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Environmental Technology Verification Report

TELEDYNE-API MODEL 101E AMBIENT HYDROGEN SULFIDE ANALYZER

Prepared by
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ETV Advanced Monitoring Systems Center

TELEDYNE-API MODEL 101E AMBIENT HYDROGEN SULFIDE ANALYZER

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Notice

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Foreword

The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the nation's air, water, and land resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, the EPA's Office of Research and Development provides data and science support that can be used to solve environmental problems and to build the scientific knowledge base needed to manage our ecological resources wisely, to understand how pollutants affect our health, and to prevent or reduce environmental risks.

The Environmental Technology Verification (ETV) Program has been established by the EPA to verify the performance characteristics of innovative environmental technology across all media and to report this objective information to permitters, buyers, and users of the technology, thus substantially accelerating the entrance of new environmental technologies into the marketplace. Verification organizations oversee and report verification activities based on testing and quality assurance protocols developed with input from major stakeholders and customer groups associated with the technology area. ETV consists of six verification centers. Information about each of these centers can be found on the Internet at http://www.epa.gov/etv/.

Effective verifications of monitoring technologies are needed to assess environmental quality and to supply cost and performance data to select the most appropriate technology for that assessment. Under a cooperative agreement, Battelle has received EPA funding to plan, coordinate, and conduct such verification tests for "Advanced Monitoring Systems for Air, Water, and Soil" and report the results to the community at large. Information concerning this specific environmental technology area can be found on the Internet at http://www.epa.gov/etv/centers/center1.html.

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List of Abbreviations

AFO	animal feeding operation
AMS	Advanced Monitoring Systems
API	Advanced Pollution Instrumentation
ASTM	American Society for Testing and Materials
CCV	continuing calibration verification
CI	confidence interval
EPA	U.S. Environmental Protection Agency
ETV	Environmental Technology Verification
GC	gas chromatography
H_2S	hydrogen sulfide
i.d.	internal diameter
Lpm	liter per minute
m	meter
mm	millimeter
ln	natural logarithm
NIST	National Institute of Standards and Technology
PE	performance evaluation
PFPD	pulsed flame photometric detection
pg	picogram
ppb	part per billion
ppm	part per million
%D	percent difference
%R	percent recovery
PMT	photomultiplier tube
QA	quality assurance
QC	quality control
QCS	quality control samples
QMP	quality management plan
RSD	relative standard deviation
scc	standard cubic centimeter
sccm	standard cubic centimeter per minute
SD	standard deviation
SO_2	sulfur dioxide
TSA	technical systems audit
UHP	ultra-high purity
USDA	U.S. Department of Agriculture
UV	ultraviolet

Chapter 1
Background

The U.S. Environmental Protection Agency (EPA) supports the Environmental Technology Verification (ETV) Program to facilitate the deployment of innovative environmental technologies through performance verification and dissemination of information. The goal of the ETV Program is to further environmental protection by accelerating the acceptance and use of improved and cost-effective technologies. ETV seeks to achieve this goal by providing high-quality, peer-reviewed data on technology performance to those involved in the design, distribution, financing, permitting, purchase, and use of environmental technologies.

ETV works in partnership with recognized testing organizations; with stakeholder groups consisting of buyers, vendor organizations, and permitters; and with the full participation of individual technology developers. The program evaluates the performance of innovative technologies by developing test plans that are responsive to the needs of stakeholders, conducting field or laboratory tests (as appropriate), collecting and analyzing data, and preparing peer-reviewed reports. All evaluations are conducted in accordance with rigorous quality assurance (QA) protocols to ensure that data of known and adequate quality are generated and that the results are defensible.

The EPA's National Exposure Research Laboratory and its verification organization partner, Battelle, operate the Advanced Monitoring Systems (AMS) Center under ETV. The AMS Center, in collaboration with the U.S. Department of Agriculture's (USDA's) National Soil Tilth Laboratory and Applied Measurement Science, recently evaluated the performance of the Teledyne-Advanced Pollution Instrumentation (API) Model 101E ambient hydrogen sulfide (H_2S) analyzer in quantifying H_2S in ambient air at a swine finishing farm.

Chapter 2
Technology Description

The objective of the ETV AMS Center is to verify the performance characteristics of environmental monitoring technologies for air, water, and soil. This verification report provides results for the verification testing of the Model 101E. Following is a description of the Model 101E, based on information provided by the vendor. The information provided below was not verified in this test.

The Model 101E measures H_2S concentrations in ambient air by thermal conversion of H_2S to sulfur dioxide (SO_2) with a molybdenum catalytic converter and ultraviolet (UV) fluorescence of the SO_2 gas. The SO_2 gas is excited using a zinc lamp, and the UV fluorescence is measured using a photomultiplier tube (PMT). The Model 101E lower detectable limit is 0.4 parts per billion (ppb). An optical shutter compensates for PMT drift, and a reference detector corrects for changes in UV lamp intensity. The Model 101E software provides automatic alarms if operational parameter diagnostic limits are exceeded.

Data can be recorded in the internal data acquisition system or transmitted to a data logger or chart recorder using either an RS-232 interface or analog outputs. The built-in data acquisition system uses the Model 101E's internal memory and permits logging multiple parameters, including averaged or instantaneous (greater than 1 hertz) concentration values; calibration data; and operating parameters such as flow rate, pressure, and lamp intensity. Data are logged as one-second to one-hour averages, depending on the data acquisition settings. Stored data are retrieved through a serial or Ethernet port or from the front panel, allowing performance of predictive diagnostics and enhanced data analysis by tracking parameter trends. Data files are saved as comma-delimited text and can be opened in Microsoft Excel or other program for analysis. The analog outputs can be configured to provide instantaneous or averaged H_2S concentration readings and/or operating parameters. For this test, H_2S concentrations and operating parameters were logged as one-minute averages and retrieved through the Ethernet port to a laptop computer running Teledyne-API's APICOM software.

Figure 2-1. Teledyne-API Model 101E Ambient H_2S Analyzer

The Model 101E weighs 20.5 kilograms (45 pounds); and it is 178 millimeters (mm, 7 inches) high, 432 mm (17 inches) wide, and 597 mm (23 inches) deep. The Model 101E base cost is $12,100. As configured for this verification test, the cost would be $14,180.

Chapter 3
Test Design and Procedures

3.1 Introduction

H_2S is formed at animal feeding operations (AFOs) during the bacterial decomposition of sulfur-containing organic compounds present in manure. Also known as a component of sewer gas, H_2S has the characteristic odor of rotten eggs and, at high levels [greater than 500 parts per million (ppm)], can cause death from even brief exposure. As a result, H_2S analyzers were identified as a priority technology category through the AMS Center stakeholder process.

This verification test was conducted according to procedures specified in the *Test/QA Plan for Verification of Ambient Hydrogen Sulfide Analyzers at a Swine Finishing Farm*,[1] with the exception of three deviations that are addressed later in this report. The testing was conducted at a large swine finishing farm near Ames, Iowa. Testing was conducted for six weeks between April 25 and June 3, 2005, during which time the Model 101E continuously measured H_2S concentrations in ambient air or synthetic air samples of known concentration ("standards"). The performance of the Model 101E was evaluated in terms of

- Accuracy
- Bias
- Precision
- Linearity
- Span and zero drift
- Response time
- Interference effects
- Comparability
- Data completeness
- Operational factors.

3.2 Site Description

The layout of the swine finishing farm is shown in Figure 3-1. The farm had ten animal barns, arranged in two parallel rows of five, with each barn housing up to 2,000 swine. Figure 3-2 shows the interior of a swine barn; natural ventilation was regulated by raising or lowering curtains, shown in the foreground. The 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 primary H_2S source was 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 was placed on-site during the test to house the monitoring equipment and to provide a sheltered work space. Figure 3-3 shows the test site as photographed from the south of the lagoons, showing the instrument trailer and swine barns in the background. The Model 101E was installed inside the instrument trailer, and a Teflon inlet line (sampling ambient air through the East window) was connected to a Teflon manifold and was used to sample ambient air. The Teflon inlet line was protected from rain by an inverted funnel. The Teflon manifold used for supplying ambient air and gas standards to the Model 101E is shown in Figure 3-4. Sample tubing lengths were minimized both for ambient air sampling and for delivery of gas standards.

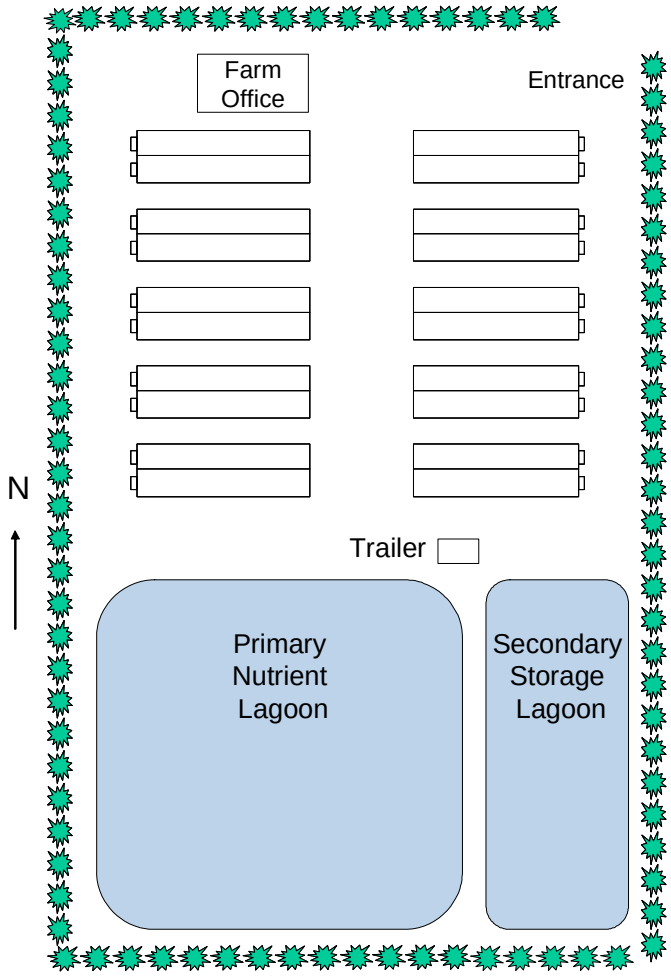

Figure 3-1. Test Site

3.3 Test Design

Table 3-1 shows the activities involved in preparing for and conducting the verification test.

Figure 3-2. Swine Barn Interior

The Model 101E was installed at the test site by vendor representatives. Battelle and USDA staff worked with the vendor representatives to establish procedures for operating the Model 101E during this verification test. The vendor representatives trained Battelle and USDA staff to check several instrument parameters to verify the operation of the Model 101E and identify signs of malfunction. A checklist, provided by the vendor representatives and included as Appendix A, was completed daily (Monday through Friday)

Figure 3-3. Test Site Lagoons

by Battelle or USDA staff. In general, Battelle or USDA staff verified that the Model 101E power was on, checked for alarms, inspected the inlet filter, and downloaded the Model 101E data (recorded as one-minute averages) on a daily basis. In the event of an instrument malfunction, Battelle and/or USDA staff could contact the vendor representatives or Teledyne-API customer service and conduct minor troubleshooting procedures as necessary, but were not expected to make any major repairs. The vendor representatives remained on-site until the installation was complete. All the testing activities, which are described in the following sections, were conducted by Battelle and/or USDA staff.

Individual data files (comma-delimited text) were opened in Microsoft Excel, where the results were analyzed using the procedures outlined in Chapter 5 of this report. Daily files containing only the Model 101E H_2S measurement data were less than 100 kilobytes. Files containing all of the stored Model 101E data (approximately 7 days), which contained the H_2S measurement data and operating parameters, were approximately 1 megabyte in size.

Gas standard dilutions were supplied to the Model 101E during testing activities for 20 minutes using a programmable dilution system (Environics Series 4040, with silanized internal components) that supplied each mixture to the Teflon manifold at flow rates at least 1 Lpm in excess of the Model 101E sampling flow rate (approximately 0.65 Lpm). The Model 101E logged one-minute averages of the instantaneous H_2S readings. The average Model 101E response to each gas standard was calculated from the last 5 minutes of data from each delivery period (5 data points). The last five minutes were selected because the Model 101E response appeared to be stable during that period (i.e., a general increase or decrease in the response was not apparent). These average Model 101E response values were used in the calculations described in Chapter 5 of this report.

Figure 3-4. Teflon Manifold

Table 3-1. Test Activities

Week of	Activities
April 11 April 18	• Install Model 101E • Establish inlet connections • Training of USDA and Battelle staff by vendor representatives • Conduct trial operations
April 25 (Testing Week 1)	• Zero air/H_2S standard challenge for analyzer response (baseline) and analyzer response time • Multipoint H_2S standard challenges for accuracy, bias, precision, linearity • One zero/span check • Three time-integrated reference samples collected and analyzed • Routine operation
May 2 (Testing Week 2)	• Three zero/span checks • Three time-integrated reference samples collected and analyzed • Install *in situ* reference method instrumentation at test site • Routine operation
May 9 (Testing Week 3)	• Two zero/span checks • Five time-integrated reference samples collected and analyzed • Routine operation
May 16 (Testing Week 4)	• Repeat zero air/H_2S standard challenge for analyzer response (baseline) and analyzer response time • Three zero/span checks • Four time-integrated reference samples collected and analyzed • Multipoint H_2S standard challenges for accuracy, bias, precision, linearity • Routine operation
May 23 (Testing Week 5)	• Two zero/span checks • Multipoint H_2S standard challenges for accuracy, bias, precision, linearity • Gas standard challenges for interference check • Troubleshoot *in situ* reference method instrumentation • Begin *in situ* reference measurements • Routine operation
May 30 (Testing Week 6)	• Three zero/span checks • Continue *in situ* reference method measurements • Demobilize *in situ* reference method instrumentation • Remove Model 101E from test site

The Model 101E H_2S readings when sampling ambient air were compared to concurrent measurements by two H_2S reference methods. For comparison with the time-integrated reference method (described in Section 3.3.5.1), the Model 101E H_2S readings were averaged to the same time period over which the reference method samples were collected (approximately 7.5 hours). For comparison with the *in situ* reference method (described in Section 3.3.5.2), Model 101E readings were averaged over 15-minute periods, centered on the *in situ* reference method sample times. The performance results of the Model 101E during this verification test are presented in Chapter 6 of this report and summarized in Chapter 7.

