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Environmental Technology Verification Program

Advanced Monitoring Systems Center

Generic Verification Protocol for Ambient Hydrogen Sulfide Analyzers at an Animal Feeding Operation

GENERIC VERIFICATION PROTOCOL

for

Verification of
Ambient Hydrogen Sulfide Analyzers at an Animal Feeding Operation

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A1.1 Foreword

This generic verification protocol is based upon a peer-reviewed specific test/quality assurance (QA) plan entitled “Test/QA Plan for Verification of Ambient Hydrogen Sulfide Analyzers at a Swine Finishing Farm.”(1) The test/QA plan was developed with vendor and stakeholder input by the ETV Advanced Monitoring Systems (AMS) Center. Peer reviewers for the test/QA plan were AMS Center stakeholder Will Ollison, American Petroleum Institute; Raul Dominguez, South Coast Air Quality Management District; and Bruce Harris, U.S. Environmental Protection Agency’s National Risk Management Research Laboratory. In preparing this generic verification protocol, specific names of individuals involved, technology vendors and technologies, test dates, and similar details in the test/QA plan were revised to be generic. The experimental design in this protocol is the same as that in the peer-reviewed test/QA plan.

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U.S. Environmental Protection Agency
  Advanced Monitoring Systems (AMS) Center Manager
  AMS Quality Manager

Battelle AMS Center
  AMS Center Manager
  Verification Testing Leader
  Verification Test Coordinator
  Quality Manager
  Technical Staff

Peer Reviewers

Hydrogen Sulfide Analyzer Vendors

Reference Laboratory

Test Facility, if applicable

Test Collaborators, if applicable

Subcontractors, if applicable

SECTION A

PROJECT MANAGEMENT

A4 VERIFICATION TEST ORGANIZATION

This protocol provides generic procedures for implementing a verification test for ambient hydrogen sulfide (H_2S) analyzers used to measure H_2S concentrations in ambient air at animal feeding operations (AFO). Verification tests are conducted under the auspices of the U.S. Environmental Protection Agency (EPA) through the Environmental Technology Verification (ETV) Program. Verification tests of monitoring technologies are coordinated by Battelle, which manages 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. In performing verification tests, Battelle follows the procedures specified in this protocol and compiles quality requirements in the "Quality Management Plan for the ETV Advanced Monitoring Systems Center" (QMP).(2)

Verification tests are performed by Battelle in cooperation with EPA and the vendors whose H_2S analyzers are being verified. The test procedures may be performed by Battelle, test facility staff, a qualified collaborator, and/or a qualified subcontractor; the specific staff members who will perform the test procedures are referred to as "technical staff" in this protocol. Each analyzer vendor is expected to install their respective analyzer, operate the analyzer through portions of the test (unless they give written consent for technical 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 his or 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.

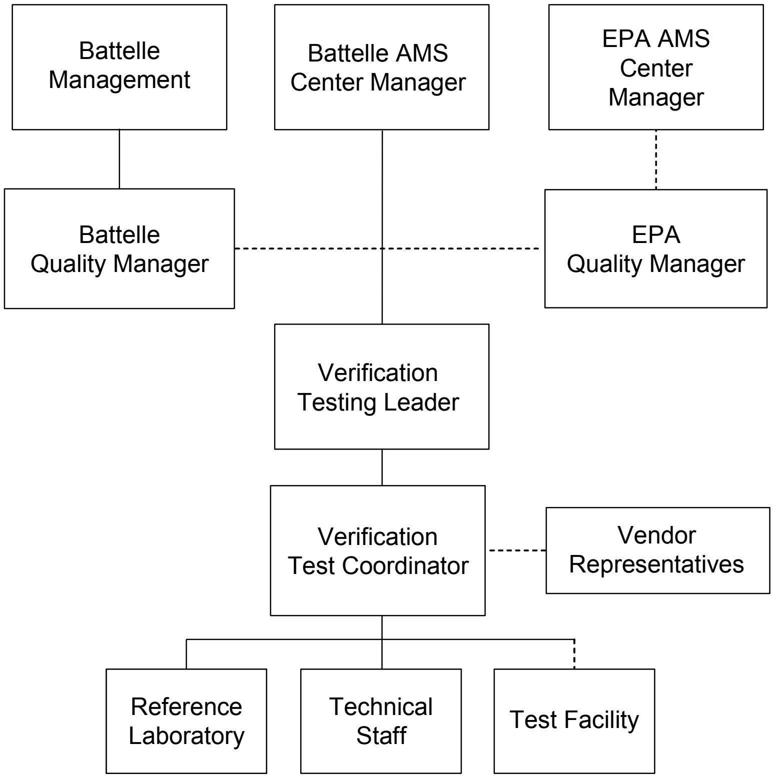

Figure 1. Organization Chart

A4.1 Battelle

The AMS Center's Verification Test Coordinator has overall responsibility for ensuring that the technical, schedule, and cost goals established for the verification test are met. More specifically, the Verification Test Coordinator will:

- Assemble a team of qualified technical staff to conduct the verification test.
- Serve as the primary point of contact for vendor representatives and technical staff.
- Direct the technical staff in performing the verification test in accordance with this protocol.
- Ensure that all quality procedures specified in this protocol and in the AMS Center QMP are followed.
- Prepare draft verification reports and verification statements, and revise according to reviewer comments.
- Coordinate distribution of the final verification reports and verification statements.

