those used for testing activities. Calibration checks will be performed upon direction by the analyzer vendor. In the event that recalibration is necessary, that recalibration will be carried out by the analyzer vendor, or by Battelle staff under the direction of the vendor. All calibrations performed will be documented by Battelle or USDA staff in the project record book dedicated to the respective analyzer.

B8 INSPECTION/ACCEPTANCE OF SUPPLIES AND CONSUMABLES

All materials, supplies, and consumables will be ordered by the Verification Test Coordinator or designee. Where possible, Battelle will rely on sources of materials and consumables that have been used previously as part of ETV verification testing without problems. Battelle will also rely on previous experience or recommendations from peer reviewers, EPA advisors, USDA staff, Applied Measurement Science, or analyzer vendors. Hydrogen sulfide gas standards will have NIST-traceable certifications.

B9 NON-DIRECT MEASUREMENTS

Data published previously in the scientific literature will not be used during this verification test.

B10 DATA MANAGEMENT

Various types of data will be acquired and recorded electronically or manually by Battelle, vendor, USDA, and Applied Measurement Science staff during this verification test. Table 7 summarizes the types of data to be recorded. All maintenance activities, repairs, calibrations, and operator observations relevant to the operation of the H₂S analyzers will be documented by Battelle or USDA staff in LRBs. A separate record book will be provided for each participating analyzer. Results from the reference methods, including raw data, analysis,

and final results, will be compiled by USDA and Applied Measurement Science staff in electronic format, and submitted to Battelle at the conclusion of reference H₂S analyses.

Table 7. Summary of Data Recording Process

Data to Be Recorded	Where Recorded	How Often Recorded	By Whom	Disposition of Data
Dates, times, and details of test events, analyzer maintenance, down time, etc.	ETV LRBs or data recording forms	Start/end of test procedure, and at each change of a test parameter or change of analyzer status	Battelle if on-site; USDA if Battelle not on-site	Used to organize and check test results; manually incorporated in data spreadsheets as necessary
Analyzer calibration information	ETV LRBs or electronically	At analyzer calibration or recalibration	Electronic data by Vendor; Battelle if on-site; USDA if Battelle not on-site	Incorporated in verification report as necessary
Analyzer H ₂ S readings	Recorded electronically by each analyzer and then downloaded to computer at least weekly	Recorded continuously	Analyzer vendor, for transfer to Battelle if on-site; transfer to USDA if Battelle not on-site	Converted to spreadsheet for statistical analysis and comparisons
Reference sample collection procedures, reference method procedures, calibrations, QA, etc.	LRBs, or data recording forms	Throughout sampling and analysis processes	USDA and Applied Measurement Science	Retained as documentation of reference method performance
Reference method H ₂ S analysis results	Electronically from H ₂ S analytical method	Every sample analysis	USDA and Applied Measurement Science	Converted to spreadsheets for calculation of ambient H ₂ S results, and statistical analysis and comparisons

Records received by or generated by any Battelle or USDA staff during the verification test will be reviewed by a Battelle staff member within two weeks of generation or receipt,

respectively, before the records are used to calculate, evaluate, or report verification results. If a Battelle staff member generated the record, this review will be performed by a Battelle technical staff member involved in the verification test, but not the staff member who originally generated the record. The review will be documented by the person performing the review by adding his/her initials and date to the hard copy of the record being reviewed. In addition, any calculations performed by Battelle or USDA staff will be spot-checked by Battelle technical staff to ensure that calculations are performed correctly. Calculations to be checked include any statistical calculations described in this test/QA plan. The data obtained from this verification test will be compiled and reported independently for each H₂S analyzer. Results for analyzers from different vendors will not be compared with each other.

Among the QA activities conducted by Battelle QA staff will be an audit of data quality. This audit will consist of a review by the Battelle Quality Manager of at least 10% of the test data. During the course of any such audit, the Battelle Quality Manager will inform the technical staff of any findings and any immediate corrective action that will be taken. If serious data quality problems exist, the Battelle Quality Manager will request that Battelle's AMS Center Manager issue a stop work order. Once the assessment report has been prepared, the Verification Test Coordinator will ensure that a response is provided for each adverse finding or potential problem, and will implement any necessary follow-up corrective action. The Battelle Quality Manager will ensure that follow-up corrective action has been taken.

