RESEARCHREPORT
ENVIRONMENT

Title: Laboratory Evaluation and Field Verification of Single Point Monitors (SPMs) for Measuring Aerial Ammonia and Hydrogen Sulfide Associated with Swine Operations - **NPB # 03-139**

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Abstract: Performance of 43-44 Single Point Monitors (SPMs) was evaluated for measuring aerial ammonia (NH_3, 0-30 ppm) and hydrogen sulfide (H_2S, 0-90 ppb) under laboratory and field conditions. Calibration gas or sample air with various levels of moisture content or dew-point temperature (t_{dp}) and gas concentrations were introduced simultaneously to the SPMs and a reference gas analyzer – chemiluminescence analyzer for NH_3 and pulsed-fluorescence analyzer for H_2S. Linear relationships were observed between readings of the SPMs and those of the respective reference analyzer, and the relationships were influenced by moisture content or t_{dp} of the calibration or sample air. Specifically, average H_2S readings by the SPMs were 66%, 80%, 87% and 97% of those by the reference analyzer for calibration gas at t_{dp} of -22 (dry), 9, 13 and 16 ºC, respectively. In comparison, average NH_3 readings by the SPMs were 42%, 86%, 102% and 178% of those by the reference analyzer for calibration gas at t_{dp} of -22, 8.5-10, 12.5-14, and 16-17 ºC, respectively. Coefficient of variation of "as-is" readings among the tested SPMs was up to 15% for H_2S and up to 25% for NH_3. Regression equations were developed to compensate for the moisture effect on SPM readings of both gases. The correctional regression equations were able to achieve over 90% of the reference H_2S readings. However, such equations were not as effective in predicting or correcting NH_3 readings by the SPMs.

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Introduction: Assurance of data quality in measuring aerial ammonia and/or hydrogen sulfide levels associated with swine operations has immense social, economical as well as technical ramifications for the industry and the public alike. The animal industry, academia and air quality regulatory agencies share the same challenge of quantifying low concentrations of the aerial pollutants in a swift, reliable, affordable and flexible manner. Sophisticated, complex instruments are commercially available and generally recommended for establishing field laboratories (e.g. mobile emission lab) that will enable continuous, accurate measurements of the pollutant levels. However, these instruments and setup are often prohibitively expensive ($150,000 - $200,000 per setup) and practically immobile once installed at a monitoring site.

Single Point Monitors (Model 7100, Zellweger Analytics, Inc., Lincolnshire, IL) have been used to monitor NH_3 and H_2S levels at swine production facilities (Bicudo et al., 2002; Predicala et al., 2001; Schmidt et al., 2002). The SPM measures gas levels based on the rate of color change of a chemical cassette tape that reacts with the target gas. The color intensity change of the tape is sensed by a photocell whose output is then converted to analog output and digital display of the gas level. The advantages of SPMs include its relatively low cost, portability for field application, and the ability to detect relatively low gas concentrations. The major drawbacks and concerns about the validity of values obtained with SPMs include their large uncertainty (20-25% of the "true" value as defined by the manufacturer), susceptibility to measurement interference by moisture content in the sample air, and inability of field or user calibration. The interchangeability of the SPM units is largely unknown. Nonetheless, SPM has been used by certain states (e.g. Minnesota) for checking compliance of state air quality standards. SPM is an approved method for measurement of ambient H_2S by the Minnesota Pollution Control Agency (MPCA).

Objectives: The goal of this project was to evaluate and validate operational performance in terms of accuracy, repeatability, sensitivity, stability, interchangeability, and immunity to moisture interference of single point monitors (SPMs) for measuring aerial NH_3 and H_2S levels under laboratory and field conditions. It was to be achieved by addressing the following objectives:

1) Set up an evaluation and validation lab that will be equipped with reference gas analyzers of traceable standards and the associated calibration apparatus.
2) Evaluate the interchangeability of 44 SPM units currently owned by NPB for the anticipated measurement ranges of NH_3 and H_2S.
3) Evaluate the accuracy and repeatability of the SPMs by calibrating each unit with calibration gases and precision, EPA-approved gas analyzers for the anticipated measurement ranges, so that individual calibration curves and equations could be established.
4) Evaluate the stability of the SPMs by monitoring their dynamic readings of known-level gas over an extended period. This test also will reveal the necessary interval for regular check or calibration.
5) Quantify interference of SPM measurement by moisture content in the sample air. An attempt will be made to develop functional relationship between moisture content (dew-point temperature) of the air and SPM readings of the target gas so that correctional adjustments can be made to eliminate or minimize the interference.

6) Verify a selected number (say, 20%) of the SPMs with a field installed ISU mobile emission lab (MEL) that contains US EPA-approved gas analyzers by comparing simultaneous readings by the SPMs (after correctional adjustment for moisture interference as determined in the lab) and by the MEL.

Materials and Methods:

5.1 Laboratory Evaluation System

A laboratory evaluation and verification system was set up to evaluate SPMs for the anticipated measurement ranges of NH_3 and H_2S (figure 1). Range span for the SPMs is set by inserting a “chem-key” that adjusts measurement time and interval according to a factory-set algorithm. The range of chem-keys for NH_3 evaluation was 0-30 ppm. In this range, SPMs update the display and analog output every 15 seconds. The range of chem-keys for H_2S evaluation was 0-90 ppb with an updating interval of 15 minutes. Amines and Hydrides chemcassettes (part no. 700342 and 700300, respectively, Zellweger Analytics) were used to evaluate NH_3 and H_2S, respectively. Calibration gases at various known concentrations were simultaneously introduced to the SPMs and the respective reference analyzer.

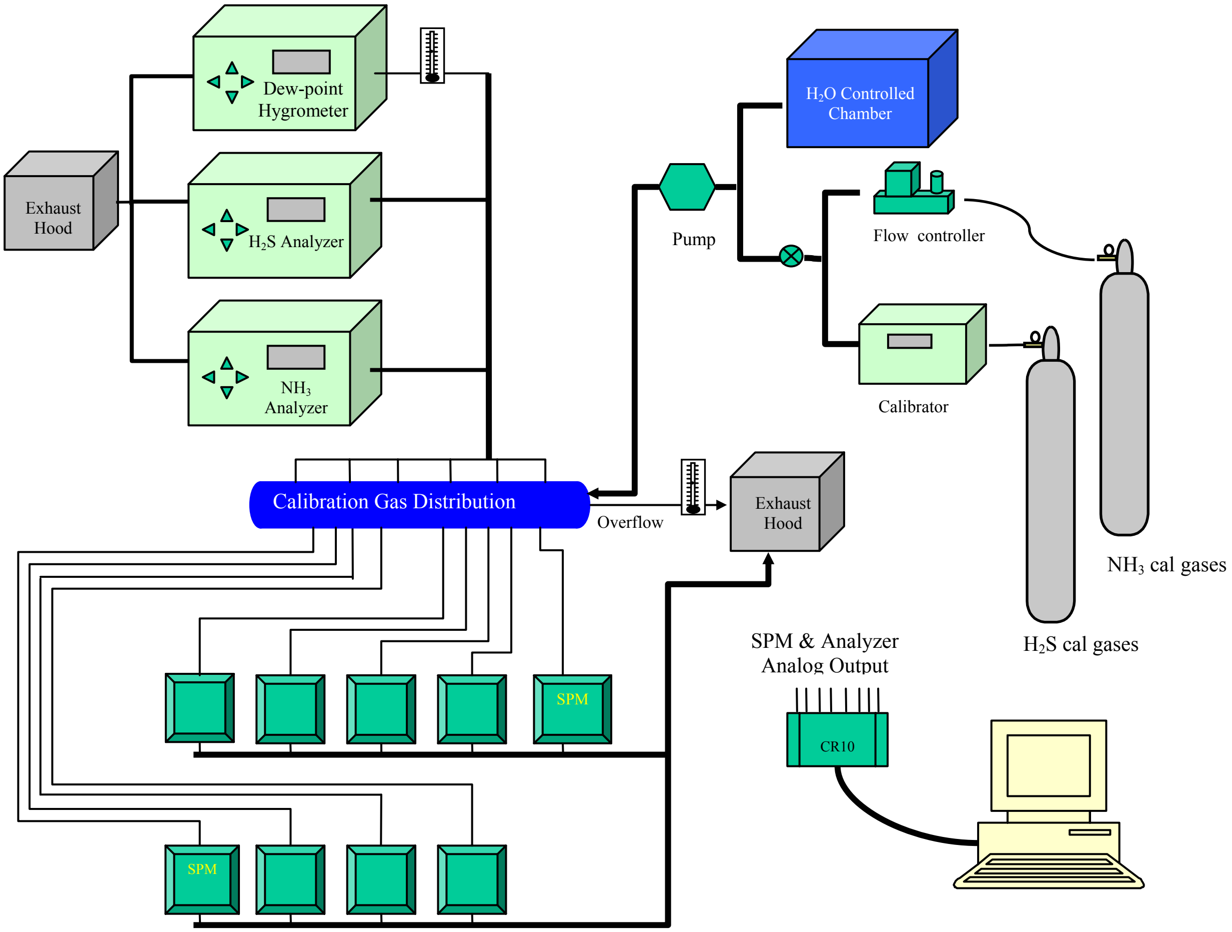

Figure 1. A schematic representation of the lab system setup for Single Point Monitor (SPM) evaluation.