- Respond to any issues raised in assessment reports and audits, including instituting corrective action as necessary.
- Ensure that confidentiality of sensitive vendor information is maintained.

The Verification Testing Leader for the AMS Center provides technical guidance and oversees the various stages of verification testing. The Verification Testing Leader will:

- Support the Verification Test Coordinator in organizing the test.
- Review the draft and final verification reports and verification statements.

The Battelle AMS Center Manager will:

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

Battelle's Quality Manager for the AMS Center will:

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

- Review the draft and final verification reports and verification statements.
- Assume overall responsibility for ensuring that this protocol is followed.

A4.2 Hydrogen Sulfide Analyzer Vendors

The responsibilities of the H_2S analyzer vendors are as follows:

- Provide an H_2S analyzer for evaluation during the verification test.
- Provide all other equipment/supplies/reagents/consumables needed to operate their analyzer for the duration of the verification test.
- Supply a representative to install and maintain their technology, and to operate it in portions of the test specified in this protocol, or provide written consent and instructions for technical staff to carry out these activities.
- Provide written instructions for routine operation of their analyzers, including a daily checklist of diagnostic and/or maintenance activities.
- Provide maintenance and repair support for their analyzers, on-site if necessary, throughout the duration of the verification test.
- 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”.(3) The roles of specific EPA staff follow.

The EPA AMS Center Quality Manager will:

- Perform at his or her option one external technical systems audit during the verification test.
- 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.
- Prepare and distribute an assessment report summarizing results of the external audit.
- Review draft verification reports and verification statements.

EPA's manager for the AMS Center will:

- Review the draft verification reports and verification statements.
- Oversee the EPA review process for verification reports, and verification statements.
- Coordinate the submission of verification reports and verification statements for final EPA approval.

A4.4 Technical Staff

Technical staff from Battelle, a subcontractor, and/or a collaborating organization will conduct sample collection and test the H_2S analyzers during the verification test. The responsibilities of technical staff may include:

- Assist vendor staff in the installation, operation, testing, and removal of the H_2S analyzers at the test site.
- Perform experimental procedures specified in this protocol and acquire data from the H_2S analyzers.
- Provide daily oversight of the H_2S analyzers during periods of routine operation, checking diagnostic indicators according to vendor directions and contacting the Verification Test Coordinator if faults in analyzer operation are observed.
- Record observations about the maintenance and operation of the H_2S analyzers during the field period.
- Assist in the collection of ambient air samples, as needed, and ship or transport them to the reference laboratory.
- Collect basic meteorological data (e.g., wind speed, wind direction, temperature, and relative humidity) at the test site during the field period and supply the data to Battelle.
- Perform statistical calculations specified in this protocol on the H_2S analyzer data and provide results of statistical calculations and associated discussion for the verification reports, as needed.
- Support the Verification Test Coordinator in responding to any issues raised in assessment reports and audits related to statistics and data reduction as needed.
- Review the draft verification reports, and verification statements, as needed.

A4.5 Reference Laboratory

One or more analytical laboratories at Battelle, a subcontractor, and/or a collaborating organization will serve as a reference laboratory to:

- Perform reference analyses of all test and QC samples described in this protocol.
- Submit the results of the reference analyses in an agreed-upon format to the Verification Test Coordinator.

A4.6 Test Facility

The test facility for this verification test will be an animal feeding operation (AFO). The test facility personnel are expected to:

- Identify a point of contact for the test who will serve as the primary interface with the Verification Test Coordinator.
- Coordinate test facility involvement in the verification test in accordance with this protocol.
- Ensure that necessary test facility resources (e.g., space and power) are committed to the verification test.

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. The purpose of a verification test generated from this protocol is to provide quantitative verification of the performance of H_2S analyzers in a field setting while monitoring ambient air containing emissions from AFOs.

Hydrogen sulfide is formed at AFOs during the bacterial decomposition of sulfur-containing organic compounds present in manure produced by livestock. Also known as a component of sewer gas, H_2S has the characteristic odor of rotten eggs and, at high levels, can cause death from even brief exposure. Ambient H_2S 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 ambient air matrix at AFOs can be very challenging analytically. The potential for measurement artifacts resulting from contact of H_2S and other gases with non-passivated surfaces in air sampling equipment should be considered when conducting measurements at AFOs.

The National Academy of Sciences 2003 report, "Air Emissions from Animal Feeding Operations,"(6) identified the need for improved methods for measuring and estimating air emissions from AFOs, including emissions of H_2S. 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) will include measurements of H_2S at several types of AFOs. 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 H_2S.