3.3.1 Accuracy, Bias, Precision, and Linearity

Three times during the verification test, the Model 101E was challenged with a certified compressed H_2S gas standard [5.12 parts per million (ppm) H_2S, Scott Specialty Gases] diluted in zero air to achieve measurements over a range of concentrations from approximately 0 to 300 parts per billion (ppb). Three non-consecutive measurements were recorded at each of five nominal concentration levels. Each concentration was supplied to the Model 101E for 20 minutes. Table 3-2 shows the nominal H_2S concentrations supplied to the Model 101E and the order in which they were supplied. As Table 3-2 indicates, the H_2S concentrations were supplied to the Model 101E in increasing order, then in random order, and finally in decreasing order. After the last measurement was recorded, the Model 101E was returned to sampling ambient air.

Table 3-2. H_2S Concentrations and Order for Multipoint Challenges

Concentration	0 ppb	30 ppb	90 ppb	150 ppb	300 ppb
Measurement Number	1	2	3	4	5
	7	10	6	9	8
	15	14	13	12	11

The Model 101E response to the series of H_2S gas standards was used to evaluate accuracy, bias, precision, and linearity. The statistical procedures used are presented in Section 5. Accuracy was calculated at each concentration and for each replicate relative to the nominal H_2S concentration. Bias was calculated for each series of multipoint H_2S challenges. The Model 101E precision was demonstrated by the reproducibility of the average Model 101E response at each nominal H_2S concentration. Linearity was assessed by establishing a multipoint calibration curve from the Model 101E response.

3.3.2 Span and Zero Drift

The baseline response of the Model 101E to zero air and a 30-ppb dilution of a compressed H_2S gas standard was determined during the first week of testing. The Model 101E was challenged alternately 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 was supplied sequentially for 20 minutes and the average response calculated for each replicate using data from the last 5 minutes of each delivery period.

The overall average and standard deviation of the Model 101E response to zero air and to the 30-ppb H_2S standard were calculated from the average response for the five replicates. Control charts showing the warning (± 2 SD) and action (± 3 SD) limits were constructed for the span and zero response for use in evaluating drift. The Model 101E was challenged with the zero air and 30-ppb H_2S sequence again during the fourth week of testing, and the results are presented in this report; however, the action and warning limits were not adjusted. Thus, drift was evaluated for the full duration of the verification test relative to the Week 1 response.

At least twice each week, zero air and a 30-ppb H_2S standard were supplied to the Model 101E for 20 minutes for a total of 14 zero/span checks. The gas standard dilution system was not flushed with the H_2S gas standard before performing eight of the span checks. Thus, the results of six span drift checks were used to evaluate span drift. Each response was compared to the Week 1 baseline response to determine whether drift occurred in the Model 101E sensitivity to zero air or the 30-ppb H_2S standard.

3.3.3 Response Time

The data collected during the Week 1 and Week 4 zero/span baseline response checks were used to determine the Model 101E response time. The 95% rise time was calculated for changes from zero air to the 30-ppb H_2S standard, and the 95% fall time was calculated for changes from the 30-ppb standard to zero air. A minimum of three individual measurements was used to determine the average rise and fall times.

3.3.4 Interference Effects

The Model 101E was challenged with a series of gases (Table 3-3) that may be present at an AFO and could interfere with the Model 101E response to H_2S. Each interferant was supplied at either 100 or 500 ppb, as listed in Table 3-3, in the presence and absence of 100 ppb of H_2S. A 100-ppb H_2S standard was supplied to the Model 101E for 20 minutes, and the responses were recorded. The Model 101E was then supplied with zero air for five minutes. The first interferant was diluted with zero air and delivered to the Model 101E for 20 minutes. After the responses were recorded, the Model 101E was supplied with zero air for five minutes. A mixture of the first interferant at (SO_2) 100 ppb with 100-ppb H_2S in zero air was supplied to the Model 101E for 20 minutes. The Model 101E responses were recorded, and zero air was supplied to the Model 101E for approximately five minutes. This process was repeated for each interferant at the concentrations listed in Table 3-3.

3.3.5 Comparability

The comparability of the Model 101E response to ambient air was evaluated by comparing its response to two H_2S reference methods (time-integrated and *in situ*), which were carried out by USDA and Applied Measurement Science. The two reference methods were based on American Society of Testing Materials (ASTM) Method D5504-01,[(2)] with the following substitution: pulsed flame photometric detection (PFPD) was used instead of sulfur chemiluminescence detection. Reference H_2S measurements in ambient air were conducted using gas chromatography (GC) with PFPD using two sample collection techniques. Although the analytical approach of the two methods was the same, they differed in sample collection and handling.

Table 3-3. 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 (mixture of C1 to C6 alkanes)	500
Ammonia	500

The two reference methods were not conducted simultaneously; therefore the results of the two methods could not be compared. As discussed in Section 4.1, not all of the QC requirements of the time-integrated and *in situ* reference methods were satisfied and, consequently, the quality of the reference method data was not confirmed. Therefore, in addition to the linear regression analysis described in the test/QA plan,[1] the reference method data were compared to the Model 101E data in a more qualitative manner. The Model 101E data were compared to the reference method data to determine whether the measured H_2S concentrations were statistically significantly different at the 95% confidence level, and the linear regression analysis was repeated including only those data that were not significantly different.

3.3.5.1 Time-Integrated Comparability

Time-integrated reference measurements were conducted by collecting ambient air samples over relatively long periods (up to eight hours) in evacuated 1.4-liter Silonite canisters (Entech Instruments, Inc.) and were taken to the USDA laboratory for analysis. Ambient air was drawn into the evacuated canisters from the same Teflon manifold to which the Model 101E was connected. The canisters were fitted with a silanized Entech flow controller and pressure gauge to restrict the air flow to approximately one to three standard cubic centimeters per minute (sccm), allowing the canisters to fill slowly over approximately eight hours. A performance evaluation (PE) audit of the canister sampling flow rate revealed that the flow rate varied between 1.01 and 2.52 sccm over 7.5 hours. The variability in the canister sampling flow rate could result in uneven weighting of the time-integrated air sample collected in the canister, potentially resulting in biased results. Samples were collected during the following time periods: April 29 to 30, May 4 to 5, May 11 to 13, and May 18 to 21. Up to three samples were collected over eight-hour intervals on each sampling day according to the following approximate schedule: 10:00 p.m. to 6:00 a.m., 6:00 a.m. to 2:00 p.m, and 2:00 p.m. to 10:00 p.m.

The Silonite canisters were cleaned before sample collection using an Entech 3120a Canister Cleaning System by heating under vacuum at 120°C, filling with humidified nitrogen, and

evacuating to a pressure of 50 millitorr. This process was repeated for 50 cycles. Canisters were then transported to the test site for sampling and returned to the laboratory for analysis. Canisters were sampled using an Entech 7500 Series Robotic Autosampler, which was connected to an Entech 7100A Preconcentrator and an Agilent 6890 GC with an OI Analytical PFPD. Canisters were heated to 100°C during sample transfer, and all transfer lines were maintained at 100°C. Helium carrier gas was used at a flow of 16 sccm. A sample of known volume [10 to 400 standard cubic centimeters (scc)], depending upon the expected concentration, was withdrawn from the canister, trapped on glass beads at -20°C (the bead trap was subsequently desorbed at 10°C), and collected on a Tenax® trap at -80°C to reduce water in the system. The Tenax trap was heated to 180°C and the desorbed components were cryofocused at -150°C before a final heating and transfer to the GC column. The column was a GS-Gaspro, 60 meter (m) × 0.32 mm inner diameter (i.d.) capillary column (J & W Scientific). The column was held at 35°C for 0.5 minutes, ramped to 230°C at 12°C per minute, and held at 230°C for the remainder of the approximately 20-minute run. The test/QA plan[1] stated that samples would be analyzed within 24 hours of collection. It was not always possible to analyze the canisters within the 24-hour time frame; in some cases, samples could not be analyzed until 4 days after collection because of instrument availability. The longer holding times may have resulted in H_2S loss in the canisters, and consequently to artificially low H_2S reference measurement results. Sample degradation in the canister was not verified since a holding time study was not performed on ambient air samples. The test/QA plan[1] stated that the acceptability of the 24-hour holding time would be verified on an ambient air sample. A deviation report was filed to address the holding time issues. A multipoint calibration curve from approximately 150 to 2,300 picograms (pg) for H_2S was constructed daily (before reference analyses were conducted) by injecting several volumes of a diluted H_2S compressed gas standard (5.12 ppm H_2S, Scott Specialty Gases) onto the GC-PFPD. Instrument blanks (i.e., zero-volume injections) were included in each analytical run. Based on the instrument blank results, the quantitation limit (average blank result plus 10 times the standard deviation of the blank) for a 10-scc injection was 2.2 ppb.

3.3.5.2 In Situ *Comparability*

In situ reference measurements were conducted by Applied Measurement Science. The instrumentation for the *in situ* method was installed in the instrument trailer at the test site. Air samples were drawn from a Teflon tube whose inlet was collocated with the Teflon manifold sampling inlet at a flow rate of approximately 5 Lpm to reduce the residence time of ambient air in the inlet. Volatile compounds in the samples were cryotrapped, thermally desorbed, and injected directly onto a Varian 3800 GC with PFPD. The duration of sample collection was adjusted so that the mass of H_2S was maintained, to the extent possible, within the range of the PFPD system, nominally from 30 pg to 3,000 pg per sample. Sample collection times varied between 6 seconds and 8 minutes. The column was a GS-Gaspro 30- m × 0.32-mm i.d. capillary column (J & W Scientific). Helium carrier gas was used at a flow of 2 sccm. The column was held at -10°C for 2 minutes, ramped to 200°C at 40°C per minute, and held at 200°C for the remainder of the approximately 20-minute run. Multilevel calibrations were performed using the same certified H_2S gas standard (5.12 ppm H_2S, Scott Specialty Gases) and programmable dilution system used for performing testing activities. *In situ* reference measurements were conducted as frequently as possible (usually every 16 minutes) over a four-day period at the end of the verification test. Due to technical problems with the reference method air sampling valve system, measurements could not be conducted over the ten days specified in the test/QA plan.[1]

Of the ambient air measurements conducted by the *in situ* reference method, 41 of the 53 reference measurements could be used for comparison to the Model 101E results. The other 12 measurements were presented as upper (result below quantitation limit) or lower (saturated H_2S peak) limits.

3.3.6 Data Completeness

Data completeness was assessed based on the overall data return achieved by the Model 101E.

3.3.7 Operational Factors

Operational factors such as maintenance needs, data output, consumables used, ease of use, and repair requirements were evaluated based on the observations of Battelle and USDA staff.

Chapter 4
Quality Assurance/Quality Control

QA/quality control (QC) procedures were performed in accordance with the quality management plan (QMP) for the AMS Center[3] and the test/QA plan for this verification test[1] with the exception of three deviations, which have been addressed in this report. First, the time-integrated reference method canister flow rate was lower than expected. This deviation did not impact the quality of this verification test. The second deviation from the test/QA plan[1] involved the reference method QC requirements, which were not fully satisfied. Third, the pre-analytical holding time for ten of the 15 time-integrated reference samples was longer than 24 hours. As discussed in Section 4.1 and Section 3.3.5.1, the second and third deviations did impact the comparisons that were performed with the reference method data.

4.1 Reference Method Quality Control Results

Table 4-1 summarizes the reference method QC requirements. Both reference methods were required to analyze continuing calibration verifications (CCV), QC samples (QCS), and field blanks. The time-integrated H_2S reference method was also required to repeat analysis of 10% of the samples to verify method precision.

4.1.1 Time-Integrated Reference Method Quality Control Results

It was determined that the USDA laboratory GC-PFPD system required calibration each day before analysis of reference samples. This eliminated the need for running CCV samples, so there was no expectation for agreement to previous calibration results. QCSs were not run as frequently as stated in Table 4-1, but often were included at the end of the analysis run. Approximately half of the analysis runs had at least one QCS that passed the requirement listed in Table 4-1. The other half either had failed QCSs or none were included in the run. Replicate H_2S precision was not determined for the same injection volume. However, the results for four out of 13 comparisons of variable-volume injections from the same sample were within 30% of one another by percent difference (%D). Measurement accuracy results are discussed in more detail in Section 4.2.1. Briefly, four PE samples were submitted to the USDA laboratory; reference method results for two of the samples were within the acceptance criterion for measurement accuracy. The other two results were 38% and undetectable H_2S levels. Finally, two field blank samples were submitted to the USDA laboratory for analysis, and both resulted in undetectable H_2S levels by the GC-PFPD system. Since the QC requirements for

Table 4-1. 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% of expected value
QCS	QCS run every 4 hours and after analysis of reference samples each day	%D of QCS result within 30% of expected value
Replicate H_2S precision	Analyze 10% of all samples twice[(a)]	%D 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 test 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 was provided as part of the PE audit.
[(c)] *In situ* H_2S reference method only.

the time-integrated reference method were not satisfied, the results were not quantitatively compared to the Model 101E both quantitatively and qualitatively [i.e., to determine whether they were significantly different from each other at the 95% confidence level (see Section 5.8, Comparability)].