A chemiluminescence NH_3/NO analyzer (Model 17C, Thermo Environmental Instruments, Franklin, MA) and a pulsed-fluorescence H_2S/SO_2 analyzer (Model 450TCL, TEI) were used as the reference analyzers, with the measurement range set at 0-30 ppm for NH_3 and 0-100 ppb for H_2S. The NH_3/NO analyzer uses an external vacuum pump to create a sample flow rate of 0.6 LPM. The H_2S/SO_2 analyzer uses an internal diaphragm pump to create a sample flow rate of 1.1 LPM. Zero and span calibrations or verifications of the analyzers were performed daily. Each SPM is equipped with an internal sampling pump. The flow rates of all SPM units were checked and found to be 0.4~0.5 LPM. Dew-point temperature (t_{dp}) of the sample air was measured with a chilled mirror dew point hygrometer (-50 to 50 °C, ±0.2°C, Model 2000, EG & G, Burlington, MA).

The calibration gas distribution system consisted of a Teflon® manifold, fittings and tubing. The column-shaped manifold measured 444 mm long, 40 mm in outside diameter, and 10 mm in inside diameter, with 24 ports on the side and 1 port at each end. The two end ports on the manifold were connected by a T-connector to the calibration gas source to minimize possible variability due to port position. Nine of the 24 ports on the side were used as inlets for a group of nine SPMs tested simultaneously (a total of 44 SPMs were tested in 5 batches). Three more ports were connected to a Teflon filter that was shared by both reference analyzers, a dew point hygrometer, and an excess flow bypass. The number of ports used and thus SPMs involved per test were limited by the flow volume available from the diluting system that delivers the source gas. The remaining ports were plugged. Teflon tubing of 1.5~1.8 m (5~6 feet) in length was used to supply test gas from the manifold to each SPM unit as well as to the gas analyzers. Variability among the ports was checked by rotating a SPM through six ports that represented all possible distances from the ends of the manifold. The results revealed no variability in port positions. Snapshots of the evaluation /calibration system setup are shown in figure 2.

Analog outputs from the SPMs (4-20 mA) and the analyzers (0-1 VDC) were sampled at 2-second intervals and stored as either 1-min averages (H_2S test) or 3-second averages (NH_3 test) using a measurement and control module (Model CR10, Campbell Scientific, Inc., Logan, UT). Channels of the measurement module were individually calibrated for both types of target gases.

Calibration gases of 4.8 ppm H_2S (+N_2 balance, ± 2% accuracy) and 233 ppm NH_3 (+air balance, ± 2% accuracy) (Matheson Tri-Gas Inc., La Porte, TX) were used to generate various gas concentrations used for the lab evaluation.

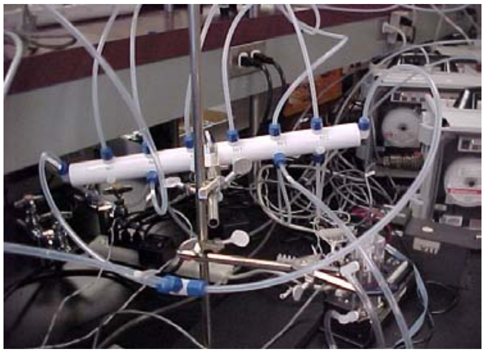

Figure 2- Lab setups for evaluation of SPM performance in measurement of H_2S and NH_3.

5.2 Lab Evaluation - Target Gases in Dry Air

Dry calibration air was generated with a dynamic span gas diluting calibrator (Model 700, Advanced Pollution Instrumentation, Inc., San Diego, CA) and a zero air generator (Model 701, API). The dynamic diluting calibrator was programmed to generate dry ($t_{dp}= -22^{\circ}C$) H_2S calibration gas at nominal concentrations of 0, 10, 20, 40, 60 or 70 ppb. Selection of the gas concentration was randomized in the testing sequence.

Because the dynamic diluting calibrator was unable to dilute 233 ppm NH_3 gas to the desired range of 0-30 ppm, a mass flow controller (0-1 LPM, stainless steel wetted parts, AALBORG Instruments & Controls, Inc, Orangeburg, NY) was connected to the NH_3 calibration gas cylinder to control the desired NH_3 gas flow rate, while the dynamic diluting calibrator was used to generate dry zero air. The NH_3 gas and dry zero air were mixed to achieve the concentrations of 0, 5, 10, 15, 20 or 25 ppm. Selection of the gas concentration was randomized in the testing sequence.

The SPMs were randomly divided into five groups. It took 15 minutes for the SPM to update the display when monitoring H_2S gas at concentrations up to 90 ppb. Four updates were collected for each H_2S level, with the first update discarded in the data analysis. For the dry H_2S calibration air evaluation, each group of tests took 6 hours, and the 44 units were tested in five days. According to the manufacturer, H_2S chemcassette tapes expire in 30 days once the sealed package is opened and each tape can run continuously for more than 30 days. Nine tapes were used and rotated among all units for the dry gas test. When tests were not in session, the tapes were stored in a 4 ºC cold storage room.

The SPMs updated readings every 15 seconds when monitoring NH_3 gas. Exposure of the SPMs to an equilibrated concentration lasted for 3 minutes before changing to the next level. Each group of SPMs was tested for 6 concentrations, completed in one hour, before switching to the next group. The NH_3 chemcassette tapes expire in 30 days after the sealed package is opened and each tape can run continuously for approximately 16 hours. Nine tapes were used and rotated among all units for the dry gas tests, which was completed in two days.

5.3 Lab Evaluation - Target Gases in Humid Air

A temperature and humidity-controlled room at the National Swine Research and Information Center (LEAP Lab II, Ames, IA) was instrumented to carry out the lab evaluation of target gases in humid air. Three dew-point temperatures (t_{dp}) at a dry-bulb temperature of 24.4°C (75°F) and four concentration levels (including zero), in a factorial arrangement, were chosen for testing of each target gas. Dew-point temperature in the room was controlled at about 9, 13 or 16 ºC (48, 55 or 61°F). Nominal concentrations of 0, 12, 35 or 70 ppb H_2S and 0, 5, 15 or 25 ppm NH_3 were chosen for the tests.

The desired testing gas concentrations were obtained by proportionally mixing the dry calibration gas with the relatively constant t_{dp} fresh air inside the environmentally controlled room. Since t_{dp} of the humid fresh air remained quite constant, t_{dp} of the humid calibration air reaching the manifold fluctuated within 2ºC for NH_3 and 0.5ºC for H_2S. As with the dry gas evaluation, SPMs were tested in five groups, with the H_2S test finished in 10 days and the NH_3 test finished in 4 days.

5.4 Lab Evaluation - Temperature Effect

The SPMs have a manufacturer-recommended operating temperature range of 0 to 40ºC. To check the potential temperature effect on their performance, four SPMs were placed inside an incubator (Fisher Scientific, Inc., Hampton, NH) set at 10, 20 or 30ºC ambient temperature. Dry H_2S calibration gas (t_{dp}= −22ºC) at nominal levels of 0, 10 or 70 ppb was used in the evaluation that was completed in two days.

5.5 Field Evaluation

Eight SPMs were randomly selected to monitor NH_3 gas at a poultry production site on October 17th, 2003. An air sample from the exhaust stream was introduced into the distribution manifold and monitored simultaneously by the reference analyzer and the SPMs. Six of the eight SPMs were set to update the output or readings at 15-second intervals, whereas the remaining two were set to be on a 15-minute duty cycle, i.e., update the readings every 15 minutes. Two SPMs stopped working shortly after start of the test. The tapes of these two units and the tapes from the 15-min duty cycle units were removed after test and stored in the 4ºC cold storage room and were re-used for the subsequent test.