A6 VERIFICATION TEST DESCRIPTION AND SCHEDULE

A6.1 Summary of Technology Category

The analyzers for which this protocol was developed are designed for quantifying gas phase H_2S in ambient air. The analyzers will be tested across a range of H_2S mixing ratios expected at a large AFO, and should be capable of H_2S quantification at least between 5 and 100 ppb H_2S. This protocol is intended for testing stand-alone, automated instruments that continuously determine H_2S concentrations in ambient air and report results in units of ppb. The H_2S analyzers may utilize analytical techniques including, but not limited to, electrochemical detection, chromatography with sulfur chemiluminescence detection (SCD), oxidation of H_2S followed by ultra-violet sulfur dioxide (SO_2) fluorescence, and others.

A6.2 Verification Schedule

An H_2S verification test from this protocol should take between six and nine months to complete after the start of testing, as shown by the general schedule in Table 1. Test planning and site preparation may take place over a period of three to four months. The period of operation of the analyzers at the facility should be approximately 5 weeks, during which time the analyzers will monitor and record H_2S in the ambient air at the test site. Periodically over the duration of the field period, the analyzers will be challenged with H_2S and other compressed gas standards. Measurements will also be conducted using a minimum of one independent H_2S reference method 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. General Verification Schedule

Month	Verification Test Activity	
	Test Planning and Site Preparation	
NA	Identify test collaborators/subcontractors and test site Recruit vendors Procure H_2S calibration and interferant gases Arrange for necessary logistical infrastructure and supplies at the test site (e.g., trailer to house testing equipment, gas standard dilution system, zero air)	
	Field Activities	**Data Analysis and Reporting**
1	Set up/install H_2S analyzers Analyzer training by vendors H_2S standard gas challenges H_2S reference sampling Routine operation	Begin preparation of report template Analyze H_2S reference samples Compile data from H_2S gas challenges
2	H_2S standard gas challenges Interferant challenges H_2S reference sampling Routine operation Remove analyzers from test site	Review and summarize operator observations Compile data from H_2S gas challenges Compile data from interferant challenges Analyze H_2S reference samples Compile data packages for reference methods
3	NA	Complete summary of operator observations Finalize data from all gas challenges Finalize results for reference analyses Complete common sections of reports Complete report sections on H_2S and other gas challenges and operator observations
4	NA	Complete report sections on comparisons to reference method
5 - 6	NA	Prepare draft reports and verification statements Peer review of draft reports
7 - 8	NA	Distribute verification reports and statements
9	NA	Finalize and post ETV reports and verification statements

NA=Not applicable.

Table 2 shows the approximate weekly schedule for testing activities for a five-week verification test. The test procedures are described in Section B of this protocol. Repeated challenges with zero air and H_2S 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 H_2S gas standards will be conducted twice each week to address analyzer span and zero drift. Multi-point challenges with H_2S 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 and other potentially interfering gases 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 H_2S to allow assessment of operational factors and data completeness under continuous operation.

Table 2. Weekly Test Activities During the Field Period

Week	Test Activities
1	Zero air/H_2S standard challenge for baseline response and analyzer response time H_2S standard challenges for linearity, accuracy, bias, precision One zero/span check Collect and analyze reference samples Routine operation
2	Two zero/span checks Collect and analyzer reference samples Routine operation
3	Two zero/span checks Collect and analyze reference samples Routine operation
4	Two zero/span checks Collect and analyze reference samples Gas standard challenges for interference check Routine operation
5	Two zero/span checks Collect and analyze reference samples H_2S standard challenges for linearity, accuracy, bias, precision Routine operation

A6.3 Test Site

The test site should be an AFO, such as a large swine finishing farm. The layout of a farm as an example test site 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) should begin at least six weeks after the farm is populated by feeder pigs. At this farm, urine and feces from the swine leave the barns through wood slats in the floor and are flushed through underground piping into a nutrient lagoon located on the southern end of the farm; supernatant liquid from the primary lagoon is pumped into a secondary storage lagoon and used to fertilize nearby fields. The perimeter of the farm is lined with trees and agricultural fields surround the perimeter. The primary H_2S source is expected to be the lagoons, so a temperature-regulated instrument trailer should be placed on-site during the test to house the monitoring equipment and to provide a sheltered work space near the lagoons. The H_2S 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.