4.1.2 In Situ *Reference Method Quality Control Results*

CCV samples were run each day when the *in situ* reference method was conducting ambient measurements. If results were not within 30% of the expected value by %D, a multilevel calibration curve was generated. At least once daily, a QCS or measurement accuracy sample was analyzed. Six QCS samples were analyzed, and all were within 30% of the expected concentration by %D. QCS samples from a second gas standard (110 ppb H_2S, Air Liquide) were analyzed six times. Two results fell outside of the calibration curve, and one was outside of the acceptance criterion; three results met the acceptance criterion. One QCS from a third gas standard (4.78 ppm H_2S, Scott Marrin) was made and was within 30% of the expected value. The measurement precision of four analyses of a 10-ppb H_2S standard was 8.1% RSD, which would relate to a %D value less than 30%. Three out of four measurement accuracy samples delivered as PE audit samples were within the acceptance criterion. Once during the verification test, the *in situ* reference method sampled zero air delivered through the ambient air inlet. The measurement result was 3.1 ppb, which is approximately the same as the method quantitation limit for a 50-cubic-centimeter sample (200 pg/sample). Since the QC requirements for the *in situ* reference method were not all satisfied, the results were compared to the Model 101E data both quantitatively and qualitatively [i.e., to determine whether they were significantly different from each other at the 95% confidence level (see Section 5.8, Comparability)].

4.2 Audits

4.2.1 Performance Evaluation Audits

A PE audit was conducted to assess the quality of the H_2S reference method measurements. In the PE audit, key aspects of the reference measurements were checked by comparing them with an independent National Institute of Standards and Technology- (NIST-) traceable standard. The PE audit of the H_2S reference methods was performed by supplying to each reference method a blind, independent, NIST-traceable H_2S standard provided by Battelle. The output of a certified H_2S permeation tube (VICI Metronics, held at 30°C) was diluted in ultra-high purity (UHP) zero air (approximately 2.7 to 3.9 Lpm) to produce H_2S concentrations between 60 and 90 ppb. The PE samples were analyzed in the same manner as the ambient air samples, and the analytical results for the PE samples were compared to the nominal concentration. The target criterion for the PE audit was agreement of the analytical result within 30% of the nominal H_2S concentration. If the PE audit results did not meet the tolerances required, they were repeated. PE audits of the reference methods were required to be performed once prior to the start of the test and two times during the test, at a minimum. A total of four PE audit samples each were submitted to the USDA laboratory and to the *in situ* reference method for analysis. The USDA time-integrated reference method results for the first and last PE audit samples met the acceptance criterion, while the other two did not. The *in situ* reference method result met the acceptance criterion for the first, third, and fourth PE audit sample.

A PE audit of the ambient air sample flow rate for the time-integrated reference method was performed by comparing it to an independent flow measurement device. The target criterion for this PE audit was in agreement within the expected range (i.e., 2 to 3 sccm). The PE audit of the canister air sampling rate revealed that the actual flow rates for the Entech Flow Controller used for this verification test ranged from 1.01 to 2.52 sccm over 7.5 hours. The flow controller was not adjusted to increase the flow rates since this would have the undesirable effect of shortening the time-integrated sample duration. This deviation from the test/QA plan[(1)] was filed. This deviation did not impact the quality of this verification test since the actual flow rate is not used in the reference method analysis. However, variability in the canister sampling flow rate over the 7.5-hour collection time would impact the comparability of the air collected in the canister and that sampled by the Model 101E.

A PE audit of the programmable dilution system was performed by comparing its output to an independent flow measurement device. One mid-range flow rate was 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 was agreement within 5% of the flow readings; all measured flows agreed within 5%. These audits were performed once during the verification test.

4.2.2 Technical Systems Audits

The Battelle Quality Manager performed a technical systems audit (TSA)on April 28 and 29, 2005, to ensure that the verification test was being performed in accordance with the AMS Center QMP,[(3)] the test/QA plan,[(1)] ASTM method D5504-01,[(2)] and any standard operating procedures (SOPs) used by USDA or Applied Measurement Science. In the TSA, the Battelle Quality Manager toured the test site and the USDA Laboratory, observed the H_2S reference

method sampling and sample recovery, inspected documentation of H_2S sample chain of custody, and reviewed Model 101E-specific record books.

The Battelle Quality Manager also reviewed the reference methods used, compared actual test procedures to those specified by the test/QA plan,[1] and reviewed data acquisition and handling procedures.

Observations and findings from this audit were documented and submitted to the Battelle Verification Test Coordinator for response. No findings were documented that required any corrective action. The records concerning the TSA are stored for at least seven years with the Battelle Quality Manager.

4.2.3 Audit of Data Quality

At least 10% of the data acquired during the verification test were audited. Battelle's Quality Manager or his designee traced the data from the initial acquisition, through reduction and statistical analysis, to final reporting, to ensure the integrity of the reported results. All calculations performed on the data undergoing the audit were checked.

4.3 Quality Assurance/Quality Control Reporting

Each assessment and audit was documented in accordance with Sections 3.3.4 and 3.3.5 of the QMP for the ETV AMS Center.[3] Once the assessment report was prepared, the Battelle Verification Test Coordinator ensured that a response was provided for each adverse finding or potential problem and implemented any necessary follow-up corrective action. The Battelle Quality Manager ensured that follow-up corrective action was taken. The results of the TSA were sent to the EPA.

4.4 Data Review

Records generated in the verification test were reviewed before these records were used to calculate, evaluate, or report verification results. Table 4-2 summarizes the types of data recorded. The review was performed by a technical staff member involved in the verification test, but not the staff member who originally generated the record. The person performing the review added his/her initials and the date to a hard copy of the record being reviewed.

Table 4-2. 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, Model 101E maintenance, down time, etc.	ETV laboratory record books or data recording forms	Start/end of test procedure, and at each change of a test parameter or change of Model 101E 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
Model 101E calibration information	ETV laboratory record books or electronically	At Model 101E calibration or recalibration	Electronic data by vendor; Battelle if on-site; USDA if Battelle not on-site	Incorporated in verification report as necessary
Model 101E H_2S readings	Recorded electronically by each Model 101E and then downloaded to computer at least weekly	Recorded continuously	Model 101E 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 and QA data, etc.	Laboratory record books and electronically by analytical method	Throughout sampling and analysis processes	USDA and Applied Measurement Science	Retained as documentation of reference method performance
Reference method H_2S analysis results	Electronically from H_2S analytical method	Every sample analysis	Applied Measurement Science	Entered into or converted to spreadsheets for calculation of ambient H_2S results and statistical analysis and comparisons
	Hard-copy printouts and data sheets	Every sample analysis	USDA	

Chapter 5
Statistical Methods and Reported Parameters

The statistical methods presented in this chapter were used to verify the performance parameters listed in Section 3.1. The average measured Model 101E response values (Y) used in the calculations presented in this section were calculated from the last 5 data points (five minutes) of each testing condition (e.g., H_2S gas standard or other gas challenge).

5.1 Accuracy

Accuracy of the H_2S Model 101E with respect to the individual H_2S gas standards was 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 Model 101E response (as defined in Section 3.3.) and X is the nominal H_2S gas standard concentration. The average, minimum, and maximum %R values are reported for each series of multilevel H_2S challenges. A %R value of 100% indicates perfect agreement between the averaged measured Model 101E response and the nominal H_2S gas standard concentration.

5.2 Bias

Bias of the Model 101E was defined as a systematic error in measurement that resulted in measured error that was consistently positive or negative compared to the true value. The bias was calculated as the average %D of the Model 101E compared to the nominal H_2S gas standard concentration and was calculated for each series of multipoint H_2S challenges, using Equation 2:

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

where *k* is the number of valid comparisons, and Y and X are the same as in Equation 1.

5.3 Precision

The precision of the Model 101E was evaluated from the triplicate responses to each H_2S gas standard supplied during the multipoint H_2S challenges (outlined in Table 3-2). The precision was defined as the percent relative standard deviation (%RSD) of the averaged triplicate measurements and calculated for each H_2S concentration listed in Table 3-2, using Equations 3 and 4:

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

$$\%RSD_i = \frac{SD_i}{\overline{Y}_i} \times 100 \tag{4}$$

where Y is the average Model 101E response calculated from the last 5 data points (5 minutes) of each gas standard delivery period, $\overline{Y}_i$ is the overall average of the Y values at H_2S concentration *i* (*i* = 30, 90, 150, and 300 ppb), and *n* is the number of measurements (3). The overall average %RSD was calculated for each series of multipoint H_2S challenges and included the %RSD for all H_2S concentrations tested.

5.4 Linearity

Linearity was assessed by a linear regression analysis using the diluted H_2S standard gas concentrations as the independent variable and results from the Model 101E being tested as the dependent variable. Linearity was expressed in terms of slope, intercept, and coefficient of determination (r^2).

5.5 Span and Zero Drift

The baseline response of the Model 101E to zero air and the 30-ppb H_2S standard was established during the first week of testing. The overall average $(\overline{Y})$ and standard deviation (SD) of the Model 101E response to zero air and the 30-ppb H_2S standard were calculated from the average Model 101E responses from each of the five replicate measurements conducted during the first week of testing. From these values, a control chart was constructed, and the $\overline{Y} \pm 2SD$ "warning limit" and the $\overline{Y} \pm 3SD$ "action limit" were calculated. Span drift was defined as having occurred if three consecutive span checks fell either above or below the warning limit. Zero drift was defined as having occurred if three consecutive zero checks fell either above or below the warning limit.

5.6 Response Time

Response time was assessed in terms of both the rise and fall times of the Model 101E when sampling the 30-ppb H_2S gas standard and zero air on the first day of testing. Rise time (i.e., 0%

to 95% response time for the change in H_2S concentration) was determined from the Model 101E response to a rapid increase in the delivered H_2S concentration. Once a stable response was achieved with the H_2S standard, the fall time (i.e., the 100% to 5% response time) was determined in a similar way, switching from the H_2S standard back to zero air.

5.7 Interference Effects

The interference effects of the Model 101E were calculated in terms of the ratio of the response of the Model 101E to the interferant relative to the actual concentration of the interfering species. For example, if 100 ppb of an interfering species resulted in a 1-ppb change in the response of the Model 101E, the interference effect was reported as 1% (i.e., 1 ppb/100 ppb). Interference effects are reported separately for each interferant both in the absence and in the presence of H_2S in zero air.

5.8 Comparability

The comparability of the Model 101E results and the time-integrated and *in situ* reference methods with respect to ambient air was assessed by linear regression using the reference method H_2S concentrations as the independent variable and the results from the Model 101E as the dependent variable. The Model 101E H_2S measurements were averaged over the appropriate sample collection period for each reference method (i.e., approximately 7.5 hours or 15 minutes). Comparability was calculated separately for the time-integrated and *in situ* reference methods and was expressed in terms of slope, intercept, and r^2.

The linear regression analysis was repeated for each reference method, including only the reference method results that were not significantly different from the Model 101E average results at the 95% confidence level. The 95% confidence interval (CI) was calculated for each Model 101E average, using Equation 5:

$$95\%\text{CI} = \overline{\text{Y}} \pm \frac{t \times \text{SD}}{\sqrt{n}} \qquad (5)$$

where $\overline{\text{Y}}$ is the average Model 101E response over the sample collection period, SD is the standard deviation of the Model 101E data over the sample collection period, *n* is the number of Model 101E readings used in the average, and *t* is the t-value of the Student's t-distribution for 95% confidence level and the degrees of freedom (*n*-1). The calculated 95% CI for each Model 101E average was compared to the corresponding reference measurement value to determine whether the results were statistically significantly different at the 95% confidence level. For comparison to the time-integrated reference method, the Model 101E readings used for each average (approximately 7.5 hours) were plotted as a histogram to determine whether they were normally distributed. Most of the samples (13 out of 14) were best represented by a log-normal distribution. For those samples, the natural logarithms (ln) of the Model 101E and reference measurements were used to calculate the 95% CI and to determine whether the results were significantly different at the 95% confidence level. This approach was also applied to the *in situ* H_2S reference method, using the Model 101E averages over 15-minute intervals, centered on the

in situ reference measurement times. The Model 101E readings used to compare to the *in situ* reference method were assumed to be normally distributed.

5.9 Data Completeness

Data completeness was calculated as the percentage of the total possible data return achieved over the entire field period. This calculation used the total hours of data recorded from each Model 101E, divided by the total hours of data in the entire field period. The field period was defined as beginning at 8:00 a.m. on April 25, 2005 and ending at 9:00 a.m. on June 3, 2005. No distinction was 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.

Chapter 6
Test Results

The results of the verification test of the Model 101E are presented in this section. The Model 101E logged one-minute averages of the instantaneous H_2S readings. The Model 101E zero value was set using UHP zero air and the span value was adjusted to a 400-ppb dilution from a certified compressed gas cylinder standard (100 ppm H_2S, Scott Specialty Gases) that was independent of the gas standard used for performing this verification test (5.12 ppm H_2S, Scott Specialty Gases). Although both standards were certified by the manufacturer to have accuracy better than ±5%, differences between the actual H_2S concentration in the two cylinders may exist. Any differences between the two gas standards would be manifested in the accuracy and bias performance parameters evaluated during this test; other performance parameters such as linearity, precision, and interference effects would not be impacted by differences in the two gas standards because of the nature of these calculations. Gas standard dilutions for calibration and testing activities were prepared using the same dynamic dilution system. All Model 101E measurement data were analyzed and included in this report as output by the Model 101E. Any negative H_2S concentration values should be considered to indicate measurements of H_2S concentrations less than those in the zero air used to set the zero value and/or drift in the Model 101E response. The Model 101E was calibrated twice prior to the start of the verification test (once after it was installed and again after the UV lamp was replaced, as described in Section 6.10); no additional calibrations were performed over the duration of this verification test.