Six SPMs were then used to monitor NH_3 concentration near a swine facility on November 14 and 17, 2003, since concentrations encountered in the field poultry test were quite low (4 ppm). Due to restriction in available sample air supply, SPMs in groups of three units were appended to an existing air quality sampling/monitoring system for the test. Air samples inside the building were introduced to the manifold and monitored simultaneously by the reference analyzer and the three SPMs.

Ten SPMs were randomly selected to monitor H_2S concentration near the swine facility between November 19 and Dec 5, 2003. Air sample at 1 m downstream from an exhaust fan was introduced to the manifold and monitored by both the reference analyzer and the SPMs. Data of the SPMs and the reference analyzer were recorded at 5-minute intervals using the same CR10 module as used in the lab tests. Hydrogen sulfide concentrations at the same swine facility were again monitored by ten SPMs between May 3 and 25, 2004. Air sample at 2 m downstream from a pit exhaust fan was introduced to the manifold and monitored by both the reference analyzer and the SPMs. Data of the SPMs and the reference analyzer were recorded at 1-minute intervals using the same CR10 module.

5.6 Data Analysis

Two potential factors contribute to the discrepancy between the SPM reading and the reference analyzer reading, i.e., the inherent resolution or accuracy of the SPM, and interference caused by moisture in the sample air. Furthermore, the degree of moisture interference may depend on the gas level. Hence, to correct the SPM readings of moist air samples, the "as-is" readings were first converted to equivalent dry readings; followed by the relationship between the dry readings of SPM and the corresponding reference readings. The following functional relationships were used to relate the SPM reading to the reference value:

$$C_{ref} = (C_{SPM\_dry} - \beta)/m \qquad [1]$$

$$C_{SPM\_dry} = C_{SPM\_as\text{-}is} - \Delta C_{SPM} \qquad [2]$$

$$\Delta C_{SPM} = a + b \cdot \Delta t_{dp} + c \cdot C_{SPM\_as-is} + d \cdot \Delta t_{dp} \cdot C_{SPM\_as-is} \qquad [3]$$

$$C_{corrected} = (C_{SPM\_as\text{-}is} - \Delta C_{SPM} - \beta)/m \qquad [4]$$

where C_{ref} is the concentration indicated by the reference analyzer, considered as the "true" value; C_{SPM_dry} is the concentration indicated by the SPM under dry air condition; $C_{SPM\_as\text{-}is}$ is concentration indicated by the SPM under moist condition; β, m are, respectively, intercept and slope of linear regression equation under dry air condition; ΔC_{SPM} is the change in concentration due to moisture interference of SPM; a, b, c, d are regression constants; Δt_{dp} is change in dew-point temperature between moist and dry sampling/calibration air/gas; and $C_{corrected}$ is corrected concentration based on "as-is" readings.

Statistical analysis was performed using the SAS GLM procedure to evaluate the effect of three ambient temperatures on the SPM readings.

The field measurements from each SPM and the reference analyzer were paired for comparison. For H_2S, the pairs were formed at 15-minute intervals. Recordings from the reference analyzer during the 15-min sampling interval immediately prior to the corresponding SPM 15-min update was selected and averaged as the corresponding reference reading. For NH_3, 15-second data were averaged into 1-min data before analyzed. Hourly averages were also analyzed and tested for significant difference between each SPM and the respective reference analyzer using two-tailed paired t-test.

5.7 Stability Evaluation

To evaluate the stability of the SPMs, laboratory tests were conducted eight months after the initial evaluation, during which majority of the units were used periodically in field monitoring with accumulated usage of between 3-4 weeks. Twenty-five SPMs were randomly selected and evaluated with dry H_2S calibration gas (t_{dp}= –22ºC) at nominal levels of 0, 10, 20, 40, 60 or 70 ppb. A new set of linear regression equations were developed for the 25 SPMs. For each unit, the magnitude of change in SPM readings for the six nominal levels (0-70 ppb) based on the two sets of regression equations was calculated, as shown in equation [5]. Statistical analysis was also performed using the SAS GLM procedure to compare differences between two slopes and intercepts of the regression equations for each SPM.

$$Change(\%) = \frac{|H_2S_{new} - H_2S_{old}|}{H_2S_{old}} \times 100 \qquad [5]$$

Results: 6.1 Lab Evaluation - Hydrogen Sulfide

A total of 44 SPMs were tested under dry air condition and 43 SPMs (one malfunctioned during the test) were tested under humid air condition for H_2S. Means and standard deviations (S.D.) of H_2S readings by the SPMs and the reference analyzer are presented in Table 1. The “within units” S.D. column shows the variation among three consecutive updates of the SPMs, whereas the “among units” S.D. column reflects the variability or interchangeability among the units. It was observed that the three consecutive updates by the same SPM for a given calibration gas level varied up to 6 ppb (or 16% of the reading) at relatively high concentrations (i.e., 60 ppb). This result indicates the rather poor repeatability of the SPMs. The “among units” coefficient of variation (CV) ranged from 9.3 to 15.4% for concentrations of 10 ~70 ppb, but much greater (up to 215%) at zero concentrations.

Comparisons in H_2S readings by the SPMs and the reference analyzer at the tested t_{dp} are shown in figure 3. Generally, SPM gave lower readings for all the tested concentrations except for the dry zero air. However, the SPM readings increased with increasing moisture content. The regression equations relating SPM and reference H_2S readings at each t_{dp} level were of the following forms:

$$\text{For } t_{dp} = -22^{\circ}\text{C}, \quad [\text{H}_2\text{S, ppb}]_{\text{SPM}} = 0.655[\text{H}_2\text{S, ppb}]_{\text{Ref}} + 2.36 \qquad (R^2 = 0.9931) \qquad [6]$$

$$\text{For } t_{dp} = 9^{\circ}\text{C}, \quad [\text{H}_2\text{S, ppb}]_{\text{SPM}} = 0.802[\text{H}_2\text{S, ppb}]_{\text{Ref}} + 1.11 \qquad (R^2 = 0.9996) \qquad [7]$$

$$\text{For } t_{dp} = 13^{\circ}\text{C}, \quad [\text{H}_2\text{S, ppb}]_{\text{SPM}} = 0.8739[\text{H}_2\text{S, ppb}]_{\text{Ref}} + 0.57 \qquad (R^2 = 0.9990) \qquad [8]$$

$$\text{For } t_{dp} = 16^{\circ}\text{C}, \quad [\text{H}_2\text{S, ppb}]_{\text{SPM}} = 0.9734[\text{H}_2\text{S, ppb}]_{\text{Ref}} + 0.72 \qquad (R^2 = 0.9991) \qquad [9]$$

Hence, when using SPMs to measure the *change* in H_2S concentration under dry air condition (t_{dp} = -22ºC), the result will be about 66% of that measured by the reference analyzer. Under moist air conditions with t_{dp} of 9, 13 and 16ºC, the result will be about 80%, 87% and 97%, respectively, of the reference readings. Under dry air condition, individual H_2S calibration curve was established for each unit and graphs are plotted and included in Appendix I.

Table 1. Summary of Single Point Monitor (SPM) readings for various calibration H_2S concentrations and dew-point temperatures in laboratory conditions.

Dew-Point Temperature	Reference Concentration	H_2S Readings by SPM and Statistics				
		Mean	Within Units		Among Units	
(ºC)	(ppb)	(ppb)	S.D.	C.V. (%)	S.D.	C.V. (%)
-22	0	0.97	0.99	102	0.74	76
	9.52	8.52	0.50	6	1.03	12
	19.54	15.73	0.62	4	1.84	12
	39.33	30.82	0.81	3	3.21	10
	59.58	40.34	1.76	4	4.24	11
	69.88	47.23	1.47	3	4.38	9
9	0.04	1.07	0.17	16	1.34	125
	11.59	11.02	0.36	3	1.49	14
	35.87	29.49	0.91	3	4.22	14
	66.8	54.8	1.69	3	7.25	13
13	0.04	0	0	N/A	0	N/A
	11.48	11.56	0.37	3	1.35	12
	35.24	31.59	0.91	3	3.78	12
	65.26	57.33	1.59	3	6.76	12
16	0.04	0.12	0.21	177	0.26	215
	11.28	12.48	0.52	4	1.77	14
	34.77	35.18	1.11	3	5.42	15
	64.71	63.24	2.00	3	7.34	12