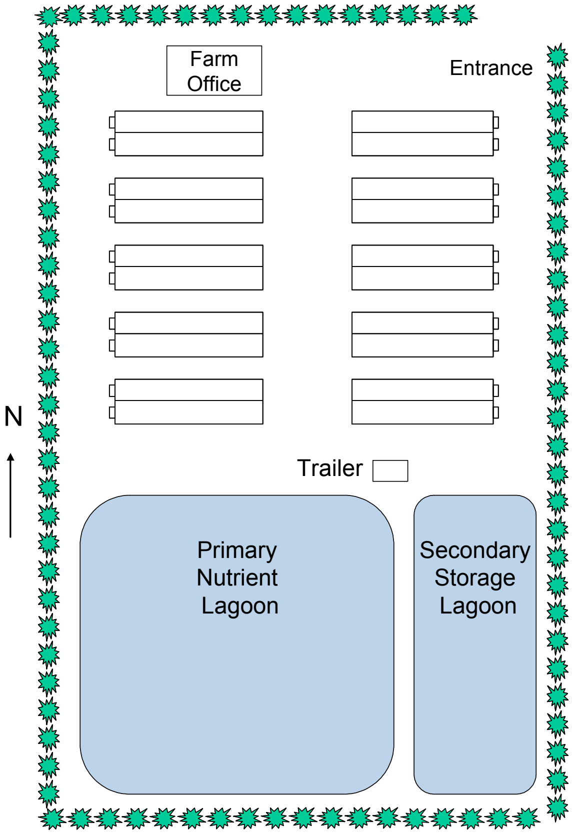

Figure 2. Example Test Site at an AFO

A7 QUALITY OBJECTIVES

In performing the verification test, Battelle will follow the technical and QA procedures specified in this protocol and will comply with the data quality requirements in the AMS Center QMP.(2) This verification test will evaluate the performance of analyzers for determining H_2S in ambient air at an AFO. This evaluation will include a comparison of the analyzer results to the results of one or more reference methods for H_2S. 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 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 H_2S standards to be used to challenge the H_2S 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 designate will perform a technical systems audit (TSA) at least once during this verification test to ensure that the quality objectives of the test are being met. The EPA Quality Manager also may conduct an independent TSA, at his or 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. Battelle technical staff will have a minimum of a bachelor’s degree in science/engineering or have equivalent work experience. Documentation of the expertise and experience of collaborators and/or subcontractors in H_2S reference method sampling and analysis must similarly be available. The Battelle Quality Manager may verify the presence of appropriate training records prior to the start of testing. If technical 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 technical staff have been trained on their analyzer.

A9 DOCUMENTATION AND RECORDS

The records for this verification test will include this protocol, 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 for each H_2S analyzer. 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 H_2S reference measurements made by the reference laboratory will be submitted to Battelle immediately upon completion of all sample analyses, review of the H_2S data, and calculation of ambient H_2S 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 H_2S under the conditions of an AFO (e.g., a swine finishing farm) by evaluating the accuracy, bias, linearity, and selectivity of H_2S measurements made by each analyzer in ambient air and/or synthetic gas mixtures, their response to rapid changes in H_2S 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 H_2S gas mixtures will also be determined. Specifically, the H_2S analyzers will be evaluated for the performance parameters summarized in Table 3 and discussed in detail in the following section.

In addition to the testing activities specified in this protocol, technical 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 technical staff to sign and date the form daily upon completion of the items on the checklist.

Table 3. Verification Test Performance Parameters

Performance Parameter	Method of Evaluation
Accuracy	Analyzer response to H_2S standards compared to nominal concentrations
Bias	Analyzer response to H_2S standards compared to nominal concentrations
Precision	Percent relative standard deviation (%RSD) of repeated analysis H_2S standards with the same concentration
Linearity	Analyzer response to H_2S standards compared to nominal concentrations
Span and Zero Drift	Stability of analyzer response to zero air and H_2S gas standard over time
Response Time	Time required to reach 95% of response to H_2S gas standards
Interference Effects	Analyzer response to potential interferants compared to nominal concentrations
Comparability	Analyzer response to ambient air compared to results of one or more 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

B1.1 Test Procedures

The following sections describe the test procedures that will be used to evaluate each of the H_2S analyzer performance parameters listed in Table 3. Procedures will be conducted on each analyzer separately unless a common manifold, such as the Teflon manifold shown in Figure 3, is used to deliver challenge gases and sample ambient air. If a manifold is used, testing activities will be performed on the H_2S analyzers simultaneously. A pump should be installed at the outlet port and configured to draw a flow through the manifold that is in excess of that required by the H_2S analyzers.

Figure 3. Example Teflon Manifold

The electronic analyzer responses will be recorded continuously throughout the verification test at a specified frequency (e.g., every minute). 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, preferably with heated, silanized 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. The dilution system should be flushed for at least 5 minutes at a higher H_2S concentration to ensure that the tubing and internal components of the dilution system have been thoroughly flushed before supplying gas standards to the analyzers. The H_2S analyzers should be calibrated prior to the start of the verification test using a dilution from the same gas standard and dilution system used for testing to avoid the potential for bias due to differences in the actual H_2S concentration of gas standards.

B1.1.1 Accuracy, Bias, Precision, and Linearity

At least twice during the verification test, the analyzers will be challenged with compressed H_2S 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 H_2S concentrations are found to be significantly higher than 100 ppb, additional H_2S gas dilutions may be tested to reflect the actual range, if possible.

At least three non-consecutive measurements will be recorded at each of a minimum 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 H_2S analyzer(s) at fixed time intervals. Table 4 shows the nominal H_2S 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 H_2S level encountered at the site is ~100 ppb. If H_2S concentrations greater than 200 ppb are encountered, the H_2S 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 H_2S levels. As Table 4 indicates, the H_2S 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.

