THE ENVIRONMENTAL TECHNOLOGY VERIFICATION PROGRAM

U.S. Environmental Protection Agency

ETV Joint Verification Statement

TECHNOLOGY TYPE:	**AMBIENT HYDROGEN SULFIDE ANALYZER**
APPLICATION:	**MEASURING HYDROGEN SULFIDE CONCENTRATIONS AT A SWINE FINISHING FARM**
TECHNOLOGY NAME:	**MODEL 101E**
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The U.S. Environmental Protection Agency (EPA) supports the Environmental Technology Verification (ETV) Program to facilitate the deployment of innovative or improved 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. Information and ETV documents are available at www.epa.gov/etv.

ETV works in partnership with recognized standards and testing organizations, with stakeholder groups (consisting of buyers, vendor organizations, and permitters), and with 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 Advanced Monitoring Systems (AMS) Center, one of six verification centers under ETV, is operated by Battelle in cooperation with EPA's National Exposure Research Laboratory. In collaboration with the U.S. Department of Agriculture (USDA) and Applied Measurement Science, the AMS Center evaluated the performance of hydrogen sulfide (H_2S) monitors to measure ambient H_2S concentrations. This verification statement provides a summary of the test results for the Teledyne-API Model 101E ambient H_2S analyzer.

VERIFICATION TEST DESCRIPTION

The objective of this verification test was to evaluate the Model 101E's performance in measuring gaseous H_2S in ambient air at an animal feeding operation (AFO). The verification test was conducted for six weeks between April 25 and June 3, 2005, at a swine finishing farm near Ames, Iowa. This site was selected to provide realistic testing conditions and was expected to exhibit a wide range of H_2S concentrations during the test period. The verification test was designed to evaluate accuracy, bias, precision, linearity, span and zero drift, response time, interference effects, comparability, data completeness, and operational factors.

The Model 101E response to a series of H_2S gas standards was used to evaluate accuracy, bias, precision, and linearity. The Model 101E was calibrated prior to this verification test with a 400-part-per-billion (ppb) dilution from an H_2S gas standard [100 parts per million (ppm) H_2S] that was independent of the gas standard (5.12 ppm H_2S) used for performing this verification test. All gas standard dilutions were prepared using the same dynamic dilution system. Each gas standard was delivered in triplicate, and the series of gas standards was delivered three times during the verification test. Dilution 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. Precision was demonstrated by the reproducibility of the Model 101E response at each nominal H_2S concentration. Linearity was assessed by establishing a multipoint calibration curve from the Model 101E responses. 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. At least twice each week, zero air and a 30-ppb H_2S standard again were supplied to the Model 101E for 20 minutes for a total of 14 zero/span checks. (Results from eight span checks could not be used to evaluate drift because the gas standard dilution system was not flushed before performing the span checks.) Each response was compared to the Week 1 baseline response to determine whether drift occurred in the response to zero air or the 30-ppb H_2S standard. The data collected during the two zero/span baseline response checks were used to determine the Model 101E response time. To determine interference effects, the Model 101E was challenged with a series of gases (supplied at either 100 or 500 ppb in the presence and absence of 100 ppb of H_2S) that may be present at an AFO and could interfere with the Model 101E response to H_2S. 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 Method D5504-01, with pulsed flame photometric detection substituted for sulfur chemiluminescence detection. 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. Data completeness was assessed based on the overall data return achieved by the Model 101E.

QA oversight of verification testing was provided by Battelle and EPA. Battelle QA staff conducted a technical systems audit, a performance evaluation audit, and a data quality audit of 10% of the test data. This verification statement, the full report on which it is based, and the test/QA plan for this verification test are all available at www.epa.gov/etv/centers/center1.html.

TECHNOLOGY DESCRIPTION

The following description of the Model 101E was provided by the vendor and does not represent verified information.

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 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 concentration values; calibration data; and operating parameters such as flow rate, pressure, and lamp intensity. Stored data are easily 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. During this test, one-minute averaged data were downloaded via the Ethernet port.

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.

VERIFICATION OF PERFORMANCE

Accuracy: The accuracy of the Model 101 E was assessed over the range of 30 ppb to 300 ppb in terms of percent recovery (%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%.

Bias: The Model 101E bias (average percent difference) observed during the Weeks 1, 4, and 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.

Precision: The precision of the Model 101E reading varied from 0.3% to 6.3% (percent relative standard deviation) 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 accuracy check. The average precision calculated from each check was 1.9%, 2.0%, and 1.2% for Weeks 1, 4, and 5, respectively.

Linearity: Linearity was evaluated in terms of slope, intercept, and r^2 of a linear regression analysis 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. (The 95% confidence interval is reported in parentheses.) During Week 4, the linear regression showed a slope of 1.25 (± 0.02), an intercept of −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.

Span and Zero Drift: For this verification test, drift is defined as three consecutive drift check results that fell outside of the warning limit (± 2 standard deviations) calculated for zero (−0.1 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.

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

Interference Effects: 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: 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. As fully described in the verification report for the Model 101E, the reference method quality control requirements, such as for preanalytical holding time, analysis of quality control standards, 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.

Operational Factors: 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.

Data Completeness: 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.

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