S.D. = standard deviation; C.V. = coefficient of variation

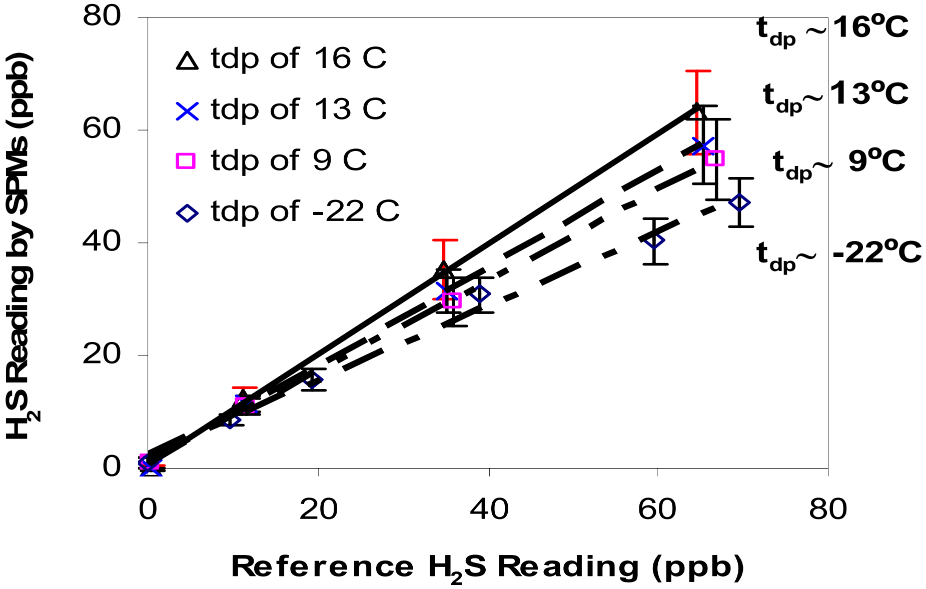

Figure 3. Comparison of H_2S measurements by SPMs (43 units) and the reference analyzer for the selected concentrations of calibration gas at dew-point temperature (t_{dp}) of -22 ºC, 9 ºC, 13 ºC and 16 ºC. The vertical bars of the data points represent standard deviation.

6.2 Lab Evaluation - Ammonia

A total of 45 units were evaluated for NH_3 measurement and the results are shown in Table 2. The “among units” CV ranged from 5% to 25% for concentrations of 0 to 26 ppm. Two units were excluded from the regression analysis due to spurious performance under the testing condition.

Comparisons in NH_3 readings by the SPMs and the reference analyzer at the tested t_{dp} are shown in figure 3. Generally, under dry air conditions the SPMs gave values slightly higher than the reference readings for concentrations of 0 and 5 ppm, but lower readings for other tested concentrations (11, 16, 21, or 26 ppm). The regression equations relating the NH_3 measurement by the SPMs and the reference analyzer under each humidity or t_{dp} level had the following forms:

$$\text{For } t_{dp} = -22^{\circ}\text{C}, \quad [NH_3, \text{ppm}]_{SPM} = 0.4182[NH_3, \text{ppm}]_{Ref} + 3.46 \quad (R^2 = 0.9866) \quad [10]$$

$$\text{For } t_{dp} \approx 9^{\circ}\text{C}, \quad [NH_3, \text{ppm}]_{SPM} = 0.8559[NH_3, \text{ppm}]_{Ref} + 2.01 \quad (R^2 = 0.9494) \quad [11]$$

$$\text{For } t_{dp} \approx 13^{\circ}\text{C}, \quad [NH_3, \text{ppm}]_{SPM} = 1.0186[NH_3, \text{ppm}]_{Ref} + 3.72 \quad (R^2 = 0.8749) \quad [12]$$

$$\text{For } t_{dp} \approx 16^{\circ}\text{C}, \quad [NH_3, \text{ppm}]_{SPM} = 1.7818[NH_3, \text{ppm}]_{Ref} + 2.37 \quad (R^2 = 0.9222) \quad [13]$$

Hence when using SPMs to measure the *change* in NH_3 concentration under t_{dp} of -22 (dry air), 9, 13 and 16ºC, the result will be, respectively, 42%, 86%, 102% and 178% of the reference values. Under dry air condition, individual NH_3 calibration curve was established for each unit and graphs are plotted and included in Appendix II.

Table 2. Summary of Single Point Monitor (SPM) readings for various calibration NH_3 concentrations and dew-point temperatures in laboratory conditions.

Dew-Point Temperature (ºC)	Reference Concentration (ppm)	NH_3 Readings by SPM and Statistics				
		Mean	Within Units		Among Units	
		(ppm)	S.D.	C.V. (%)	S.D.	C.V. (%)
-22	0.03	2.96	0.08	3	0.24	8
	5.24	5.73	0.13	2	0.48	8
	10.93	8.32	0.21	3	0.70	8
	16.50	11.08	0.46	4	0.92	8
	21.48	12.39	0.29	2	0.83	7
	25.81	13.75	0.40	3	0.72	5
8.5-10	0	0.02	0	0	0.06	396
	5.53	8.31	0.33	4	1.52	18
	13.84	15.77	1.22	8	1.47	9
	23.71	20.81	1.59	8	2.72	13
12.6-14	-0.02	0.01	0	7	0.07	958
	5.68	12.30	0.50	4	2.10	17
	13.83	21.69	1.00	5	2.86	13
	23.25	24.41	1.15	5	2.30	9
16-17	0.03	0.09	0.02	23	0.42	453
	5.49	14.70	0.66	5	2.47	17
	9.54	22.01	1.00	5	3.53	16
	13.62	23.77	1.08	5	5.91	25

S.D. = standard deviation; C.V. = coefficient of variation

The linear relationship between the SPM and the reference readings at dry conditions is shown in figure 4a. The seemingly quadratic relationships between the SPM and the reference readings of NH_3 under moist conditions as shown in figures 4b-d were at least partially attributed to the experimental procedure. Namely, for a given t_{dp} in the humidity-controlled room, sample air of higher NH_3 concentration required relatively larger proportion of the dry calibration gas, which resulted in somewhat less humidity or lower t_{dp} in the mixed sample air. This lower t_{dp} sample air presumably caused relatively lower SPM readings. In other words, the four points displayed in figure 4b-d were collected under progressively declining t_{dp} of the sample air (10.2~8.6ºC in figure 4b; 14.4~12.6ºC in figure 4c; 17.6~16.7ºC in figure 4d). The actual t_{dp} values were used in subsequent analysis of moisture interference on NH_3 readings of SPMs (discussed later).

Fewer than 43 units were involved in calculating the average readings for the last two points of figures 4c-d. Specifically, when t_{dp} was about 13ºC (figure 4c), 20% of the SPMs displayed the "30^+" out of range error at a reference value of 24 ppm NH_3. When t_{dp} was about 16ºC (figure 4d), the "30^+" out of range error occurred to 90% of the SPMs at >14 ppm NH_3, thereby resulting in a shorter curve.