Meteorological conditions collected by a nearby (less than 2 miles) meteorological station are presented in Figure 6-1. The ambient data set collected by the Model 101E is shown in the bottom panel, along with the wind direction, wind speed, and ambient temperature data. The average ambient H_2S concentration measured by the Model 101E during the verification test was 14.8 ppb, with a range of −2.2 to 843.9 ppb. The meteorological conditions, which were recorded as 1-hour averages, varied widely over the duration of the verification test. The average ambient temperature was 14.3°C, with a range of −4.9 to 29.0°C. The average Model 101E ambient H_2S concentrations are shown in Figure 6-2 plotted on polar coordinates as a function of wind direction. When winds were from the south, the Model 101E was exposed to emissions from the nutrient lagoons. As shown in Figure 6-2, the highest H_2S concentrations were observed during southwesterly winds, which passed across the primary nutrient lagoon before reaching the instrument trailer. During northerly winds, the Model 101E sampled barn emissions and measured much lower H_2S concentrations. Winds were most frequently from the northwest and southeast, as shown by the diamonds in Figure 6-2. Under southerly winds, spikes in the measured H_2S concentration were often observed at the start of rain, as shown in Figure 6-1.

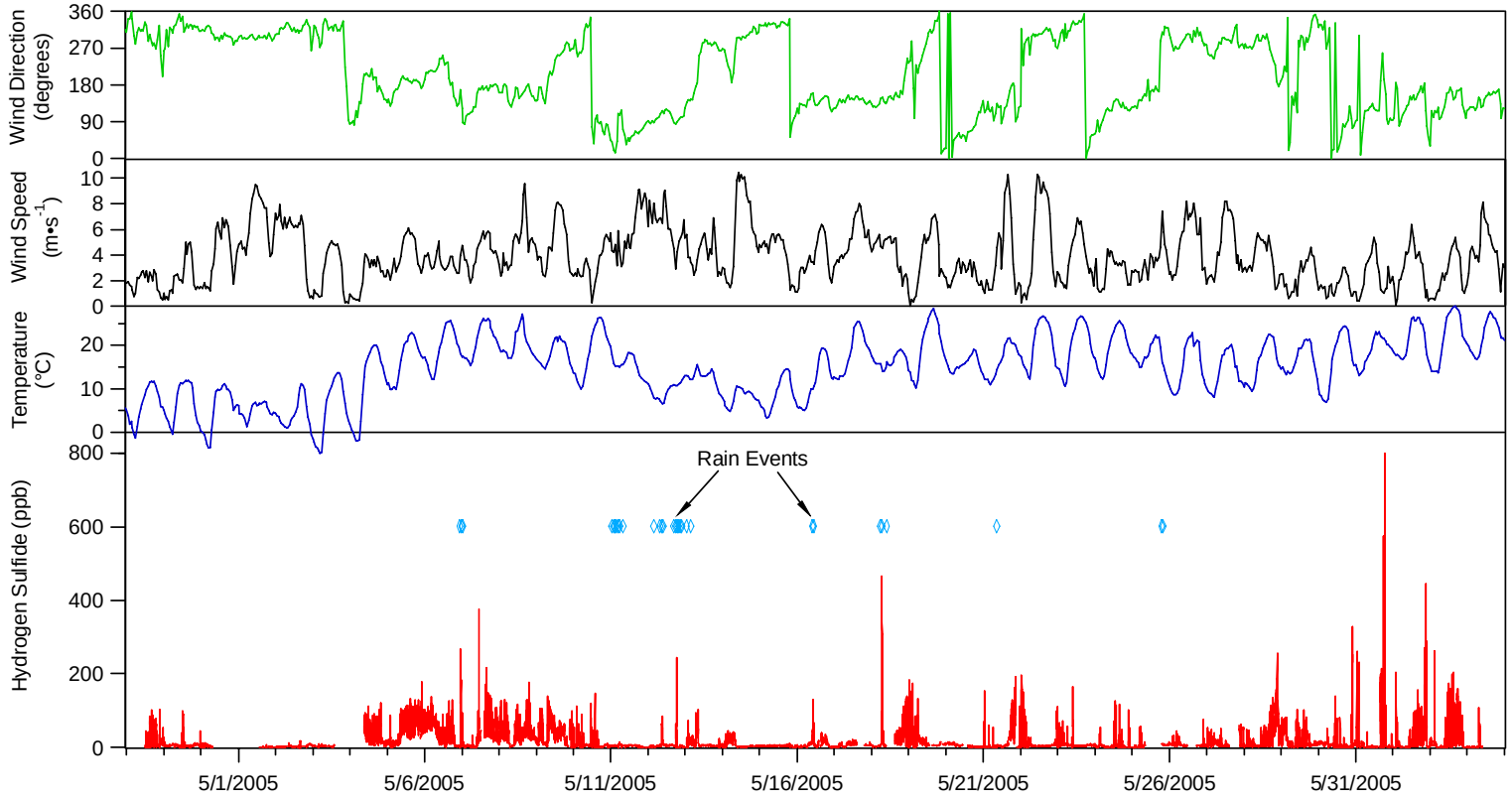

Figure 6-1. Meteorological Conditions and Model 101E Ambient H_2S Measurements

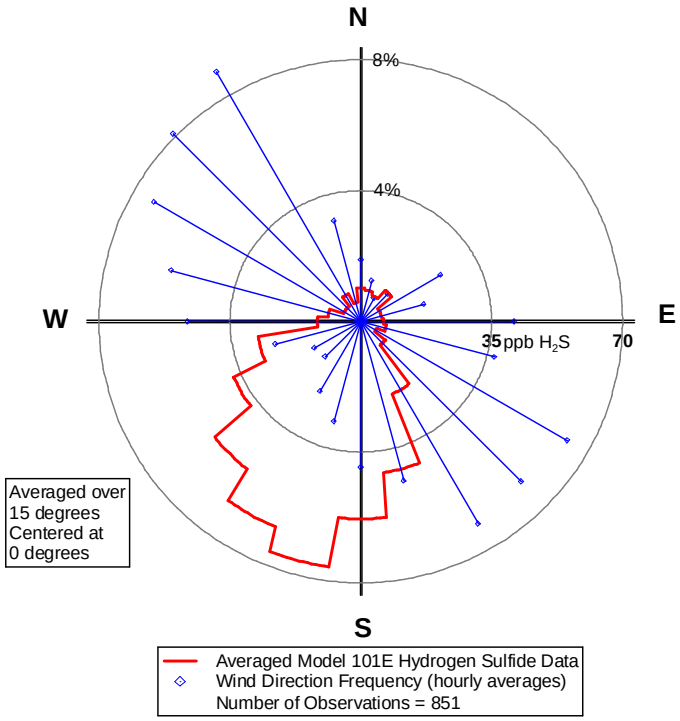

Figure 6-2. Hourly Averaged Model 101E H_2S Measurements Plotted as a Function of Wind Direction

6.1 Accuracy

Accuracy checks were conducted during Week 1, Week 4, and Week 5 of the verification test. The Model 101E was challenged with compressed H_2S gas standards diluted in zero air at several concentrations (30 ppb to 300 ppb H_2S). The H_2S gas standards were diluted in zero air and delivered to the Teflon manifold at a flow rate of 3 to 4 Lpm, with a vent to ambient pressure. Accuracy checks were conducted during Week 1, Week 4, and Week 5 of the verification test.

Figure 6-3 presents the H_2S concentrations recorded by the Model 101E during each accuracy check gas challenge, along with the nominal H_2S concentration levels supplied to the Model 101E for Week 1, Week 4, and Week 5. The averages of the last five minutes (5 data points) of the measurements at each nominal H_2S concentration and the calculated %R are presented in Table 6-1, along with the average %R for each week. The SD for each average measured concentration is also reported in Table 6-1 for reference purposes. As shown in Table 6-1, the Model 101E %R values ranged from 114% to 132%, with an average of 129% for the Week 1 check. The Model 101E %R values for the Week 4 check ranged from 111% to 127% with an average of 124%. For the Week 5 check, the Model 101E %R values ranged from 113% to 122%, with an average of 120%. Except for measurements of zero air, all of the Model 101E concentrations reported for Week 1 were higher than for Week 4, which were higher than Week 5.

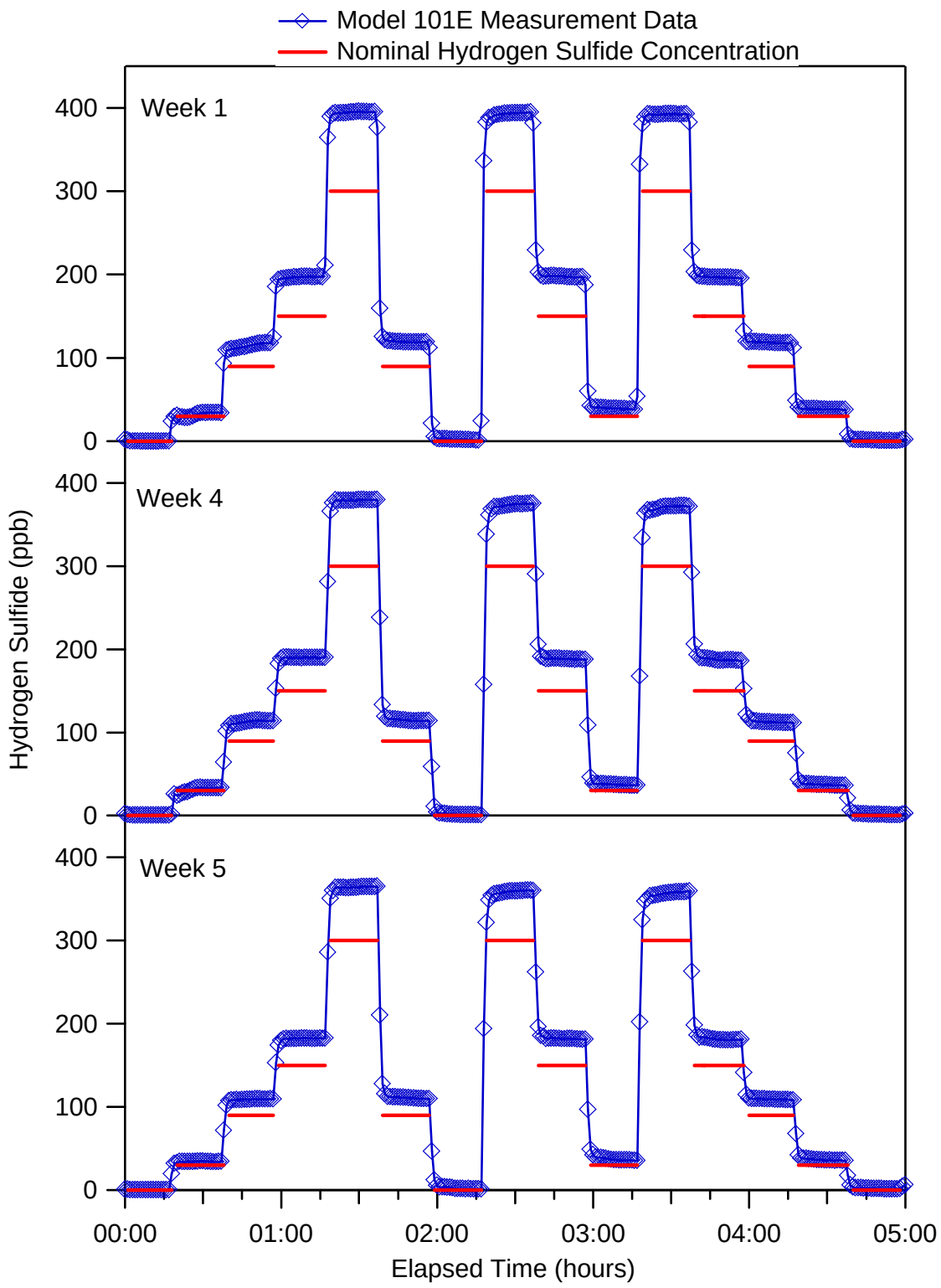

Figure 6-3. Model 101E Accuracy Results

Table 6-1. Accuracy Results

Measurement Number	H_2S Gas Standard Concentration (ppb)	Week 1 Average[a] Model 101E Response (ppb)	Week 1 SD (ppb)	Week 1 %R	Week 4 Average[a] Model 101E Response (ppb)	Week 4 SD (ppb)	Week 4 %R	Week 5 Average[a] Model 101E Response (ppb)	Week 5 SD (ppb)	Week 5 %R
1	0	-0.0	0.1	NA	0.5	0.1	NA	0.3	0.1	NA
2	30	34.3	0.1	114	33.3	0.1	111	33.9	0.2	113
3	90	117.7	0.2	131	113.9	0.2	127	109.2	0.1	121
4	150	197.3	0.1	132	190	0.1	127	182.2	0.2	122
5	300	395	0.1	132	379.7	0.1	127	364.7	0.1	122
6	90	119	0.1	132	113.9	0.1	127	109.7	0.2	122
7	0	1.4	0.3	NA	0.9	0.1	NA	1.2	0.1	NA
8	300	394.2	0.3	131	375.2	0.3	125	360.1	0.2	120
9	150	196.9	0.3	131	187.8	0.1	125	181.2	0.3	121
10	30	38.5	0.3	129	36.4	0.2	121	35.6	0.3	119
11	300	392.4	0.2	131	372.3	0.4	124	358.7	0.5	120
12	150	196	0.5	131	186.6	0.4	124	180.6	0.3	120
13	90	117.8	0.1	131	111.8	0.1	124	108.3	0.2	120
14	30	38	0.1	127	36.2	0.1	121	35.5	0.1	118
15	0	0.6	0.0	NA	0.9	0.1	NA	1.2	0.1	NA
Average				129			124			120
Minimum				114			111			113
Maximum				132			127			122
Bias ($\overline{\%D}$)				+29			+24			+20

[a] Average Model 101E response calculated from the last 5 minutes of data collected during each gas standard delivery (n=5).
NA = not applicable.