Table 4. Approximate H_2S 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

The analyzer response to the series of H_2S gas standards will be used to evaluate accuracy, bias, precision, and linearity. Section B1.2 presents the statistical procedures that will be used to evaluate the data generated during the verification test. Accuracy will be calculated at each concentration and for each replicate relative to the nominal H_2S concentration. Bias will be calculated for each series of multi-point H_2S challenges. The analyzer precision will be demonstrated by the reproducibility of the analyzer response at each nominal H_2S concentration after a stable reading is achieved. Linearity will be assessed by establishing a multi-point calibration curve from the analyzer response.

B1.1.2 Span and Zero Drift

The "baseline" response of each analyzer to zero air and a mid-level (e.g., 30 ppb) dilution of a compressed H_2S gas standard will be determined during the first week of testing. Each analyzer will be alternately challenged with the diluted H_2S 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 H_2S 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 H_2S 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 H_2S 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 H_2S 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 a mid-level (e.g., 30 ppb) H_2S standard and the 95% fall time will be calculated for changes from the mid-level 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, such as the potential interferants listed in Table 5, that may be present at an AFO and could interfere with the analyzer response to H_2S. Each interferant should be supplied at approximately its ambient concentration, in the presence and absence of 100 ppb H_2S. Example concentrations are also shown in Table 5. Zero air will be supplied to the analyzers for at least twenty minutes and the responses will be recorded. A 100 ppb H_2S 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 (e.g., SO_2) will be diluted with zero air to the appropriate concentration (e.g., 100 ppb) 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 (100 ppb SO_2) with 100 ppb H_2S 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 at the concentrations chosen. The interferant challenges need not all be completed in a single day.

Table 5. Interferants and Approximate Concentrations for Interference Checks

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

[(a)] Equal mixture of methane, ethane, propane, butane, pentane, and hexane

B1.1.5 Comparability

The comparability of the H_2S analyzer response to ambient air will be evaluated by comparing the analyzer response to an H_2S reference method, which will be carried out by the reference laboratory. The reference method should follow ASTM International Method D5504-01(8) for the determination of sulfur compounds using GC, and may use pulsed flame photometric detection (PFPD) instead of SCD. As discussed in Section B2, reference samples may be collected as time-integrated air samples in silanized canisters and/or air samples may be cryotrapped *in situ* and analyzed immediately at the field site. If two sample collection method are used, results from the two 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 produced differences in the measured H_2S concentrations. Reference results from each sample collection method will be compared separately to the H_2S analyzer measurements. Details of the reference sample collection procedure and analytical methods are provided in sections B2 and B4, respectively. The QC procedures for the reference methods are described in section B5.

B1.1.1.5a Time-integrated Comparability

Time-integrated air samples may be collected in silanized canisters and transported to the reference laboratory for analysis. Sample duration and frequency should be optimized based on canister size and flow rate and the availability of the reference laboratory. Sampling in 1.4 L canisters with a fill rate of approximately 2 standard cubic centimeters per minute (sccm) will serve as an example. In this case, samples would be collected over two eight-hour intervals on each sampling day on approximately the following schedule: 10:00 p.m. to 6:00 a.m. and 6:00 a.m. to 2:00 p.m. These sampling times allow time for analysis by the reference laboratory in the afternoon following sample collection. Samples collected in canisters should be analyzed within 24 hours of sample collection.(8) Time-integrated reference measurements should be conducted on a minimum of ten days during the field period. The samples may be collected twice per week or collected at a higher frequency during shorter measurement intensives. The results of a minimum of 15 time-integrated reference method measurements that are greater than the reference method quantitation limit should be compared to the time-averaged analyzer responses over the same time periods to give the time-integrated comparability of H_2S analyzers.

B1.1.1.5b *In situ* Comparability

In situ H_2S reference measurements may be conducted in addition to or instead of time-integrated measurements. The instrumentation for the *in situ* method should 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 (e.g., two to 30 minutes). Volatile compounds in the samples will be cryotrapped, thermally desorbed, and injected directly onto the GC-PFPD or GC-SCD system. To the extent possible, the duration of sample collection will be coordinated with the sampling frequency of the H_2S analyzers being tested. *In situ* reference measurements should be conducted for approximately 8 hours per day for ten days during the verification test. The results of a minimum of 60 *in situ* H_2S reference method measurements should be compared to the analyzer responses to ambient air recorded at the same time. If the measurement frequency of the *in situ* H_2S reference method and the H_2S analyzer being tested do not match in time within ± 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 technical staff. A checklist of should be prepared for each analyzer by the vendor representative and completed daily by technical staff to verify the operation of each H_2S analyzer and to identify signs of malfunction. An example checklist is shown in Appendix A. A separate LRB will be maintained at the test site for each analyzer undergoing testing, and will be used to enter additional daily observations on operational 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 H_2S analyzers with respect to the individual H_2S gas standards will be assessed as the percent recovery (%R), using Equation 1:

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

where Y is the average measured H_2S analyzer value and X is the nominal H_2S gas standard concentration. The average, minimum, and maximum %R values will be reported for each series of multi-level H_2S challenges. A %R value of 100% indicates perfect agreement between the H_2S analyzer value and the nominal H_2S gas standard concentration.

