THE ENVIRONMENTAL TECHNOLOGY VERIFICATION PROGRAM

U.S. Environmental Protection Agency

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ETV Joint Verification Statement

TECHNOLOGY TYPE:	**AMBIENT HYDROGEN SULFIDE ANALYZER**		
APPLICATION:	**MEASURING HYDROGEN SULFIDE CONCENTRATIONS AT A SWINE FINISHING FARM**		
TECHNOLOGY NAME:	**APSA-360**		
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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 Horiba Instruments, Inc., APSA-360 ambient H_2S analyzer.

VERIFICATION TEST DESCRIPTION

The objective of this verification test was to evaluate the APSA-360's performance in measuring gaseous H_2S in ambient air at an animal feeding operation (AFO). The verification test was conducted between April 25 and June 3, 2005, at a swine finishing farm near Ames, Iowa; the APSA-360 operated at the test site from May 16 through June 3, 2005 (Weeks 4, 5, and 6 of the verification test). 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 APSA-360 response to a series of H_2S gas standards was used to evaluate accuracy, bias, precision, and linearity. The APSA-360 was factory-calibrated prior to this verification test and verified 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 dilution was delivered in triplicate, and the series of gas standards was delivered twice during the verification test. 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 APSA-360 response at each nominal H_2S concentration. Linearity was assessed by establishing a multipoint calibration curve from the APSA-360 responses. The baseline response of the APSA-360 to zero air and a 30-ppb dilution of a compressed H_2S gas standard was determined during the first day of testing, which, for the APSA-360, occurred in Week 4 of the verification test. At least twice each week, zero air and a 30-ppb H_2S standard were supplied to the APSA-360 for 20 minutes for a total of 7 zero/span checks. (Results from two 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 4 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 zero/span baseline response check were used to determine the APSA-360 response time. To determine interference effects, the APSA-360 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 APSA-360 response to H_2S. The comparability of the APSA-360 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 for Testing and 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 APSA-360.

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 APSA-360 was provided by the vendor and does not represent verified information.

The APSA-360 continuously measures the concentration of H_2S (including other sulfide compounds) in ambient air using an H_2S converter and sulfur dioxide (SO_2) ultraviolet luminescence as the measurement principle. A hydrocarbon reduction membrane eliminates hydrocarbon interference in the sample gas. The APSA-360 can be configured to measure SO_2 and/or H_2S by switching measuring lines into and out of the built-in H_2S converter at regular intervals or with the measuring line fixed to SO_2 or H_2S. The APSA-360 verified in this test was configured to measure only H_2S. The basic system can be operated by controls on the front panel when it is connected to a calibration gas, but it can also be upgraded for remote monitoring by adding a computer, a

controller, and a recorder using the APSA-360 AP-Remote software for Microsoft Windows. The APSA-360 can be calibrated automatically or manually and has a lower detection limit of 4 ppb.

Data logged by the AP-Remote software can be exported into Microsoft Excel. The APSA-360 has internal storage for up to several weeks of data depending on the sample rate. The data are accessible by the front panel or the AP-Remote software. Data may also be recorded by an external data logger that is connected to the analog and digital outputs of the APSA-360. As configured for the verification test, the 4-20 mA instantaneous H_2S reading was output to an analog input channel of a Campbell Scientific Model CR43 data logger that was made available by the USDA. The data logger program sampled the APSA-360 signal every 10 seconds and recorded one-minute averages calculated from six instantaneous readings. The external data logger was used for the verification test because the AP-Remote software at the time was operational only for the Horiba ambient carbon monoxide, nitrogen oxides, SO_2 (only Model APSA-360CE), ozone, and total hydrocarbon analyzers. In the future, AP-Remote will be available for the APSA-360 H_2S Analyzer.

The APSA-360 weighs 25 kilograms (55 pounds); it is 221 millimeters (mm, 8.7 inches) high, 430 mm (17 inches) wide, and 550 mm (22.7 inches) deep (excluding front and rear extrusions). The list price of the APSA-360 H_2S-only analyzer is approximately $18,000. The APSA-360 that alternately measures SO_2 and H_2S is list priced at approximately $24,000.