6.2 Bias

Bias in the Model 101E response to H_2S gas standards was assessed for each of the accuracy checks presented in Section 6.1 and calculated separately for each sequence of multilevel H_2S challenges. The Model 101E bias observed during the Week 1, Week 4, and Week 5 accuracy checks were +29%, +24%, and +20%, respectively. The consistently high bias is indicative of systematic error, which would also affect the Model 101E accuracy, and could be caused by a number of factors, including, but not limited to, differences in H_2S gas standards used for calibration and testing activities, the gas standard dilution system, and Model 101E instrumental errors. The slow decrease in bias (from +29% to +20%) over the duration of the verification test is indicative of drift in the Model 101E sensitivity. The Model 101E bias values are presented in Table 6-1.

6.3 Precision

Table 6-2 presents the calculated precision of the Model 101E determined from the average Model 101E responses to the triplicate challenges at each H_2S concentration level during the Week 1, Week 4, and Week 5 accuracy checks. The precision of the Model 101E reading varied from 0.3% to 6.3% during the Week 1 accuracy check, from 0.9% to 4.8% during the Week 4 accuracy check, and from 0.4% to 2.7% during the Week 5 check. The highest %RSD values for each accuracy check were observed for the lowest concentration standard (30 ppb). The average precision calculated from each check was 1.9%, 2.0%, and 1.2% for Weeks 1, 4, and 5, respectively.

Table 6-2. Calculated Precision of the Model 101E

	Week 1		Week 4		Week 5	
H_2S Gas Standard Concentration (ppb)	**Overall Average Model 101E Response (ppb)**	**%RSD**	**Overall Average Model 101E Response (ppb)**	**%RSD**	**Overall Average Model 101E Response (ppb)**	**%RSD**
30	36.9	6.3	35.3	4.8	35	2.7
90	118.2	0.6	113.9	1.1	109.1	0.6
150	196.7	0.3	188.1	0.9	181.3	0.4
300	393.8	0.3	375.8	1.0	361.2	0.9
Average %RSD		1.9		2		1.2

6.4 Linearity

Figure 6-4 shows the linearity results for the Week 1, Week 4, and Week 5 accuracy checks. For each check, a linear regression was calculated from the results presented in Table 6-1 (average Model 101E response versus the nominal H_2S gas standard concentration) over the range of 0 to 300 ppb. The 95% CI for the slope and intercept of the regression line were also calculated (shown in the following text within parenthesis). For Week 1, the slope of the regression line was 1.32 (± 0.02), with an intercept of -0.64 (± 2.6) and r^2 value of 0.9999. During Week 4, the linear regression showed a slope of 1.25 (± 0.02), an intercept -0.37 (± 3.5), and an r^2 of 0.9998. The linear regression analysis of the Week 5 data resulted in a slope of 1.20 (± 0.01), an intercept 0.24 (± 2.6), and an r^2 of 0.9999. Over the range of concentrations tested (0 to 300 ppb H_2S), the Model 101E demonstrated a high degree of linearity.

6.5 Span and Zero Drift

The baseline response of the Model 101E to zero air and a 30-ppb H_2S dilution was determined during the first week of the verification test and repeated during Week 4. The average responses of the Model 101E during each replicate delivery of zero air and 30 ppb H_2S are shown in Table 6-3. Each average utilized the last five data points for each zero air or H_2S standard delivery. The warning ($\overline{Y} \pm 2SD$) and action ($\overline{Y} \pm 3SD$) limits were calculated for zero air and 30 ppb H_2S and also are shown in the table.

Span and zero drift checks were performed at least twice each week during the verification test, for a total of 14 drift checks, including the replicate challenges shown in Table 6-3 for Week 4. The gas standard dilution system was not flushed with the H_2S gas standard before performing eight of the span checks prior to May 27, 2005. Results from these span checks are included in this report, but were not used to evaluate drift. The results of the span and zero drift checks are shown in Table 6-4. Each average utilized the last five data points for each zero air or H_2S standard delivery. A control chart was prepared from the data shown in Tables 6-3 and 6-4 to demonstrate graphically whether drift occurred over the duration of the verification test. The control chart is shown in Figure 6-6. The Model 101E also was equipped with a zero air scrubber and H_2S permeation tube, which allowed the Model 101E to perform automated internal span and zero checks. The Model 101E was configured to perform span and zero checks on a daily basis at 21:00, running zero air and the internal H_2S permeation source for 20 minutes each. The last automated zero/span check was performed at the beginning of the fifth week of testing so that testing activities would not be interrupted by the automated checks. The average results of these automated span and zero checks are included in Figure 6-6.

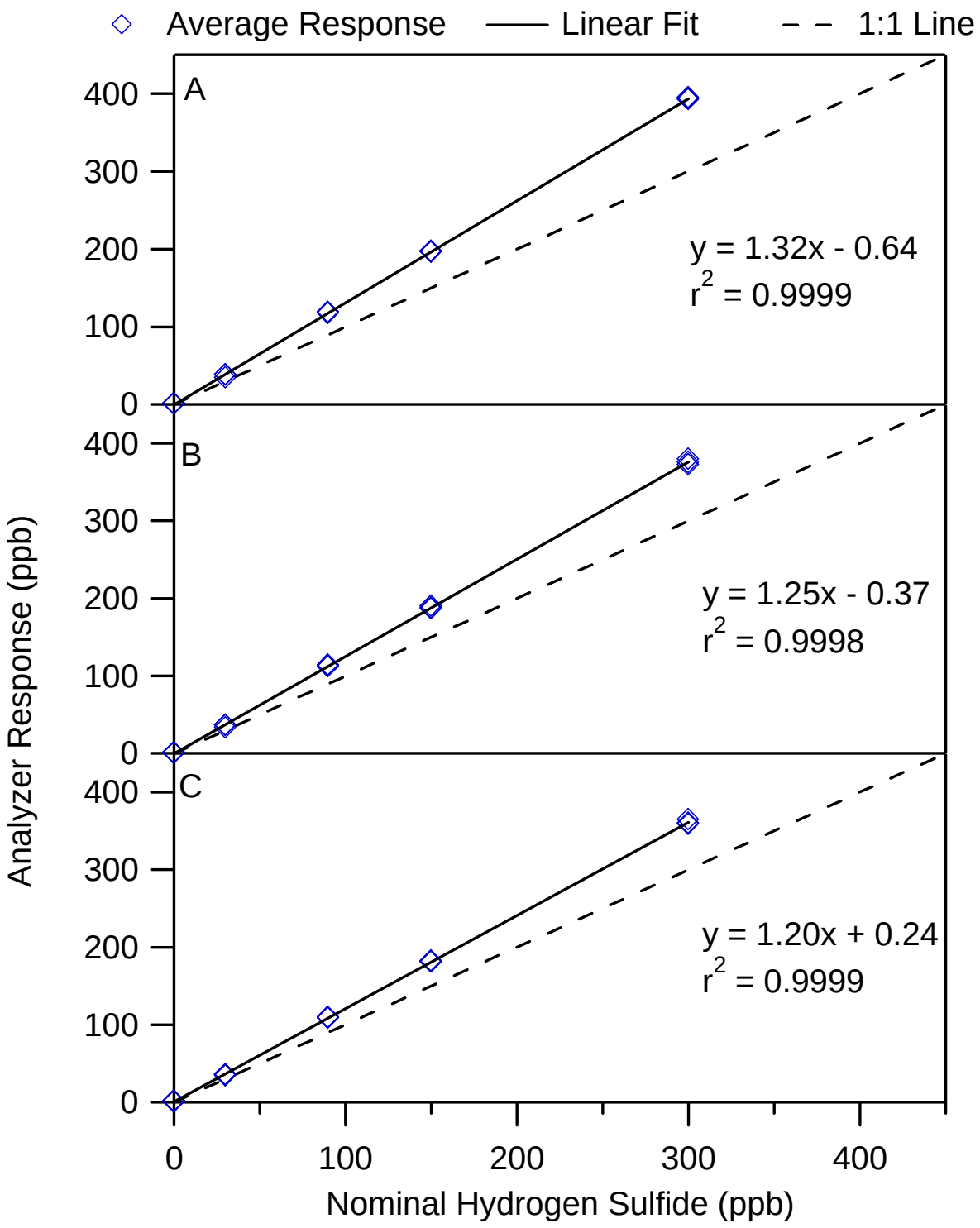

Figure 6-4. Model 101E Linearity Results

Table 6-3. Span and Zero Baseline Response

	Zero Response[a]				30-ppb Span Response[a]			
Drift Check Date	**Average (ppb)**	**SD (ppb)**	**Min-imum (ppb)**	**Max-imum (ppb)**	**Average (ppb)**	**SD (ppb)**	**Min-imum (ppb)**	**Max-imum (ppb)**
Week 1 Wednesday	-0.1	0.1	-0.1	0.0	35.2	0.4	34.6	35.4
Week 1 Wednesday	0	0.1	-0.1	0.1	34.9	0.3	34.4	35.1
Week 1 Wednesday	-0.1	0.1	-0.1	0.0	35.7	0.1	35.6	35.8
Week 1 Wednesday	-0.1	0	-0.1	-0.1	35.7	0.1	35.5	35.8
Week 1 Wednesday	0	0.1	-0.1	0.1	35.6	0.1	35.4	35.6
Baseline Response		**-0.05**				**35.4**		
Overall SD		**0.03**				**0.3**		
Warning Limit		**-0.1 – 0.0**				**34.7 – 36.1**		
Action Limit		**-0.2 – 0.0**				**34.4 – 36.4**		
Week 4 Tuesday	0.3	0.0	0.2	0.4	35.5	0.1	35.3	35.6
Week 4 Tuesday	0.3	0.0	0.3	0.4	35	0.1	34.9	35.1
Week 4 Tuesday	0.3	0.1	0.3	0.4	34.8	0.1	34.6	34.9
Week 4 Tuesday	0.3	0.1	0.2	0.3	34.5	0.1	34.4	34.6
Week 4 Tuesday	0.2	0.0	0.2	0.3	34.4	0.4	33.6	34.7
Baseline Response		**0.29**				**34.8**		
Overall SD		**0.05**				**0.4**		
Warning Limit[b]		**0.2 – 0.4**				**34.0 – 35.7**		
Action Limit[b]		**0.1 – 0.4**				**33.5 – 36.1**		

[a] Statistics calculated from the last 5 data points (5 minutes) for each zero air or H_2S standard challenge (n=5).

[b] The warning and action limits for the Week 4 zero and 30-ppb H_2S challenges are shown for reference purposes, but were not used for determining zero or span drift.

Table 6-4. Span and Zero Drift Check Results

	Zero Check						30 ppb Span Check					
Check Number	**Average (ppb)**	**SD (ppb)**	**Mini-mum (ppb)**	**Maxi-mum (ppb)**	**Within Warning Limit?**	**Within Action Limit?**	**Average (ppb)**	**SD (ppb)**	**Mini-mum (ppb)**	**Maxi-mum (ppb)**	**Within Warning Limit?**	**Within Action Limit?**
Week 1 Friday	0.0	0.1	-0.1	0.0	Yes	Yes	28[a]	0.3	27.7	28.3	[a]	[a]
Week 2 Monday	-0.3	0.1	-0.4	-0.2	No	No	14.7[a]	0.4	14.1	15.1	[a]	[a]
Week 2 Friday	-0.2	0.2	-0.4	0.2	No	No	12.2[a]	0.2	12	12.4	[a]	[a]
Week 2 Saturday	-4.8	0.0	-4.8	-4.7	No	No	25.7[a]	0.1	25.6	25.8	[a]	[a]
Week 3 Monday	0.7	0.0	0.7	0.8	No	No	23.5[a]	0.1	23.5	23.6	[a]	[a]
Week 3 Friday	0.4	0.1	0.3	0.4	No	No	21[a]	0.6	20.4	21.9	[a]	[a]
Week 4 Monday	0.6	0.1	0.5	0.8	No	No	36.3	0.1	36.2	36.3	No	Yes
Week 4[b] Tuesday	0.4	0.1	0.2	0.3	No	No	34.8	0. 4	34.4	35.5	Yes	Yes
Week 4 Thursday	0.7	0.0	0.6	0.7	No	No	31.5[a]	0.3	31.3	31.9	[a]	[a]
Week 4 Friday	1.0	0.0	1.0	1.1	No	No	34.8	0.1	34.7	34.9	Yes	Yes
Week 5 Monday	0.3	0.1	0.2	0.4	No	No	24.7[a]	0.7	24	25.7	[a]	[a]
Week 5 Friday	0.3	0.0	0.3	0.3	No	No	34.5	0.1	34.4	34.6	No	Yes
Week 6 Sunday	0.5	0.1	0.4	0.6	No	No	35.5	0.1	35.3	35.6	Yes	Yes
Week 6 Tuesday	0.0	0.0	0.0	0.1	No	Yes	34.3	0.1	34.1	34.4	No	No
Week 6 Thursday	0.3	0.1	0.2	0.4	No	No	34.2	0.2	34.1	34.4	No	No

[a] Gas standard dilution system was not flushed before this span check was performed.
[b] Data presented were for the average of five replicate challenges of zero air and 30 ppb H_2S.