B1.2.2 Bias

Bias of the H_2S 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 H_2S analyzer compared to the nominal H_2S gas standard concentration and will be calculated for each series of multi-point H_2S challenges, using Equation 2:

$$\%\overline{D} = \frac{1}{k}\sum_{i=1}^{k}\left(\frac{Y - X}{X}\right)_i \times 100 \qquad (2)$$

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

B1.2.3 Reproducibility

The reproducibility of the H_2S analyzers will be evaluated from the triplicate responses to each H_2S gas standard supplied during the multi-point challenges (outlined in Table 4). The reproducibility will be defined as the percent relative standard deviation (%RSD) of the triplicate measurements and calculated for each H_2S concentration listed in Table 4, using Equations 3 and 4:

$$SD = \sqrt{\frac{\sum\left(Y - \overline{Y}\right)^2}{n-1}} \qquad (3)$$

$$\%RSD_i = \frac{SD_i}{\overline{Y}_i} \times 100 \qquad (4)$$

where Y is the individual analyzer response at each concentration, $\overline{Y}$ is the average analyzer response from the triplicate measurements at H_2S concentration i (i = 10, 30, 50, and 100 ppb), and SD the standard deviation of the analyzer responses at that concentration. The overall average %RSD will also be calculated for each series of multi-point H_2S challenges and will include the %RSD for all H_2S concentrations tested.

B1.2.4 Linearity

Linearity will be assessed by a linear regression analysis using the diluted H_2S standard gas concentrations as the independent variable and results from the H_2S 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 H_2S analyzers to zero air and the 30 ppb H_2S standard will be established on the first day of testing, as outlined in Section B1.1.2. The mean $(\overline{Y})$ and standard deviation (SD) of the analyzer response to zero air and 30 ppb H_2S 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 $\overline{Y} \pm 2SD$ "warning limit" and the $\overline{Y} \pm 3SD$ "action limit" calculated. Span drift will be defined as having occurred if three consecutive span checks fall either above or below the warning limit. Zero drift will also be defined as having occurred if three consecutive zero checks 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 H_2S analyzer when sampling the 30 ppb H_2S 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 H_2S concentration) will be determined from the analyzer response to a rapid increase in the delivered H_2S concentration. Once a stable response is achieved with the H_2S standard, the 95% fall time (i.e., the 100% to 5% response time) will be determined in a similar way, switching from the H_2S standard back to zero air.

B1.2.7 Interference Effects

The interference effects of the H_2S 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 H_2S in zero air.

B1.2.8 Comparability

Comparability between the H_2S analyzer results and the reference method results will be assessed by linear regression using the reference method H_2S concentrations as the independent variable and results from the H_2S 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 H_2S reference method and the *in situ* H_2S reference method. It is expected that the measured concentration of H_2S 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. As appropriate, tests of statistical significance may be used in addition to or in place of linear regression analysis.

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 H_2S 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 technical 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 H_2S Reference Method

The time-integrated reference method will utilize air samples that will be collected in evacuated silanized canisters, which will be transported from the field site to the reference laboratory for analysis. A restrictive sampler will be used to control the fill rate over the appropriate time period and maintain sub-ambient pressure in the canister at the completion of sampling (i.e., fill to ~80% capacity). Under sub-ambient pressure, H_2S 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.(9) All components that contact ambient air samples will be Teflon or passivated metal (e.g., Silcosteel® or Silonite) to minimize scavenging of H_2S by bare metal or other surfaces. In accordance with ASTM Method D5504-01,(8) canister samples will be analyzed by GC-PFPD or GC-SCD within 24 hours.

As indicated in ASTM Method D5504-01,(8) it has been demonstrated that H_2S 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 H_2S 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* H_2S Reference Method

Reference samples need not be collected for the *in situ* H_2S 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 or GC-SCD analysis.

B3 SAMPLE HANDLING AND CUSTODY REQUIREMENTS

Custody of all reference samples will be documented from sample collection through sample recovery, transport, and analysis. Samples will be carried by technical staff or shipped to the reference 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 provided by the reference laboratory 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 Verification Test Coordinator 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 ANALYTICAL REFERENCE METHODS

Although the ASTM H_2S method is primarily for determination of sulfur compounds in natural gas and gaseous fuels, it has successfully been applied to H_2S detection in ambient air.(8) Both of the reference methods described in this protocol follow the ASTM method(8) and adhere to the general measurement principle of H_2S determination by GC with SCD or other detection technique. A cryofocus interface and thermal desorption may be utilized to deliver the ambient air sample to the GC for separation. Instead of SCD, PFPD may be used to detect H_2S. GS-Gaspro capillary columns (J & W Scientific) may be used for separating H_2S in ambient air. QC procedures for both reference methods are described in section B5.

B4.1 Time-integrated H_2S Reference Method

A multi-point calibration curve for H_2S will be constructed before reference analyses are conducted using dilute standards prepared from NIST-traceable certified H_2S compressed gas standards. Variable injection volumes may be used to establish the calibration curve or several gas concentrations will be prepared using a dynamic dilution system, transferred into Silonite canisters, and analyzed in the same manner as the reference samples. All analyses of reference and QA/QC samples will be conducted by the reference laboratory. The reference laboratory will be responsible for providing the analytical instrumentation, calibrating that instrumentation, performing method QA/QC (see Section B5), and maintaining calibration records for any instrumentation used. The reference laboratory will be required to provide Battelle with documentation on calibration and QC of the reference analyses.