VERIFICATION OF PERFORMANCE

Accuracy: The accuracy of the APSA-360 was assessed over the range of 30 ppb to 300 ppb in terms of percent recovery (%R), which ranged from 106% to 133%, with an average of 128% for the Week 4 check. The APSA-360 %R values for the Week 5 check ranged from 120% to 135%, with an average of 131%.

Bias: The APSA-360 bias (average percent difference) observed during the Week 4 and Week 5 accuracy checks (30 ppb to 300 ppb) was +28% and +31%, respectively. The consistently high bias is indicative of systematic error, which would also affect the APSA-360 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 APSA-360 instrumental errors.

Precision: The precision of the APSA-360 reading varied from 0.4% to 7.5% (percent relative standard deviation) during the Week 4 accuracy check and from 0.1% to 1.6% during the Week 5 accuracy check. The average precision calculated from each check was 2.2% and 0.5% for Weeks 4 and 5, respectively.

Linearity: Linearity was evaluated in terms of slope, intercept, and r^2 over the range from 0 ppb to 300 ppb H_2S. For Week 4, the slope of the regression line was 1.33 (± 0.02), with an intercept of −2.56 (± 3.62) and r^2 value of 0.9998. (The 95% confidence interval is reported in parentheses.) During Week 5, the linear regression showed a slope of 1.35 (± 0.01), an intercept −2.47 (± 1.76), and an r^2 of 1.000.

Span and Zero Drift: For this verification test, drift was defined as three consecutive drift check results that fell outside of the warning limit (± 2 standard deviations) calculated for zero (−1.3 ppb to −0.9 ppb) and a 30-ppb span gas (34.6 to 35.5 ppb). Seven drift checks were conducted over a period of two weeks. Drift was not observed in the APSA-360 response to zero air. The last three span drift checks fell above the warning limit, indicating that drift in the APSA-360 response to the 30-ppb H_2S span gas did occur. The final span drift check value was 1.4 ppb greater than the baseline response.

Response Time: The average 95% rise time was 5 minutes, and the average 95% fall time was 4 minutes.

Interference Effects: No interference effect was observed in the APSA-360 response to SO_2, a blend of C1 to C6 alkanes, and ammonia. The APSA-360 showed an interference effect for carbonyl sulfide in zero air of 31% and in 100 ppb H_2S of 10%. Carbon disulfide and dimethyl sulfide resulted in an interference effect of 2% to 5%. The interference effect for methyl mercaptan was 59% in zero air and 63% in 100 ppb H_2S.

Comparability: Comparability was evaluated in terms of the slope, intercept, and r^2 of a linear regression analysis of the APSA-360 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 APSA-360, 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.

Only two quantitative time-integrated reference results were available for the period during which the APSA-360 was operational at the field site. Therefore, time-integrated comparability could not be evaluated by linear regression analysis. Both of the two time-integrated reference measurements were significantly different from the corresponding APSA-360 averages at the 95% confidence level.

The regression line slope for 41 quantitative *in situ* reference measurements was 0.15 (± 0.5), with an intercept of 26 (± 22) and an r^2 value of 0.0325. Thirteen of the 41 quantitative *in situ* reference values (32%) were not significantly different from the corresponding APSA-360 15-minute averages. The regression analysis of those 13 data points yielded a slope of 0.99 (± 0.34), an intercept of 1.8 (± 13), and an r^2 value of 0.9374.

Operational Factors: The APSA-360 was not functioning properly when first installed at the test site. The APSA-360 was sent to Horiba in California for repair and returned to the test site, after which it was successfully installed by USDA staff. A user with minimal experience and the instruction manual could install and operate the APSA-360. No maintenance was required after the APSA-360 was repaired by Horiba. Daily checks of the APSA-360 were simple and quick.

Data Completeness: The APSA-360 operated during 45% of the verification test because it was not running properly for the entire test (April 25 to June 3). Once the APSA-360 was installed at the test site (May 16 to June 3), 98% of the data were collected and retrieved.

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