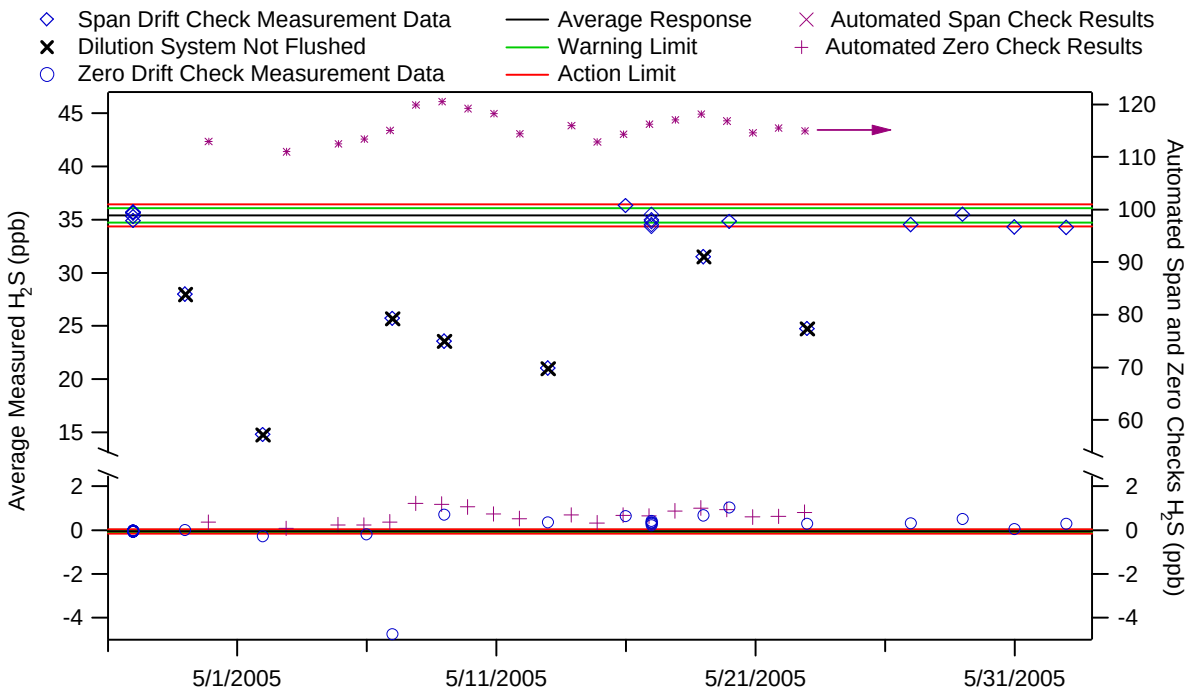

Figure 6-5. Span and Zero Drift Control Chart

Based on the data presented in Table 6-3 and Figure 6-5, drift in the Model 101E zero did occur during the verification test; zero drift is defined as three consecutive drift check results that fell outside of the warning limit of -0.1 ppb to +0.0 ppb established during the first week of the verification test. With the exception of one very low value (-4.8 ppb for Week 2, Saturday), the Model 101E response to zero increased during the verification test, but appeared to level off at Week 3. The results of the automated zero check appear to follow the same trend as the manual zero drift checks performed as a part of this verification test. The final zero span check result was 0.4 ppb greater than the average baseline zero response.

The warning limit established for the Model 101E response to the 30-ppb H_2S span gas was 34.7 to 36.1 ppb. Drift in the Model 101E response to the 30-ppb H_2S span gas did not occur during the verification test. The final span drift check result was 1.2 ppb less than the average baseline span response.

6.6 Response Time

Response time was determined during Week 1 and Week 4 from the amount of time required for the Model 101E to reach 95% of the change in response during the zero air and 30-ppb H_2S span gas replicate deliveries shown in Figure 6-6. Table 6-5 presents a summary of the response time determinations for the Model 101E. The response time (both rise and fall, averaged for Week 1 and Week 4) was 3 minutes.

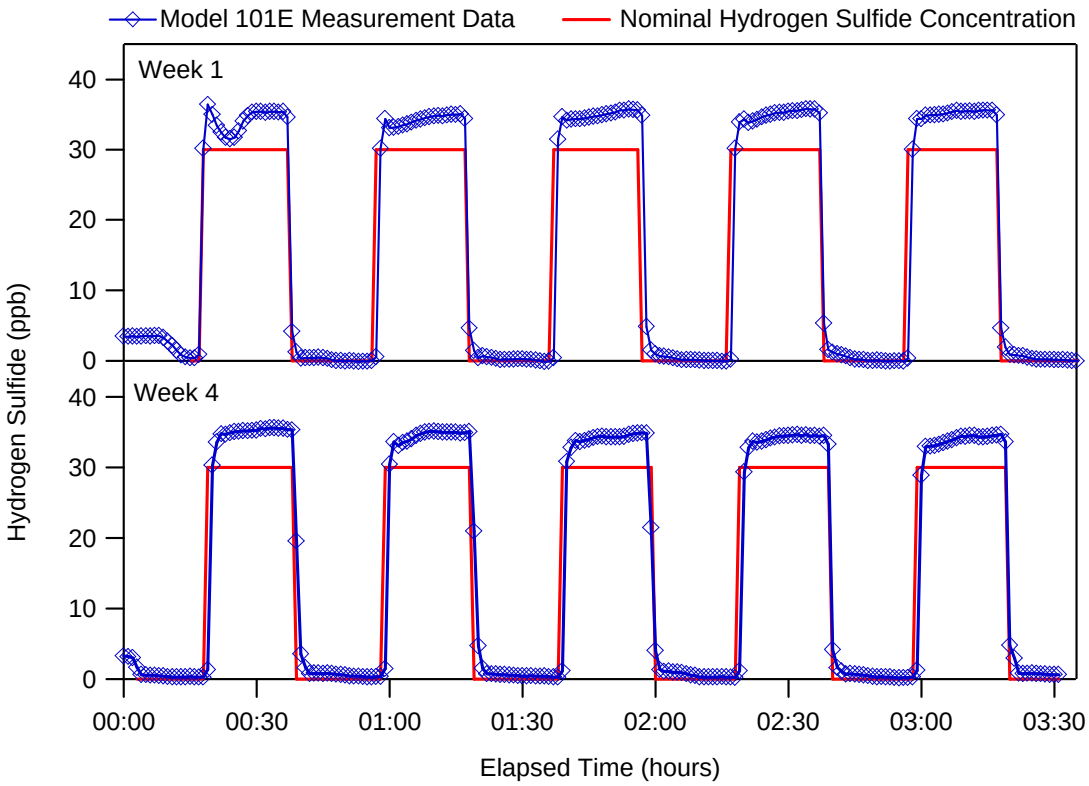

Figure 6-6. Model 101E Response Time Results

6.7 Interference Effects

The effect of potential interferant gases on the response of the Model 101E was assessed by supplying the Model 101E with a series of seven gases (listed in Table 6-6) in zero air and a 100-ppb H_2S standard. The response of the Model 101E during the introduction of these gases is summarized in Table 6-6.

Table 6-5. Response Time Determinations

Replicate	Week 1		Week 4	
	0 ppb to 30 ppb 95% Rise Time (minutes)	30 ppb to 0 ppb Fall Time (minutes)	0 ppb to 30 ppb 95% Rise Time (minutes)	30 ppb to 0 ppb 95% Fall Time (minutes)
1	[a]	2	4	[a]
2	3	2	3	3
3	3	3	4	3
4	3	3	4	3
5	3	4	4	3
Average	3	3	4	3

[a] The Week 1 sequence of zero/30-ppb H_2S replicate challenges began with a 30-ppb H_2S standard; the Week 4 sequence began with zero air.

Table 6-6. Interference Effect Evaluation

Interferant	Approximate Interferant Concentration (ppb)	Interference Effect (%)	
		Zero Air Matrix	100-ppb H_2S Matrix
Sulfur dioxide	100	0	0
Carbonyl sulfide	100	20	6
Carbon disulfide	100	6	9
Methyl mercaptan	100	33	33
Dimethyl sulfide	100	12	12
Hydrocarbon blend	500 (total)	0	0
Ammonia	500	0	0

No interference effect was observed in the Model 101E response to SO_2, a blend of C1 to C6 alkanes, and ammonia. The Model 101E showed an interference effect for carbonyl sulfide in zero air of 20% and in 100-ppb H_2S of 6%. Carbon disulfide resulted in an interference effect of 6% in zero air and 9% in the 100-ppb H_2S matrix. The interference effect of methyl mercaptan on the Model 101E was 33% in both zero air and 100-ppb H_2S. Dimethyl sulfide resulted in a 12% interference effect in both matrices.

6.8 Comparability

As stated previously, the Model 101E was calibrated with an H_2S compressed gas cylinder that was independent of the standard used in the verification testing. The instrumentation for both reference methods was calibrated using the same gas standard used in the verification testing of the Model 101E. To reduce the potential impact on the comparability results due to differences in calibration gases, the Model 101E data were corrected using the results of the linearity checks (Section 6.4) closest in time to the reference sample collection date. Thus, both reference method and Model 101E calibrations were referenced to the same H_2S gas standard for the comparability evaluations, and any differences observed between the Model 101E and reference method data can be attributed to the analytical approach rather than the calibration source.

It should be noted that the reference method quality control requirements were not fully satisfied, and, therefore, the accuracy of the reference method results could not be verified. In addition, the swine finishing farm ambient air, which can contain high levels of ammonia and other small, polar molecules, was very challenging analytically and may have caused measurement artifacts resulting from contact of H_2S and other gases with non-passivated surfaces in the air sampling system. The comparability results presented here should be considered cautiously in light of the reference method quality control results and the challenges associated with the complex ambient air matrix.

6.8.1 Time-Integrated Comparability

The results of 8 time-integrated reference method measurements were compared to the time-averaged Model 101E responses over the same periods (approximately 7.5 to 8 hours, n=407 to 498 data points) to determine the time-integrated comparability. One of these measurements was a grab sample, collected by allowing the canister to fill rapidly without a flow controller on the inlet (n=3). Six time-integrated reference method measurements were below the quantitation limit (2.2 ppb). An additional time-integrated measurement was performed, but the Model 101E data were not being logged to the Model 101E internal memory during that sample period. The maximum preanalytical holding time stated in the test/QA plan[(1)] was 24 hours; however, holding times exceeded 24 hours for 12 of the 15 time-integrated reference measurements. The long holding times may have resulted in degradation of H_2S in the canisters. The reference method measurements were compared to the Model 101E data by linear regression analysis and by determining whether the measurements were significantly different at the 95% confidence level.

Figure 6-7 shows the time-integrated reference H_2S measurements (red and green traces), the Model 101E raw H_2S data (blue trace), and the Model 101E averages for the reference measurement sample periods (black trace). As is evident in the figure by green traces for the reference measurements, the results for 5 of the 8 (63%) quantitative time-integrated reference measurements were not statistically significantly different from the Model 101E averages. (The grab sample is not shown and was not within the 95% CI of the Model 101E value.) The Model 101E and time-integrated reference method data are presented in Appendix B.

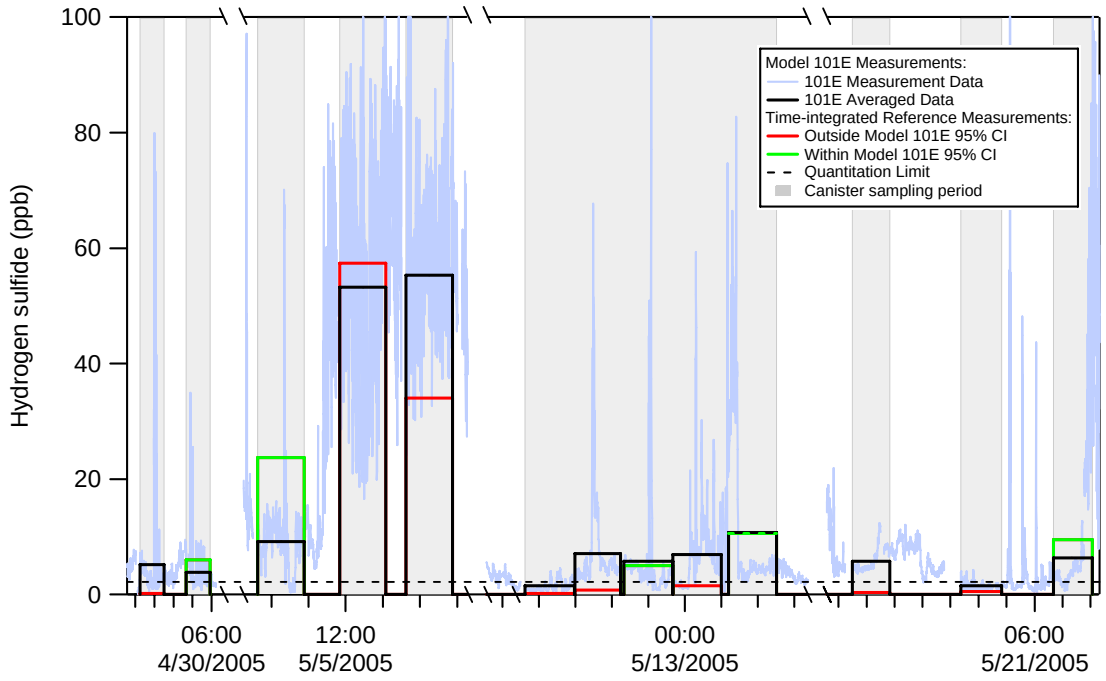

Figure 6-7. Comparison of Time-Integrated Reference Measurements with Averages from the Model 101E

A linear regression analysis of the Model 101E averages during the reference sampling periods versus the H_2S concentration determined by the time-integrated reference method was calculated. The data are presented as a scatter plot in Figure 6-8 to illustrate the correlation between the reference results and the Model 101E data. The scatter plot includes reference method results that were within (green diamonds) and outside (red diamonds) the Model 101E 95% CI. The slope of the regression line including all available quantitative results was 1.03 (±1.10), with an intercept of -1.7 (± 31) and an r^2 value of 0.7807. When only the five results that were not significantly different at the 95% confidence level were included in the linear regression analysis, the slope was 0.22 (± 1.1), with an intercept of 4.7 (± 14) and an r^2 value of 0.3673.

6.8.2 In Situ *Comparability*

The results of 41 *in situ* reference method results were compared to 15-minute averages (*n*=15) calculated from the Model 101E data that were centered in time on the *in situ* reference measurement times. The 95% CI was calculated for each Model 101E average and compared to the *in situ* reference measurement to determine if the results were significantly different at the 95% confidence level. Figure 6-9 shows selected *in situ* reference measurements (red and green diamonds), the Model 101E H_2S data, and the Model 101E 15-minute averages. Any upper and lower limits reported for the *in situ* reference method are also shown in Figure 6-9. As demonstrated by the green diamonds in Figure 6-9, 37% (15 of 41) of the quantitative *in situ* reference values were not significantly different from the corresponding Model 101E 15-minute averages. The Model 101E and *in situ* reference method data are presented in Appendix C.