B4.2 *In situ* H_2S Reference Method

A multi-point calibration curve for H_2S will be constructed at the test site before reference method measurements will be conducted, using dilute standards prepared from NIST-traceable certified H_2S compressed gas standards or certified permeation tubes and sampled in the same way as ambient air. All analyses of reference and QA/QC samples for the *in situ* reference method will be conducted by the reference laboratory. The reference laboratory will be responsible for providing the analytical instrumentation, calibrating that instrumentation, performing method QA/QC (see Section B5), and maintaining calibration records for any instrumentation used and 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 QC requirements for the reference methods during this test**.** Although these requirements differ from the suggested QA procedures outlined in ASTM method D5504-01,(8) they are more appropriate for the detection of H_2S at ppb levels (versus part per million levels) in an ambient air matrix. Reference methods will be required to analyze continuing calibration verifications (CCV), quality control samples (QCS), and field blanks. The time-integrated H_2S reference method will also be required to repeat analyses of 10% of the samples to verify method precision. The reference analytical procedures 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 H_2S analyzer results. If possible, matrix spike samples should also be analyzed. A minimum of 15 time-integrated reference measurements and/or 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 (mid-range H_2S gas standard) run before analysis of reference samples each day	%D of CCV result within 30% of expected value
QCS	QCS (mid-range H_2S gas standard) run every 4 hours and after analysis of reference samples each day	%D of QCS result within 30% compared to expected value
Reproducibility	Analyze 10% of all samples twice(a)	Results within 30% of one another
Measurement accuracy	Analyze H_2S 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_2S, data must be flagged

(a) Time-integrated H_2S reference method only.
(b) This standard will be provided as part of the Performance Evaluation audit (Section C.1.1).
(c) *In situ* H_2S reference method only.

B6 INSTRUMENT/EQUIPMENT TESTING, INSPECTION, AND MAINTENANCE

The equipment used for the reference sampling and analysis (e.g., GC, detector, gas standard dilution equipment, flow controllers, flow meters) will be tested, inspected, and maintained as per the standard operating procedures of the reference laboratory and/or the manufacturer recommendations, so as to meet the performance requirements established in this document. When technical staff operate and maintain the H_2S 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 GC-PFPD or GC-SCD systems used for the reference H_2S analyses will be calibrated before any reference samples will be analyzed and recalibrated as needed based on the results from CCV samples. 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 H_2S analyzers undergoing testing will be calibrated initially by the respective analyzer vendors at the time of installation at the test site using H_2S 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 technical staff in the LRB 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, test collaborators, subcontractors, or analyzer vendors. H_2S gas standards will have NIST-traceable certifications, when possible.

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, collaborator, and/or subcontractor 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 H_2S analyzers will be documented by technical staff in LRBs. A separate LRB will be provided for each participating analyzer. Results from the reference methods, including raw data, analysis, and final results, will be compiled by the reference laboratories in electronic format, and submitted to Battelle at the conclusion of reference H_2S analyses.

Records received by or generated by any technical 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 technical staff will be spot-checked by Battelle QA and/or technical staff to ensure that calculations are performed correctly. Calculations to be checked include any statistical calculations described in this protocol. The data obtained from this verification test will be compiled and reported independently for each H_2S 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.

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	Technical staff	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; LRB entries by technical staff	Incorporated in verification report as necessary
Analyzer H_2S readings	Recorded electronically by each analyzer and then downloaded to computer at least weekly	Recorded continuously	Analyzer vendor, for transfer to technical staff	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	Reference laboratory	Retained as documentation of reference method performance
Reference method H_2S analysis results	Electronically from H_2S analytical method	Every sample analysis	Reference laboratory	Converted to spreadsheets for calculation of ambient H_2S results, and statistical analysis and comparisons

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 protocol is to establish mechanisms necessary to ensure this. Internal QC measures described in this protocol, 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 with the Battelle Quality Manager 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 H_2S 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 H_2S reference methods will be performed by supplying to each reference method a blind, independent, NIST-traceable compressed gas or permeation tube H_2S 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 H_2S 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 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, H_2S stability in the sampling container (if applicable), and analytical accuracy of the GC-PFPD or GC-SCD 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, which will be defined prior to the PE audit. A PE audit of the flow rates produced by the 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 liters per minute (Lpm)] within the dilution system. The target criterion for this PE audit is agreement within 5% of the flow readings. An additional PE audit of the H_2S concentration produced by the dilution system will be conducted by supplying the reference method(s) with each H_2S concentration used for testing the performance of the H_2S analyzers (i.e., 10, 30, 50, and 100 ppb). The acceptance criterion for this PE audit is agreement within 30% of the nominal H_2S concentration. If the PE audit results do not meet the tolerances required, they will be repeated. If the outlying results persist, the nominal concentrations used in the calculations (Section B1.2) may be corrected according to the reference method results. These audits will be performed once during the verification test, and will be the responsibility of the Verification Test Coordinator or 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 QMP,(2) this protocol, published reference methods, and any Standard Operating Procedures (SOPs) used by the reference methods. 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 protocol, and review data acquisition and handling procedures. In the TSA, the Battelle Quality Manager will tour the test site, observe the H_2S reference method sampling and sample recovery, inspect documentation of H_2S sample COC; and review analyzer-specific record books. He or she will also check gas standard certifications and analyzer data acquisition procedures, and may confer with the analyzer vendors, reference laboratory, and technical staff. The Battelle Quality Manager may also visit the reference laboratories where the H_2S 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 or designee 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 TSA will be submitted to EPA. Assessment reports will include the following:

- Identification of any adverse findings or potential problems
- Response to adverse findings or potential problems
- Recommendations for resolving problems
- Confirmation that solutions have been implemented and are effective
- 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. This protocol and final reports will be reviewed by EPA AMS Center QA staff and EPA AMS Center program management staff. Upon final review and approval, both documents will 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

Data validation is conducted as part of the data review described in Section B10 and C1.2 of this protocol. This verification will include a visual inspection of handwritten data to ensure that all entries were properly recorded or transcribed, and that any erroneous entries were properly noted (i.e., single line through entry, with an error code, initials of the recorder, and date of the entry). Data manually incorporated into spreadsheets for use in calculations will be checked against handwritten data to ensure that transcription errors have not occurred. Calculations will be spot-checked to ensure the accuracy and appropriateness of the calculations. Calculations performed manually will be reviewed and repeated using a handheld calculator or commercial software (e.g., Microsoft Excel). Calculations performed using standard commercial software (e.g., Microsoft Excel) will be reviewed by inspection of the equations used and selected calculations will be verified by handheld calculator.

A number of data validation procedures will also be performed. Section C of this protocol provides a description of the validation safeguards employed for a verification test performed under this protocol. Data validation efforts include the completion of QC activities and the performance of TSA and PE audits as described in Section C. An audit of data quality will be conducted by the Battelle Quality Manager or designee to ensure that data review, verification, and validation procedures were completed, and to verify the overall quality of the data.

D3 RECONCILIATION WITH USER REQUIREMENTS

The purpose of a verification test performed under this protocol is to evaluate the performance of ambient H_2S analyzers. To meet the requirements of the user community, the data obtained in such a verification test should include thorough documentation of the performance of each analyzer during the verification test. The data review, verification, and validation procedures described in the previous sections will ensure that verification test data meet these requirements, are accurately presented in the verification reports generated from the test, and that data not meeting these requirements are appropriately flagged and discussed in the verification reports. The QC acceptance criteria described in Section B5 will be used to ensure that the reference methods provide accurate measurements of the ambient air and test samples.

This generic verification protocol is based upon a peer-reviewed specific test/QA plan entitled “Test/QA Plan for Verification of Ambient Hydrogen Sulfide Analyzers at a Swine Finishing Farm.”(1) The test/QA plan was reviewed by H_2S analyzer vendors, ETV AMS Center staff, EPA, test collaborators, and expert peer reviewers. The data from any verification test of H_2S analyzers performed under this protocol will be compiled into an ETV verification report for each analyzer. The report will be subjected to review by the H_2S analyzer vendors, test collaborators, EPA, and external expert peer reviewers. These reviews will assure that this protocol, verification test(s) of H_2S analyzers, and the resulting report(s) meet the needs of potential users of H_2S analyzers. The final report(s) will be submitted to EPA in Microsoft Word or Corel WordPerfect and Adobe Portable Document Format (PDF) and subsequently posted on the ETV website.

SECTION E

REFERENCES

1. Test/QA Plan for Verification of Ambient Hydrogen Sulfide Analyzers at a Swine Finishing Farm, Version 1.0, U.S. EPA Environmental Technology Verification Program, Battelle, Columbus, Ohio, March 31, 2005.
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 Malordorous 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. 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.
9. Restek Corporation. "Stability of Low-level (1ppb - 20 ppb) Reactive Surfurs in SilcoCan™ Canisters." Applications note #59347-INT, 2001.

Appendix A
Example Daily Checklist

H_2S Analyzer Name

ETV Verification of Ambient Hydrogen Sulfide Analyzers
at an Animal Feeding Operation

Observe Analyzer Front Panel

9 Verify that power is on

9 Check for alarms Alarm = ___________________

9 Visually inspect filter

  9 Clean

  9 Dirty (replace if dirty) 9 Replaced

9 Download Data Download Time = ____________

9 Send data to Battelle (daily M-F) Most recent Date _____

_____

9 Send data to Vendor (at least weekly) Most recent Date __________

Action: If any of above issues fails, note in logbook and contact:

(Vendor contact information)

Operator Name: _______________________________________

Signature: ____

Date: ____________________

Comments:____

____

____

____

Note: Please remember to sign and date this form in non-erasable ink.