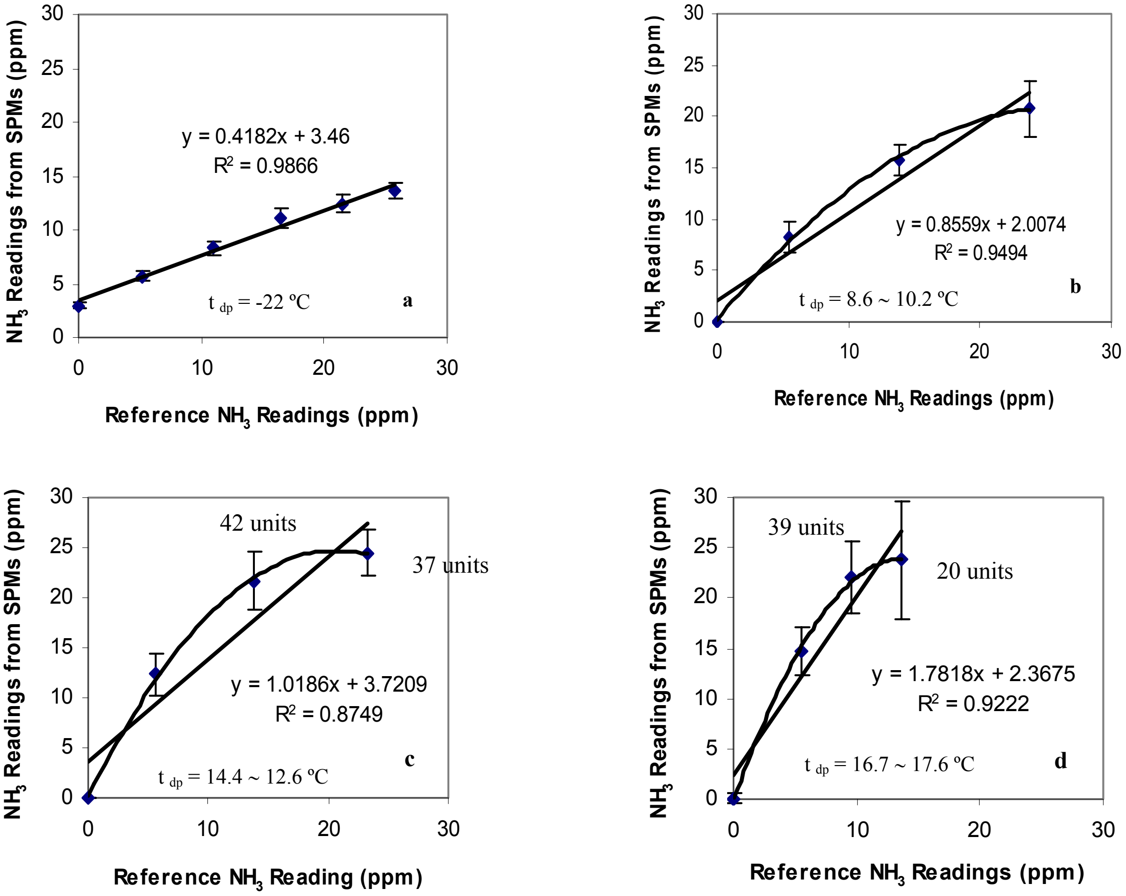

Figure 4. **Comparison of NH_3 measurements by SPMs and the reference analyzer at selected concentrations of calibration gas and dew-point temperature (t_{dp}) of a) -22 ºC; b) 10.2, 9.9, 9.3, 8.6 ºC progressively; c) 14.4, 14.0, 13.5, 12.6 ºC progressively; and d) 17.6, 17.3, 17.0, 16.7 ºC progressively. The vertical bars represent standard deviation. Values were averaged from 43 units unless otherwise labeled.**

6.3 Temperature Effect

Hydrogen sulfide concentrations measured by four SPMs at ambient temperatures of 10, 20 and 30 ºC are presented in Table 3. Significant differences were observed at zero ppb ($P<0.001$) but not at 10 or 70 ppb. It was unclear whether the significant differences at zero air was caused by the temperature effect or more likely a result of the inherent uncertainty of readings or detection at zero level.

Table 3. Effect of ambient temperature on hydrogen sulfide measurement by Single Point Monitor (SPM) (mean and standard deviation of four replicates)

H_2S Concentration (ppb)	Ambient Temperature (ºC)		
	10	20	30
0	0.1 ± 0.2 [a]	1.5 ± 0.6 [b]	2.4 ± 0.3 [c]
10	7.8 ± 0.2 [a]	8.1 ± 0.3 [a]	7.9 ± 0.3 [a]
70	38.9 ± 1.2 [a]	38.0 ± 0.4 [a]	38.4 ± 2.8 [a]

Row values with different superscript letters were significantly different ($P<0.001$)

6.4 Regression Analysis of Individual Units

For each type of gas, 43 regression equations (of equation 3 form) were established to correct SPM readings to the reference levels (Appendix III and IV). Examples of comparative results before and after correction of the SPM readings under humid conditions (t_{dp} = 8~16 ºC) are plotted in figure 5 (H_2S) and figure 6 (NH_3). The corrected H_2S concentrations (from equation 4) generally showed a linear trend (R^2 >0.99), having a slope close to 1 and an intercept less than 1 (figure 5). In comparison, the corrected NH_3 concentrations had larger variability, as evidenced by the lower R^2 value of 0.92 (vs. 0.99 for H_2S).

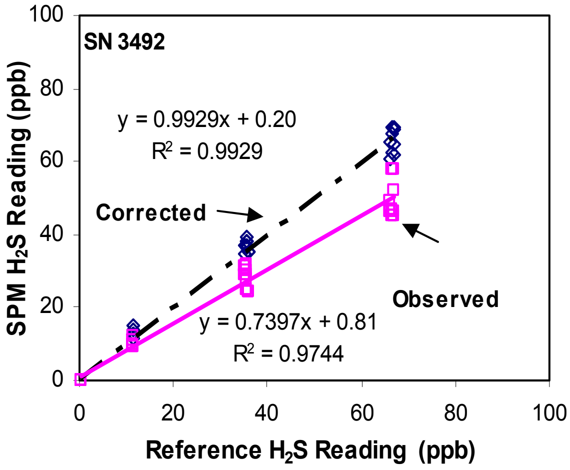

Figure 5. Comparison of H_2S concentrations (SN 3492) before and after correction for moisture content in the sample air.

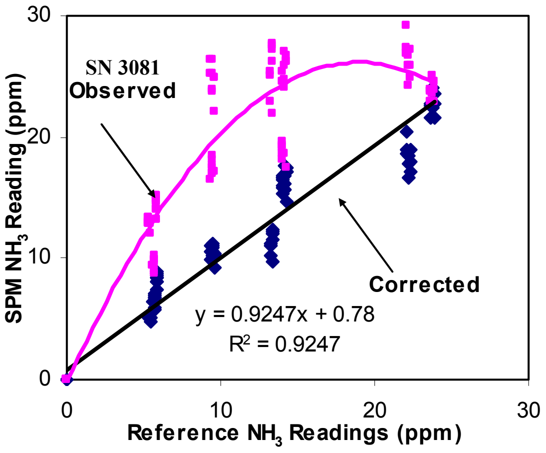

Figure 6. Comparison of NH_3 concentrations (SN 3081) before and after correction for moisture content in the sample air.

6.5 Interchangeability and Overall Regression for Hydrogen Sulfide

Interchangeability among the SPMs was examined under the dry air testing conditions for H_2S gas. Because the usefulness of individual regressions for NH_3 gas was rather marginal, unit interchangeability was not investigated. Since readings by all

SPMs exhibited linear relationships to those of the reference analyzer, slopes were chosen as a parameter to characterize each unit's behavior and unit interchangeability.

Among the 44 SPMs being tested under dry air, 34 (77%) of them had a slope between 0.6 and 0.7, averaging 0.65. Three units (7%) had a slope of 0.48, 0.79 or 0.84. The considerable range of slopes and relatively high "among units" CV (Tables 1 and 2) demonstrate rather weak interchangeability among the SPMs.

Regression analysis was performed on the H_2S data collected from all SPMs in an attempt to derive a general correctional equation. A closer examination of the operational performance of the SPMs led to exclusion of three units from the overall regression analysis. The overall regression equation had the following form,

$$\Delta SPM_{H2S} = 0.701 - 0.0824 \cdot \Delta t_{dp} - 0.374 \cdot SPM_{H2S} + 0.0185 \cdot \Delta t_{dp} \cdot SPM_{H2S} \qquad (R^2 = 0.9036) \quad [14]$$

The H_2S concentrations predicted with the *overall* equation and with the *individual* regression equations were compared against the reference values and are plotted in figure 7. The *individual* correctional regression equations gave appreciably better prediction results than the *overall* equation.

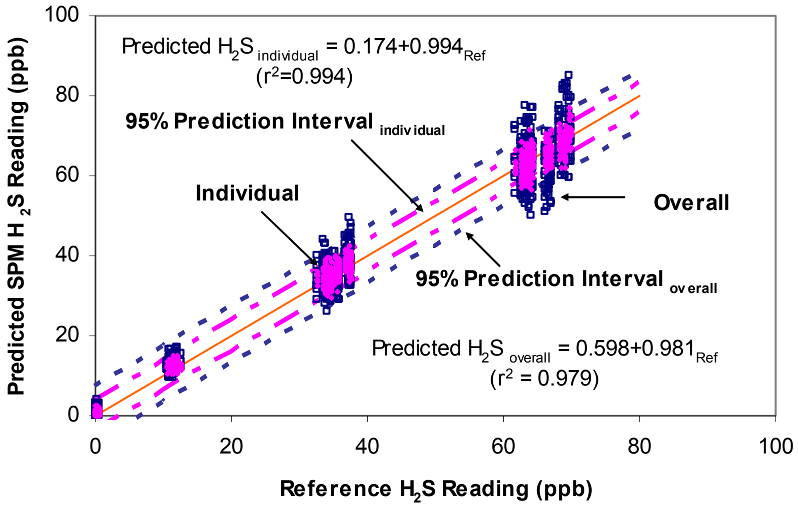

Figure 7. Corrected H_2S readings with *overall* regression equation vs. *individual* regression equations, and the respective 95% prediction intervals.

6.6 Field Evaluation

6.6.1 Hydrogen Sulfide

Two field evaluations were conducted at different time periods (fall and late spring) at the same swine facility. In the first field test, more than 1500 observations were collected at t_{dp} of -10 to 8 °C, with median dew-point temperature around zero. Most (68%) of the measured H_2S readings were lower than 10 ppb. Two units malfunctioned after 5 or 7 days of operation. Thus, data analysis was based on the remaining eight units.