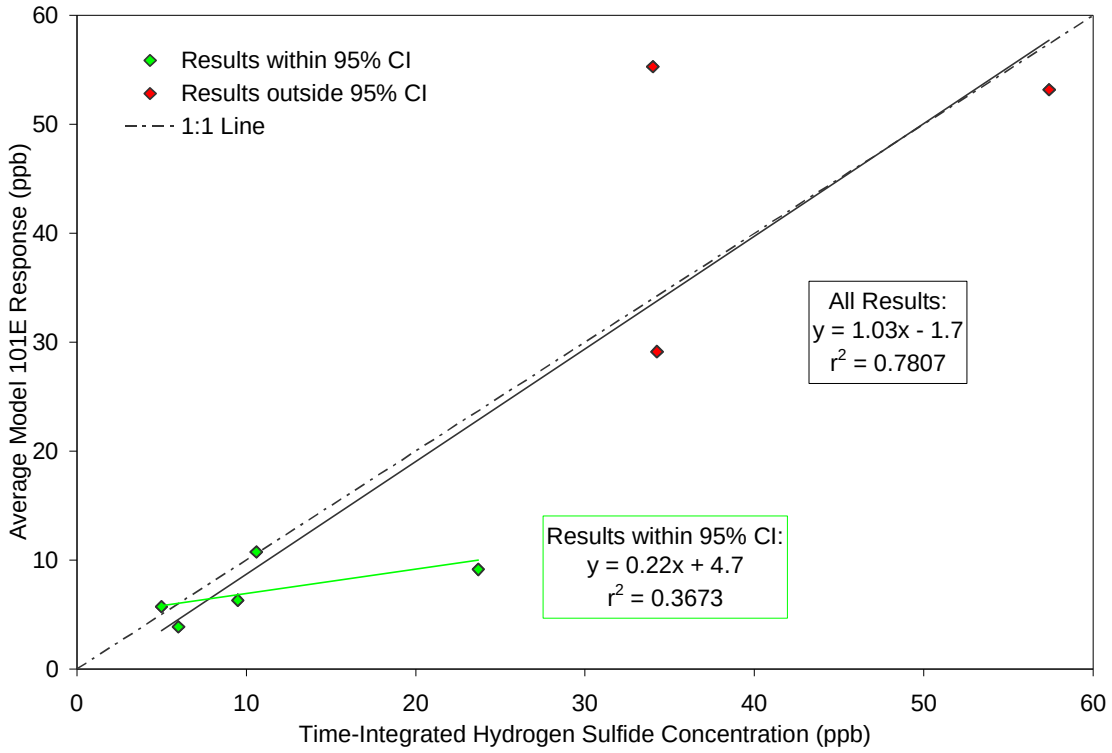

Figure 6-8. Scatter Plot of Model 101E Results versus Time-integrated Reference Measurements

A linear regression analysis of the Model 101E averages during the reference sampling periods versus the H_2S concentration determined by the *in situ* reference method is presented in Figure 6-10 as a scatter plot to illustrate the correlation between the reference results and the Model 101E data. The scatter plot includes reference method results that were within (green diamonds) and outside (red diamonds) the Model 101E 95% CI. The slope of the regression line including all available quantitative results was 0.16 (± 0.6), with an intercept of 26 (± 22) and an r^2 value of 0.0313. When only the 15 results that were not significantly different at the 95% confidence level were included in the linear regression analysis, the slope was 1.06 (± 0.26), with an intercept of 2.2 (± 8.5) and an r^2 value of 0.9606.

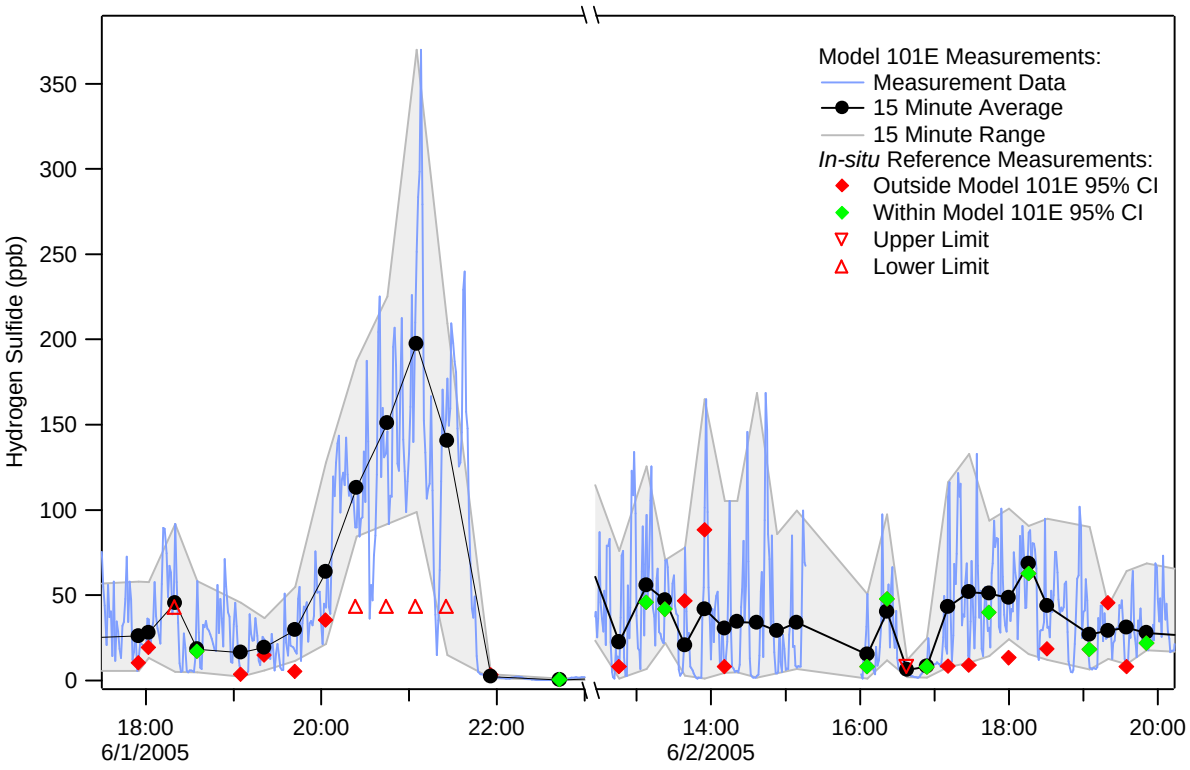

Figure 6-9. Comparison of Selected *In Situ* Reference Measurements with Model 101E Averages and Measurement Data

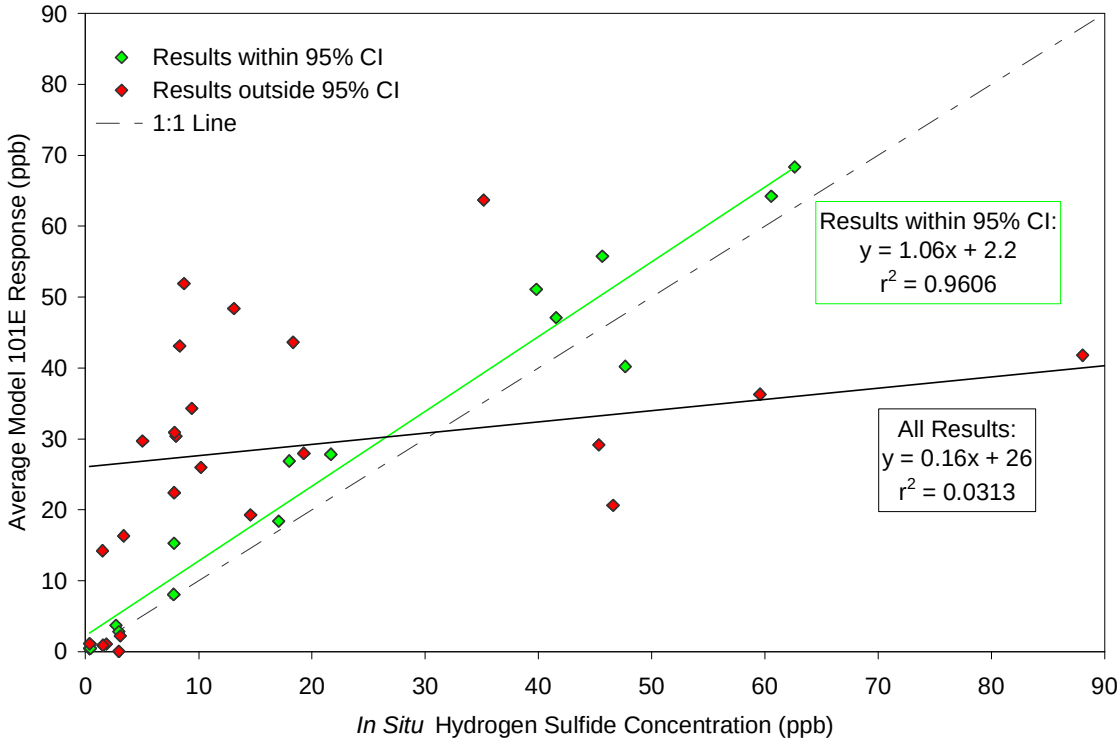

Figure 6-10. Scatter Plot of Model 101E Results versus *In Situ* Reference Measurements

6.9 Data Completeness

The Model 101E operated for 100% of the available time during the verification test; 88% of the available data were retrieved from the Model 101E, as discussed further in Section 6.10. The data loss is attributed to a glitch in the data download software or the on-board data acquisition parameters.

6.10 Operational Factors

The Model 101E was installed at the test site by the vendor representative, and installation was completed in less than one day. One calibration was performed on the Model 101E by USDA and Battelle staff prior to the start of the verification test and repeated after installation of a new UV lamp; no other calibrations were performed. The Model 101E could have been installed and operated by a user with minimal experience and access to the Model 101E manual, which was quite thorough. A checklist was provided by the vendor representatives to establish whether the Model 101E was in proper working order during the test. The checklist, shown in Appendix A, was completed by Battelle or USDA staff during daily checks of the Model 101E operating status. The inlet filter was changed once during the verification test; the filter change was completed in less than 15 minutes. The only other maintenance performed by Battelle or USDA was replacement of the UV lamp, which failed before the beginning of the verification test. A brief telephone call to Teledyne-API's customer service support center diagnosed the problem quickly and a new lamp was received at the USDA laboratory the following day. Changing the lamp was simple and straightforward and took less than 30 minutes. The Model 101E was recalibrated approximately one day after the lamp installation.

The Model 101E data were collected on a laptop computer provided by the USDA. The Teledyne-API proprietary software, APIcom was provided by the vendor representatives for use in downloading, viewing, saving, and graphing the Model 101E data. An ethernet router (provided by the vendor representatives) was used to connect the data output port to the laptop computer via an ethernet connection. Individual records could be downloaded individually (i.e., only H_2S concentration data) or as combined files with additional parameters, such as detector values, Model 101E box temperature, etc. The Model 101E on-board memory stored approximately 7 days of data. Files containing 7 days of data for nine parameters were approximately 1 megabyte in size.

Some difficulties were encountered with the data download process. On three occasions, more than 19 hours of data were lost. It was eventually discovered that the Model 101E stopped logging data after certain data download commands were employed (for download options "since last download" and "download all records"). The data logging could be restarted by scrolling through and resetting the data acquisition parameters from the Model 101E panel; curiously, none of the data acquisition parameters appeared to have changed as a result of this process. Teledyne-API customer support was contacted regarding the issue, but no problems were found in the Model 101E programs. Once the cause of the problem was determined, test operators were careful to confirm that the Model 101E was still logging data by downloading a few records to the laptop computer or by viewing the logged data from the Model 101E panel display after each data download. The APIcom software and router occasionally lost communication with the Model 101E, but this was relatively easily remedied by restarting the

software or restarting the Model 101E and the laptop computer (to reset the Model 101E IP address).

Chapter 7
Performance Summary

The performance of the Model 101E was evaluated for its accuracy, bias, precision, linearity, span and zero drift, response time, interference effects, and comparability by evaluating the Model 101E response while sampling H_2S and other gas standards at known concentrations and ambient air. The Model 101E was calibrated prior to this verification test with a 400-ppb dilution from an H_2S gas standard (100 ppm H_2S) that was independent of the gas standard (5.12 ppm H_2S) used for performing the verification test. All gas standard dilutions were prepared using the same dynamic dilution system. The results of this evaluation are described below.

The accuracy of the Model 101E was assessed over the range of 30 ppb to 300 ppb in terms of %R, which ranged from 114% to 132%, with an average of 129% for the Week 1 check. The Model 101E %R values for the Week 4 check ranged from 111% to 127%, with an average of 124%. For the Week 5 check, the Model 101E %R values ranged from 113% to 122%, with an average of 120%.

The Model 101E bias observed during the Weeks 1, 4, and Week 5 accuracy checks (30 ppb to 300 ppb) was +29%, +24%, and +20%, respectively. The consistently high bias is indicative of systematic error, which would also affect the Model 101E accuracy, and could be caused by a number of factors, including, but not limited to, differences in H_2S gas standards used for calibration and testing activities, the gas standard dilution system, and Model 101E instrumental errors.

The precision of the Model 101E reading varied from 0.3% to 6.3% during the Week 1 accuracy check, from 0.9% to 4.8% during the Week 4 accuracy check, and from 0.4% to 2.7% during the Week 5 check. The average precision calculated from each check was 1.9%, 2.0%, and 1.2% for Weeks 1, 4, and 5, respectively.