SECTION C

ASSESSMENT AND OVERSIGHT

C1 ASSESSMENTS AND RESPONSE ACTIONS

Every effort will be made in this verification test to anticipate and resolve potential problems before the quality of performance is compromised. One of the major objectives of this test/QA plan is to establish mechanisms necessary to ensure this. Internal quality control measures described in this test/QA plan, which is peer reviewed by a panel of outside experts, implemented by the technical staff and monitored by the Verification Test Coordinator, will give information on data quality on a day-to-day basis. The responsibility for interpreting the results of these checks and resolving any potential problems resides with the Verification Test Coordinator. Technical staff have the responsibility to identify problems that could affect data quality or the ability to use the data. Any problems that are identified will be reported to the Verification Test Coordinator, who will work to resolve any issues. Action will be taken to control the problem, identify a solution to the problem, and minimize losses and correct data, where possible. Independent of any EPA QA activities, Battelle will be responsible for ensuring that the following audits are conducted as part of this verification test.

C1.1 Performance Evaluation Audits

A Performance Evaluation (PE) audit will be conducted to assess the quality of the H₂S reference method measurements made in this verification test. In the PE audit, key aspects of the reference measurement will be checked by comparison with an independent instrument, or an independent NIST-traceable standard. The PE audit of the H₂S reference methods will be performed by supplying to each reference method a blind, independent, NIST-traceable H₂S standard provided by Battelle. The PE samples will be analyzed in the same manner as for all other ambient air samples, and the analytical results for the PE samples will be compared to the

nominal concentration. The target criterion for this PE audit is agreement of the analytical result within 30% of the nominal H₂S concentration. If the PE audit results do not meet the tolerances required, they will be repeated. If the outlying results persist, a change in reference instrument and a repeat of the PE audit may be considered. This audit will be performed once prior to the start of the test and two times during the verification test, and will be the responsibility of the Verification Test Coordinator or her designee. Since the PE audit samples will be sampled by the reference methods in the same way as reference samples, they will assess each component of the reference method, including inertness of metal sampling components, H₂S stability in the sampling container (if applicable), and analytical accuracy of the GC-PFPD systems.

A PE audit of the ambient air sample flow rate for the time-integrated reference method will be performed by comparing to an independent flow measurement device. The target criterion for this PE audit is agreement within the expected range (i.e., 2 to 3 milliliters per minute). If used in this verification test, a PE audit of the programmable dilution system will be performed by comparing to an independent flow measurement device. One mid-range flow rate will be audited for each flow controller (i.e., 0.03, 0.3, and 5 Lpm) within the dilution system. The target criterion for this PE audit is agreement within 5% of the flow readings. These audits will be performed once during the verification test, and will be the responsibility of the Verification Test Coordinator or her designee.

C1.2 Technical Systems Audits

The Battelle Quality Manager will perform a technical systems audit (TSA) at least once during this verification test. The purpose of this audit is to ensure that the verification test is being performed in accordance with the AMS Center QMP², this test/QA plan, published reference methods, and any Standard Operating Procedures (SOPs) used by USDA or Applied Measurement Science. In the TSA, the Battelle Quality Manager, or a designee, may review the reference methods used, compare actual test procedures to those specified or referenced in this plan, and review data acquisition and handling procedures. In the TSA, the Battelle Quality

manager will tour the test site, observe the H₂S reference method sampling and sample recovery, inspect documentation of H₂S sample chain of custody; and review analyzer-specific record books. He will also check gas standard certifications and analyzer data acquisition procedures, and may confer with the analyzer vendors, USDA, and Applied Measurement Science personnel. He may also visit the USDA laboratories where the time-integrated H₂S reference method analysis is conducted, to review procedures and adherence to this plan and applicable SOP's. A TSA report will be prepared, including a statement of findings and the actions taken to address any adverse findings. The EPA AMS Center Quality Manager will receive a copy of Battelle's TSA report. At EPA's discretion, EPA QA staff may also conduct an independent on-site TSA during the verification test. The TSA findings will be communicated to technical staff at the time of the audit and documented in a TSA report.