Overall, the H_2S readings by the SPMs were about 70% of those as measured by the reference analyzer (Table 4). The relatively lower concentration values registered by the SPMs mainly resulted from the low t_{dp} of the sample air under this field measurement condition. This field result was consistent with the lab test results where the SPMs displayed approximately 66% and 80% of the reference values when the sample air has a t_{dp} of -22 and 9°C, respectively.

Table 4. Slopes of linear equations relating Single Point Monitor (SPM) “as-is” and corrected H_2S readings to reference values during 1st H_2S field test. SPM as-is readings were in the range of 10-90 ppb.

SPM Serial Number	As-is		Individual Correction		General Correction	
	Slope *	R^2	Slope *	R^2	Slope *	R^2
3085	0.693	0.980	0.911	0.953	0.967	0.956
3132	0.709	0.980	0.971	0.940	0.978	0.951
3465	0.701	0.983	0.990	0.963	0.980	0.964
3497	0.761	0.980	0.891	0.956	1.074	0.952
3446	0.679	0.979	1.010	0.946	0.965	0.953
3318	0.647	0.976	1.074	0.937	0.899	0.949
3118	0.683	0.982	1.130	0.948	0.936	0.958
3496	0.704	0.980	0.979	0.950	0.982	0.946
Mean	**0.697**	0.980	**0.995**	0.949	**0.973**	0.954
Standard Deviation	**0.032**	0.002	**0.079**	0.008	**0.050**	0.006

* Slope is between SPM and reference readings

Readings from the eight SPMs were corrected using either the individual correctional regression equations or the overall correctional regression equation derived from the laboratory evaluation. Results showed that SPM readings less than 10 ppb were better off not to be corrected. Therefore, only readings between 10 and 90 ppb were corrected. The results were compared with the reference values and linear equations were established (Table 4). The individually corrected readings were 0.995 (±0.079 S.D., R^2=0.95) of the reference values, and the overall corrected readings were 0.973 (±0.050 S.D., R^2=0.95) of the reference values. Hence, results in Table 4 show that H_2S readings by SPMs can be corrected with the overall regression equation derived from lab evaluation to achieve > 90% agreement with the reference values.

In the field test conducted in May 2004, between 250 to 800 data points were collected at t_{dp} of 0 to 27ºC, with median dew-point temperature around 13ºC. About half of the measured H_2S readings were < 10 ppb, while the remaining half were 10 to 100 ppb.

Overall, the H_2S readings by the SPMs were about 75% of those as measured by the reference analyzer (Table 5). Readings from the ten SPMs were again corrected using either the individual correctional regression equations or the overall correctional regression equation derived from the laboratory evaluation. The results were compared with the reference values and linear equations were established (Table 5). The individually corrected readings were 0.938 (±0.064 S.D., R^2=0.94) of the reference values, and the overall corrected readings were 0.927 (±0.045 S.D., R^2=0.94) of the reference values.

The moisture interference on H_2S reading was tested up to 16ºC in laboratory. A portion of the field observations (about 120 data points from 6 units) with t_{dp} over 18ºC were analyzed for effect of moisture interference on SPM readings (figure 8). Higher than reference readings were observed of the SPMs when t_{dp} was greater than 18ºC. This further confirms that SPM readings are highly influenced by moisture content in the sample air. It is crucial to concurrently measure the moisture level of the air to obtain more reliable results.

Table 5. Slopes of linear equations relating Single Point Monitor (SPM) “as-is” and corrected H_2S readings to reference values during 2nd H_2S field test.

SPM	As-is		Individual Correction		Group Correction	
Serial Number	Slope	R^2	Slope	R^2	Slope	R^2
3496	0.786	0.957	0.972	0.966	0.969	0.966
3132	0.732	0.969	0.943	0.975	0.947	0.976
3446	0.735	0.955	0.962	0.949	0.937	0.953
3318	0.742	0.966	1.051	0.965	0.915	0.971
3085	0.731	0.966	0.902	0.969	0.929	0.970
3118	0.685	0.966	1.004	0.963	0.868	0.972
3459	0.798	0.905	0.910	0.907	1.015	0.902
3317	0.791	0.907	0.821	0.908	0.923	0.892
3495	0.718	0.905	0.892	0.914	0.87	0.910
3465	0.749	0.912	0.918	0.916	0.892	0.914
Mean	**0.747**	0.941	**0.938**	0.943	**0.927**	0.943
Standard Deviation	**0.036**	0.029	**0.064**	0.028	**0.045**	0.034

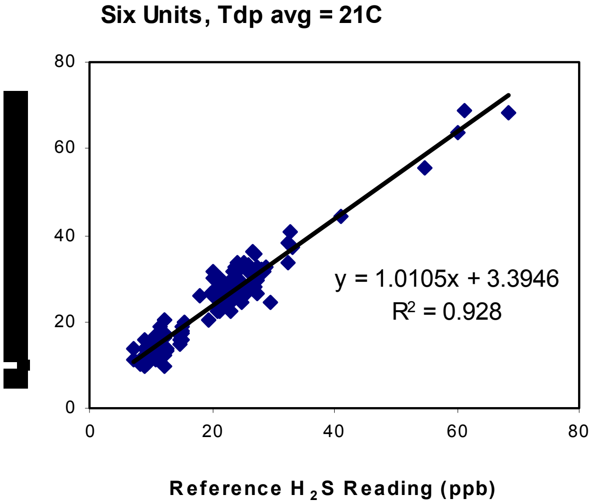

Figure 8. Correlation of H_2S readings from six SPM units with reference readings during a field measurement with dew-point temperature (t_{dp}) in the range of 18 to 27°C.

6.6.2 Ammonia

During the first field test at the poultry facility, 8 hours of data were collected before the dew-point hygrometer malfunctioned. Ammonia levels were in the range of 3.4 to 5.4 ppm, and t_{dp} was in the range of 4 to 7 °C. Two SPMs malfunctioned due to tape failure. Data were analyzed for the remaining six units.

Hourly averages of as-is readings at the poultry facilities were calculated and results are listed in Table 5. All six SPMs showed slightly higher corrected readings during the first two hours of measurement (Table 5). The reasons were unknown. In general, “as-is” readings of the SPMs were higher than the reference values ($P<0.05$). Corrected NH_3 concentrations from five of the six SPM units were not significantly different from the reference readings ($P>0.05$).

Table 5. Hourly average ammonia concentrations from six Single Point Monitors (SPMs) and the reference analyzer (TEI) during field test at a poultry production site.

Time	Ref	3134		3318		3118		3132		3317DC		3496DC	
		As-is	Crt	As-is	Crt	As-is	Crt	As-is	Crt	As-is	Crt	As-is	Crt
12:18	**4.0**	6.4	5.6	7.1	7.3	6.0	7.6	6.8	6.4	8.2	6.7	7.4	7.0
13:18	**4.0**	5.4	4.0	5.9	5.5	6.0	5.8	5.6	4.6	6.9	5.2	6.2	5.4
14:18	**3.8**	5.0	3.4	5.3	4.4	5.5	4.9	5.2	3.8	6.1	3.9	5.6	4.4
15:18	**3.9**	5.0	3.3	5.3	4.3	5.5	4.8	5.2	3.8	5.9	3.8	5.5	4.2
16:18	**3.9**	4.6	2.9	5.0	3.8	5.2	4.5	4.9	3.3	5.5	3.2	5.2	3.9
17:18	**4.0**	4.7	3.0	5.0	4.0	5.2	4.5	5.0	3.5			5.3	4.0
18:18	**3.9**	4.6	2.8	4.9	3.7	5.1	4.3	4.9	3.4			5.1	3.7
19:18	**3.9**	4.8	3.0	5.1	3.9	5.2	4.3	5.0	3.5			5.8	4.5
Mean	**3.9**	5.1*	3.5	5.4*	4.6	5.5*	5.1*	5.3*	4.0	6.5*	4.6	5.8*	4.6
S.D.	0.07	0.60	0.92	0.73	1.23	0.35	1.12	0.63	1.02	1.05	1.41	0.73	1.09

Note: Ref = reference analyzer DC = duty cycle; Crt = corrected; S.D. = standard deviation;
* Significant at P < 0.05

Ammonia concentrations and t_{dp} for the field test at the swine facility are shown in Table 6. It can be noted that "as-is" readings of the SPMs tended to overestimate NH_3 concentration. However, application of the derived regression equations over-corrected the readings, thereby resulting in significantly lower corrected readings (slopes of 0.59 to 0.90).