Linearity was evaluated in terms of slope, intercept, and r^2 over the range from 0 ppb to 300 ppb H_2S. For Week 1, the slope of the regression line was 1.32 (± 0.02), with an intercept of -0.64 (± 2.6) and r^2 value of 0.9999. During Week 4, the linear regression showed a slope of 1.25 (± 0.02), an intercept -0.37 (± 3.5), and an r^2 of 0.9998. The linear regression analysis of the Week 5 data resulted in a slope of 1.20 (± 0.01), an intercept 0.24 (± 2.6), and an r^2 of 0.9999.

Drift (defined as three consecutive drift check results that fell outside of the (±2 standard deviation) warning limit calculated for zero (-0.10 ppb to +0.0 ppb) and a 30-ppb span gas (34.7 to 36.1 ppb). Eleven consecutive zero drift check results fell above the warning limit, indicating that drift occurred. The final zero drift check value was 0.4 ppb greater than the baseline

response. Although four out of seven drift check results fell outside the warning limit, drift did not occur in the Model 101E response to the 30-ppb H_2S span gas. The final span drift check value was 1.2 ppb lower than the baseline response.

The average 95% response time was 3 minutes for both the rise time and fall time.

No interference effect was observed in the Model 101E response to SO_2, a blend of C1 to C6 alkanes, and ammonia. The Model 101E showed an interference effect for carbonyl sulfide in zero air of 20% and in 100-ppb H_2S of 6%. Carbon disulfide resulted in an interference effect of 6% in zero air and 9% in the 100-ppb H_2S matrix. The interference effect for methyl mercaptan was 33% in both zero air and 100-ppb H_2S. Dimethyl sulfide resulted in a 12% interference effect in both matrices.

Comparability was evaluated in terms of the slope, intercept, and r^2 of a linear regression analysis of the Model 101E averages versus the reference measurements and was calculated separately for the time-integrated and *in situ* reference methods. It should be noted that the reference method quality control requirements, such as for preanalytical holding time and analysis of quality control and performance evaluation standards, were not fully satisfied. Therefore, the accuracy of the reference method results could not be verified. In addition, the swine finishing farm ambient air, which can contain high levels of ammonia and other small, polar molecules, was very challenging analytically and may have caused measurement artifacts resulting from contact of H_2S and other gases with non-passivated surfaces in the air sampling system. The comparability results presented here should be considered cautiously in light of the reference method quality control results and the challenges associated with the complex ambient air matrix. For the eight quantitative time-integrated reference measurements, the slope of the regression line was 1.03 (± 1.10), with an intercept of -1.7 (± 31) and an r^2 value of 0.7807. Five of the 8 (63%) time-integrated reference measurements were not significantly different from the corresponding Model 101E averages at the 95% confidence level. When only these five values were included in the linear regression analysis, the slope was 0.22 (± 1.1), with an intercept of 4.7 (± 14) and an r^2 value of 0.3673. The regression line slope for 41 quantitative *in situ* reference measurements was 0.16 (± 0.6), with an intercept of 26 (± 22) and an r^2 value of 0.0313. Fifteen of the 41 quantitative *in situ* reference values (37%) were not significantly different from the corresponding Model 101E 15-minute averages. The regression analysis of those 15 data points yielded a slope of 1.06 (± 0.26), an intercept of 2.2 (± 8.5), and an r^2 value of 0.9606.

A user with minimal experience and the instruction manual could install and operate the Model 101E. Daily checks of the Model 101E were simple and quick. Some difficulty was encountered in maintaining the ethernet connection between the laptop computer used for downloading data (using Teledyne-API's APICOM software), but it generally took less than 10 minutes to restore the connection. The Model 101E data logging was terminated when data were downloaded using certain commands, such as “download all records.” This resulted in loss of potential data. Teledyne-API customer support was contacted about this issue, but no cause could be determined. However, once the problem was identified, Battelle and USDA staff verified that data logging was occurring after each data download and were able to restore data logging if it had been terminated. Customer service telephone support was readily available and very helpful whenever contacted by Battelle or USDA staff. The only maintenance required during the

verification test was one inlet filter change. A new UV lamp was installed prior to the start of the verification test; the installation was completed in less than 30 minutes.

The Model 101E operated 100% of the time, and 88% of the data were retrieved. The loss of 22% of the potential data was caused by the termination of data logging discussed above.

Chapter 8
References

1. *Test/QA Plan for Verification of Ambient Hydrogen Sulfide Analyzers at a Swine Finishing Farm*, Battelle, Columbus, Ohio, April 2005.

2. 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.

3. *Quality Management Plan (QMP) for the ETV Advanced Monitoring Systems Center,* Version 5.0, U.S. EPA Environmental Technology Verification Program, Battelle, Columbus, Ohio, March 2004.

Appendix A
Model 101E Checklist

Teledyne-API Model 101E

ETV Verification of Ambient Hydrogen Sulfide Analyzers
at a Swine Feeding Farm

Observe Analyzer Front Panel

- ☐ Verify that power is on
- ☐ Check for alarms — Alarm = _____
- ☐ Visually inspect filter
  - ☐ Clean
  - ☐ Dirty (replace if dirty) ☐ Replaced
- ☐ Download Data — Download Time = _____
- ☐ Send data to Battelle (daily M-F) — Most recent Date _____
- ☐ Send data to Teledyne-API (at least weekly) — Most recent Date _____

Action: If any of issues above 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.

Appendix B
Model 101E and Time-Integrated Comparability Data

Time-Integrated Reference Method							Model 101E						Reference Result Within 95% CI?
Start Date and Time	Stop Date and Time	Result (ppb)	Distribution	ln Result	Holding time (hr)	Final QCS	Average Result (ppb)	SD (ppb)	ln Average	ln SD	*n*	95% CI	
4/29/05 7:30	4/26/05 15:0	<2.2	log-normal	NA	13	[a]	5.15	9.62	1.20	0.72	451	1.14 - 2.34	NA
4/29/05 22:00	4/30/05 5:30	6.0	log-normal	1.79	39	[a]	3.88	2.91	1.20	0.54	451	1.15 - 2.34	Yes
4/30/05 7:25	4/30/05 14:55	<2.2	log-normal	NA	28	[a]	[b]	[b]	[b]	[b]	[b]	[b]	NA
5/4/05 21:45	5/5/05 5:15	23.7	log-normal	3.17	43	Pass	9.14	7.51	1.95	0.81	451	1.88 - 3.83	Yes
5/5/05 11:00	5/5/05 18:30	57.4	normal	NA	33	Pass	53.19	16.55	[c]	[c]	451	51.67 - 54.72 ppb	No
5/5/05 21:45	5/6/05 5:15	34.0	log-normal	3.53	23	Pass	55.29	13.91	3.98	0.24	451	3.96 - 7.94	No
5/11/05 21:45	5/12/05 5:52	<2.2	log-normal	NA	97	Fail	1.47	0.97	0.20	0.29	488	0.15 - 0.35	NA
5/12/05 5:55	5/12/05 13:25	<2.2	log-normal	NA	88	Fail	7.10	7.78	1.69	0.62	447	1.63 - 3.32	NA
5/12/05 14:00	5/12/05 22:00	5.0	log-normal	1.61	75	Fail	5.73	14.27	1.27	0.77	498	1.20 - 2.47	Yes
5/12/05 22:00	5/13/05 6:00	<2.2	log-normal	NA	68	Fail	6.91	7.25	1.53	0.92	480	1.45 - 2.98	NA
5/13/05 7:10	5/13/05 15:05	10.6	log-normal	2.36	50	Fail	10.74	13.86	1.86	0.88	470	1.78 - 3.64	Yes
5/18/05 15:11	5/18/05 15:14	34.3	normal	NA	5	Pass	29.14	0.10	[c]	[c]	3	28.90 - 29.38 ppb	No
5/19/05 15:00	5/19/05 22:30	<2.2	log-normal	NA	46	[a]	5.73	2.03	1.70	0.30	408	1.67 - 3.36	NA
5/20/05 14:13	5/20/05 21:43	<2.2	log-normal	NA	25	[a]	1.50	0.69	0.32	0.42	407	0.27 - 0.59	NA
5/21/05 10:05	5/21/05 17:35	9.5	log-normal	2.25	44	Fail	6.33	7.31	1.45	0.82	447	1.37 - 2.82	Yes

ln = natural logarithm

[a] No final QCS data provided.

[b] Model 101E data not logged by internal memory during this sample.

[c] Model 101E data were normally distributed, so the natural logarithm was not calculated.

Appendix C
Model 101E and *In Situ* Comparability Data

In situ Reference Method			Model 101E (ppb)				Reference Result Within 95% CI?
Sample Midpoint	Result (ppb)	Final QCS	Result at Sample Midpoint	Average Result	SD	95% CI	
5/30/05 14:04	1.51		42.18	14.24	21.24	1.97 - 26.50	No
5/30/05 14:20	<1.48		1.93	2.57	0.86	2.10 - 3.04	NA
5/30/05 14:36	<1.48		4.68	2.80	1.64	1.89 - 3.70	NA
5/30/05 15:26	2.69		4.14	3.71	2.05	2.57 - 4.85	Yes
5/30/05 15:49	<1.78	Pass	4.53	2.76	1.32	2.03 - 3.50	NA
5/30/05 19:08	<1.48		0.60	0.57	0.22	0.45 - 0.70	NA
5/30/05 19:24	<1.48		1.80	1.39	1.06	0.80 1.97	NA
5/30/05 21:42	12.79		196.72	155.68	86.62	107.71 - 203.66	No
5/30/05 21:56	168.62		1.19	2.60	3.48	0.67 - 4.52	No
5/30/05 22:12	2.95		4.35	2.82	1.25	2.13 - 3.51	Yes
5/31/05 11:20	0.38		0.69	0.42	0.22	0.30 0.54	Yes
5/31/05 11:48	0.37	(a)	1.14	1.12	0.37	0.91 - 1.32	No
5/31/05 22:17	2.96		-0.04	0.04	0.07	0.01 - 0.08	No
6/1/05 17:55	10.21		13.28	25.99	14.15	18.15 - 33.82	No
6/1/05 18:02	19.28		35.79	27.97	11.38	21.66 - 34.27	No
6/1/05 18:20	>42.49		91.90	45.45	28.69	29.56 - 61.34	NA
6/1/05 18:35	17.05		58.21	18.40	16.33	9.35 - 27.44	Yes
6/1/05 19:05	3.37		2.20	16.33	14.73	8.17 - 24.49	No
6/1/05 19:21	14.59		23.84	19.28	8.14	14.77 - 23.79	No
6/1/05 19:42	5.04		17.25	29.71	14.68	21.58 - 37.84	No
6/1/05 20:03	35.18	(a)	42.82	63.70	32.15	45.90 - 81.51	No
6/1/05 20:24	>42.85		89.75	113.04	26.30	98.47 - 127.61	NA
6/1/05 20:45	>42.85		146.08	150.83	42.35	127.38 - 174.29	NA
6/1/05 21:05	>42.85		251.48	197.34	83.40	151.15 - 243.53	NA
6/1/05 21:26	>42.85		177.01	140.52	58.50	108.12 - 172.92	NA
6/1/05 21:56	3.09		2.04	2.24	0.70	1.85 - 2.63	No
6/1/05 22:43	0.44		0.36	0.45	0.24	0.31 - 0.58	Yes
6/1/05 23:16	1.85		1.74	1.06	0.54	0.73 - 1.37	No
6/2/05 11:53	59.55		51.85	36.29	24.27	22.85 - 49.73	No
6/2/05 12:08	9.40		4.88	34.30	31.13	17.06 - 51.54	No
6/2/05 12:25	60.56		69.88	64.24	30.20	47.51 - 80.96	Yes
6/2/05 12:46	7.83		1.13	22.42	25.92	8.06 - 36.78	No
6/2/05 13:08	45.65		97.29	55.77	36.33	35.65 - 75.89	Yes
6/2/05 13:23	41.57		70.48	47.08	18.59	36.79 - 57.38	Yes
6/2/05 13:39	46.60	Pass	77.87	20.63	21.12	8.94 - 32.33	No
6/2/05 13:55	88.07		101.18	41.79	47.62	15.42 - 68.17	No
6/2/05 14:11	7.99		4.48	30.36	28.47	14.59 - 46.13	No
6/2/05 16:06	7.83		50.79	15.28	13.62	7.74 - 22.82	Yes
6/2/05 16:22	47.66		40.22	40.21	21.91	28.08 - 52.35	Yes
6/2/05 16:38	<7.69		7.50	6.15	3.59	4.16 - 8.14	NA
6/2/05 16:54	7.80		8.70	8.08	5.55	5.00 - 11.15	Yes
6/2/05 17:11	8.32		107.99	43.11	35.44	23.48 - 62.74	No

In situ Reference Method			Model 101E (ppb)				Reference Result Within 95% CI?
Sample Midpoint	Result (ppb)	Final QCS	Result at Sample Midpoint	Average Result	SD	95% CI	
6/2/05 17:28	8.70		10.39	51.90	34.87	32.59 - 71.21	No
6/2/05 17:44	39.82		31.04	51.08	26.39	36.47 - 65.70	Yes
6/2/05 18:00	13.12		49.37	48.38	20.66	36.94 - 59.82	No
6/2/05 18:16	62.63		86.63	68.35	20.83	56.81 - 79.89	Yes
6/2/05 18:31	18.32	Pass	30.98	43.62	22.55	31.13 - 56.11	No
6/2/05 19:05	18.01		7.61	26.89	25.11	12.98 - 40.80	Yes
6/2/05 19:20	45.34		27.28	29.17	8.36	24.54 - 33.80	No
6/2/05 19:35	7.87		9.98	30.88	16.99	21.47 - 40.29	No
6/2/05 19:51	21.67		18.13	27.83	13.28	20.48 - 35.19	Yes
6/3/05 4:33	1.56	[a]	0.81	0.88	0.22	0.74 - 1.00	No

[a] QCS not analyzed at end of sampling on this date because the liquid nitrogen supply ran out.