C1.3 Data Quality Audits

The Battelle Quality Manager will audit at least 10% of the verification data acquired in the verification test. The Battelle Quality Manager will trace the data from initial acquisition, through reduction and statistical comparisons, to final reporting. All calculations performed on the data undergoing the audit will be checked.

C1.4 QA/QC Reporting

Each assessment and audit will be documented in accordance with Section 3.3.4 of the AMS Center QMP.² The results of the technical systems audit will be submitted to EPA.

Assessment reports will include the following:

- C Identification of any adverse findings or potential problems
- C Response to adverse findings or potential problems
- C Recommendations for resolving problems

- C Confirmation that solutions have been implemented and are effective
- C Citation of any noteworthy practices that may be of use to others.

C2 REPORTS TO MANAGEMENT

The Battelle Quality Manager, during the course of any assessment or audit, will identify to the technical staff performing experimental activities any immediate corrective action that should be taken. If serious quality problems exist, the Battelle Quality Manager is authorized to request that Battelle's AMS Center Manager issue a stop work order. Once the assessment report has been prepared, the Verification Test Coordinator will ensure that a response is provided for each adverse finding or potential problem and will implement any necessary follow-up corrective action. The Battelle Quality Manager will ensure that follow-up corrective action has been taken. The test/QA plan and final report are reviewed by EPA AMS Center QA staff and EPA AMS Center program management staff. Upon final review and approval, both documents will then be posted on the ETV website (www.epa.gov/etv).

SECTION D

DATA VALIDATION AND USABILITY

D1 DATA REVIEW, VALIDATION, AND VERIFICATION REQUIREMENTS

The key data review requirements for the verification test are the analysis of QC samples described in Section B5, a comparison of field data sheet comments against final data to flag any suspect data, and a review of final data to resolve any questions about apparent outliers. The QA audits described within Section C of this document, including the audit of data quality, are designed to assure the quality of the data.

D2 VALIDATION AND VERIFICATION METHODS

Section C of this test/QA plan provides a description of the validation safeguards employed for this verification test. Data validation and verification efforts include the collection of QC samples as required in this document, and the performance of TSA and PE audits as described in Section C.

D3 RECONCILIATION WITH USER REQUIREMENTS

This test/QA plan and the resulting ETV verification report(s) will be subjected to review by the H₂S analyzer vendors, USDA, Applied Measurement Science, EPA, and external expert peer reviewers. These reviews will assure that this test/QA plan and the resulting report(s) meet the needs of potential users and permittees of H₂S analyzers. The final report(s) will be submitted to EPA in Word Perfect and Adobe pdf format and subsequently posted on the ETV website.

SECTION E

REFERENCES

1. ASTM International. Standard Test Method for Determination of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Chemiluminescence. Designation: D5504-01, 2001.
2. Quality Management Plan for the ETV Advanced Monitoring Systems Center, Version 5.0, U.S. EPA Environmental Technology Verification Program, Battelle, Columbus, Ohio, March 2004.
3. Environmental Technology Verification Program Quality Management Plan, EPA/600/R-03/021, U.S. Environmental Protection Agency, Cincinnati, Ohio, December 2002.
4. Minnesota Pollution Control Agency. "Feedlot Air Quality Summary: Data Collection, Enforcement and Program Development." <http://www.pca.state.mn.us/hot/pubs/feedlot-aq.pdf>, March 1999.
5. Zahn, J. A., et al. "Correlation of Human Olfactory Responses to Airborne Concentrations of Malodorous Volatile Organic Compounds Emitted from Swine Effluent," J. Environ. Qual., 30, 624-634, 2001.
6. National Academy of Sciences. "Air Emissions from Animal Feeding Operations: Current Knowledge, Future Needs." National Research Council, 2003.
7. Animal Feeding Operations Consent Agreement and Final Order, Federal Register, Volume 70 (19), January 31, 2005.
8. Restek Corporation. "Stability of Low-level (1ppb - 20 ppb) Reactive Sulfurs in SilcoCan™ Canisters." Applications note #59347-INT, 2001.