Hence, correction of SPM NH_3 readings with the regression equations improved results for lower concentrations and low t_{dp} at the poultry facility, but not so for the higher concentration, higher t_{dp} conditions at the swine facility. It remains unknown whether the gas sample from the swine building caused interference with the NH_3 measurement, or the chem-cassette tape had partially lost sensitivity due to aging.

Table 6. Field evaluation of SPM readings for NH_3 measurement at a swine production site

Serial Number	Hours of operation	Concentration range (ppm)	t_{dp} range (°C)	As-is		Corrected	
				Slope	R^2	Slope	R^2
3134	16	8 - 23	8 - 13	1.052	0.653	0.901	0.601
3318	15			0.953	0.595	0.904	0.559
3118	10	12 - 18	10 - 16	1.154	0.714	0.751	0.748
3132	17			1.282	0.886	0.829	0.898
3496DC	66	8 - 23	8 - 17	-	-		
3446DC	23	7 - 18	10 - 16	1.013	0.451	0.586	0.85

Notes: - No correlation could be established; DC = duty cycle; Slope is between SPM and reference readings

6.7 Stability Evaluation

Some SPMs exhibited positive changes while others exhibited negative changes, with the ranges shown in Table 9. To reduce the cancellation effect of the positive and negative changes, the changes were first converted to absolute values before computing the relative changes. The results are presented in figure 9. Changes between 10-70 ppb were less than 12%. The larger change at zero level was mainly due to the small denominator. Slopes and intercepts from three units (12%) were significantly different at P<0.05. However, all units were not significantly different at significance level of 0.01. Hence, the SPMs generally exhibited good stability.

Table 9. Maximum and minimum relative changes of readings at nominal levels from 25 SPMs over 8-month period

Reference (ppb)	Relative change (%)	
	Min	Max
0	-77	18
10	-21	8
20	-15	7
40	-11	6
60	-9	6
70	-9	7

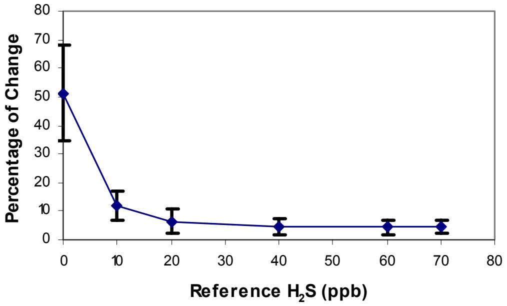

Figure 9. Relative changes (%) of H_2S readings from 25 SPM units at nominal levels of 0-70 ppb H_2S during 8 months period. Vertical bars represent standard deviation. (Calculation based on absolute values)

Discussion: Measurement of hydrogen sulfide gas with SPMs involves an uncertainty that is consistent with the manufacture specified performance, i.e., 20-25% of the "true" value. The performance of SPMs in measuring aerial ammonia is worse. However, considering certain positive features of SPM, i.e., portability, stability, and low detection ability, they are still of value for measuring H_2S associated with swine operations. It is important to have a concurrent knowledge of the moisture content of the sample air so that SPM as-is readings can be corrected using the equations developed in this study. The corrected results can achieve 90% of reference analyzer's reading for H_2S gas.

Lay Interpretation: Single Point Monitor is a portable, relatively low cost instrument that can detect relatively low levels of gaseous ammonia and hydrogen sulfide. It is an approved method for measurement of ambient hydrogen sulfide levels by the Minnesota Pollution Control Agency. This project quantified SPM performance based on a side-by-side comparison with sophisticated, accurate analyzers. The SPM reading is affected by moisture content in the sampling air. In a typical field condition of swine facility with ambient hydrogen sulfide range from 0 to 90 parts per billion (ppb), SPMs tend to record lower concentration (70 – 101% of the "true" values). Hence concurrent knowledge of moisture content in the sample air is necessary to compensate for the moisture interference. The moisture interference on SPM measurement can be mathematically compensated quite well for hydrogen sulfide gas by laboratory-derived equations, achieving 90% agreement with the reference value. In comparison, such compensation was not as effective for ammonia measurement.

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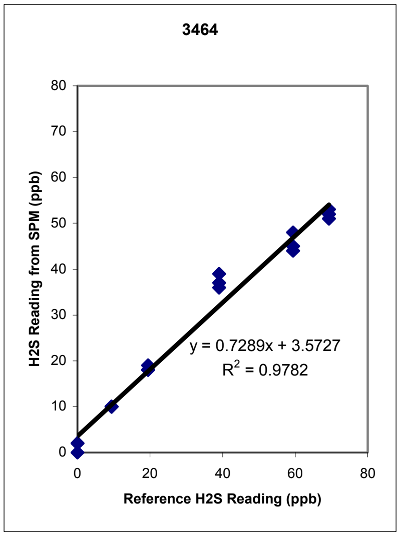
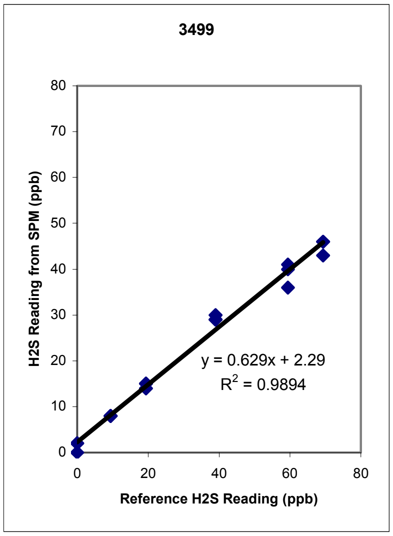
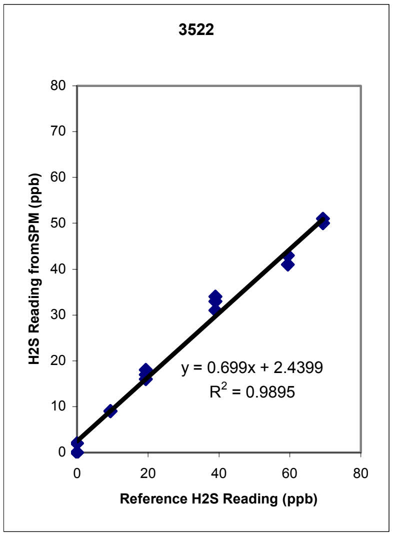
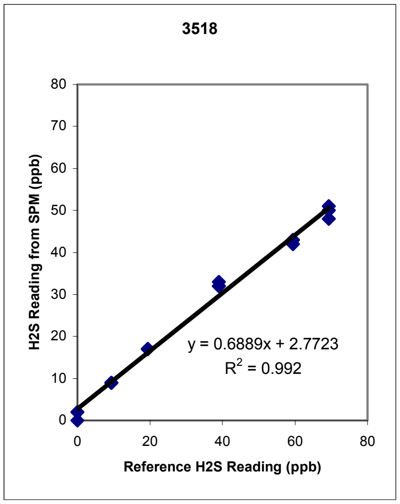
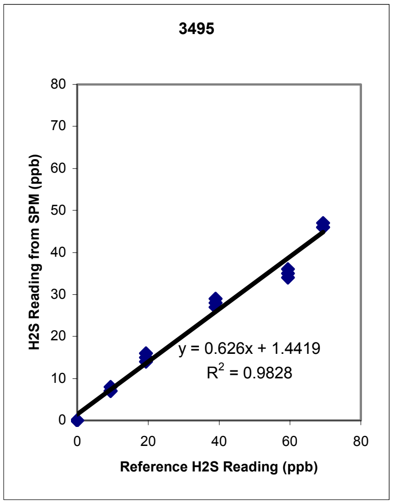
Appendix I. Calibration equations of H_2S measurement for individual SPM units (44)

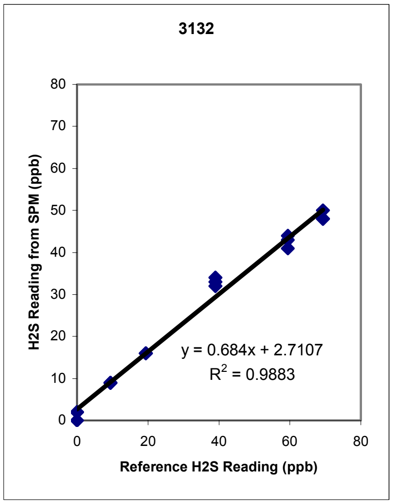


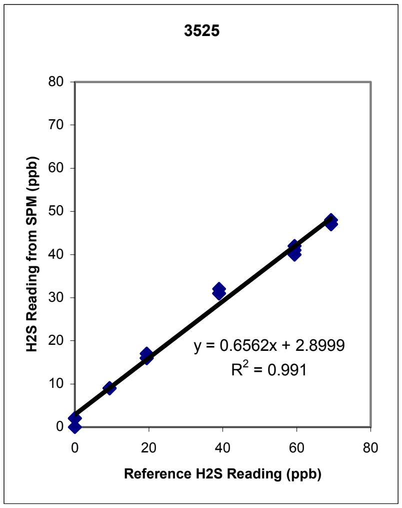


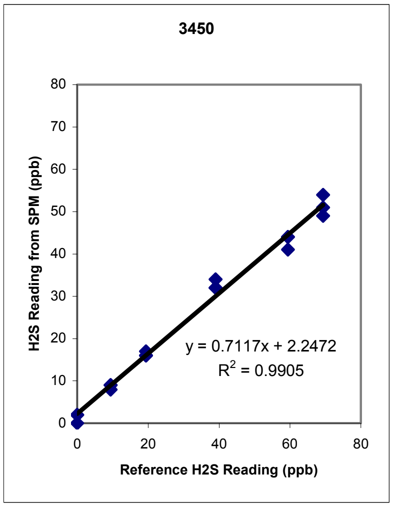


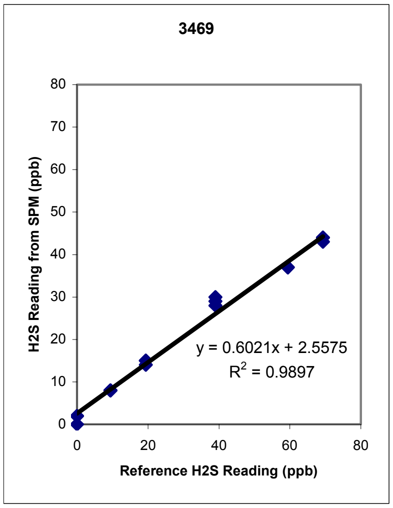




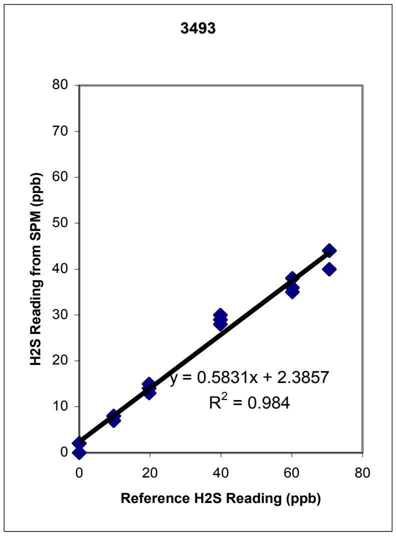








Appendix I. Calibration equations of H_2S measurement for individual SPM units (continued)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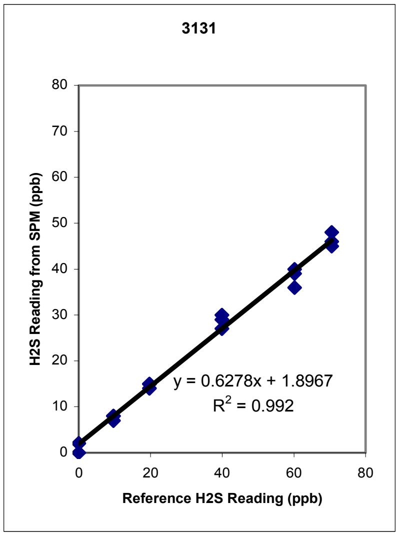
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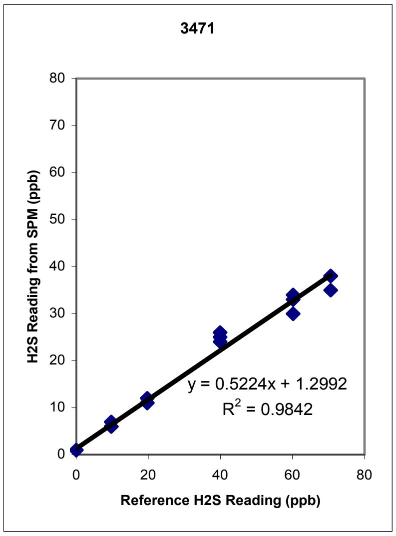
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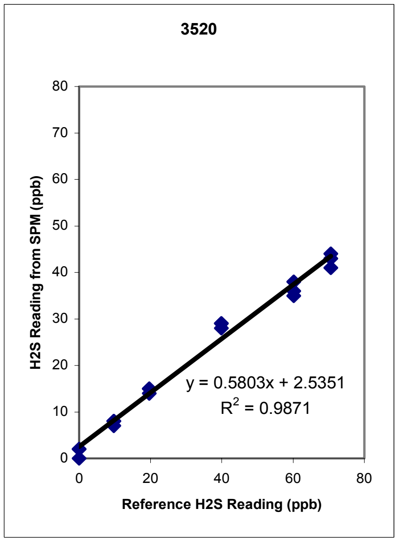
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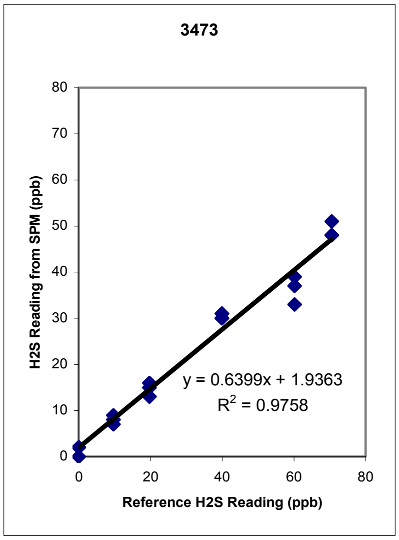
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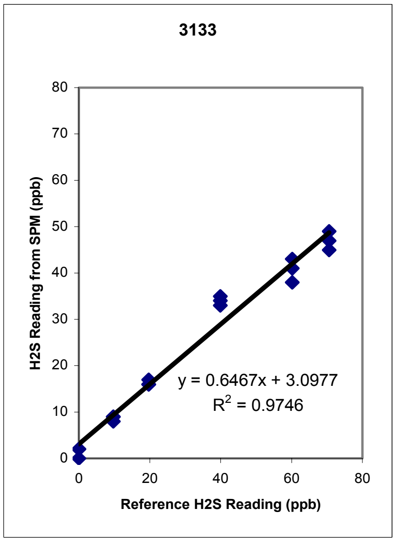
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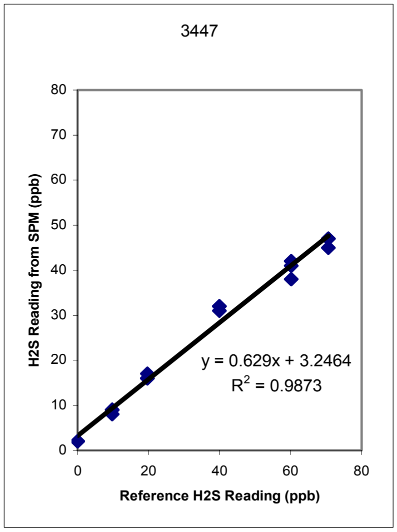
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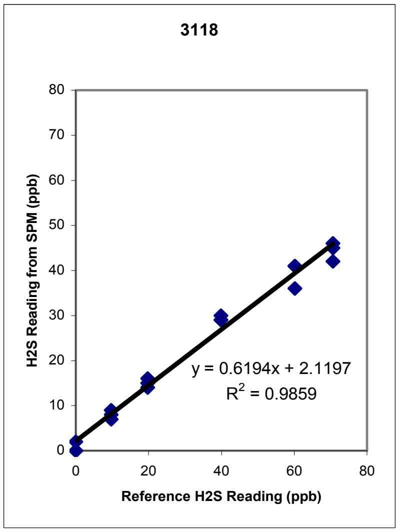
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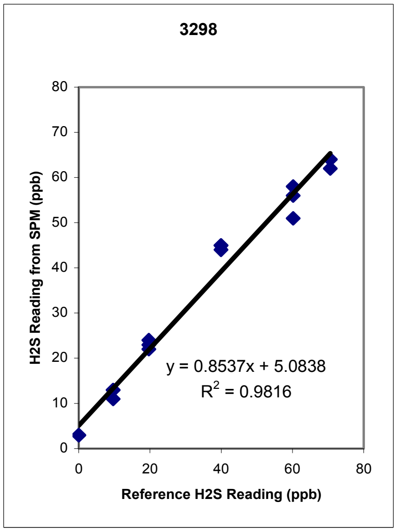
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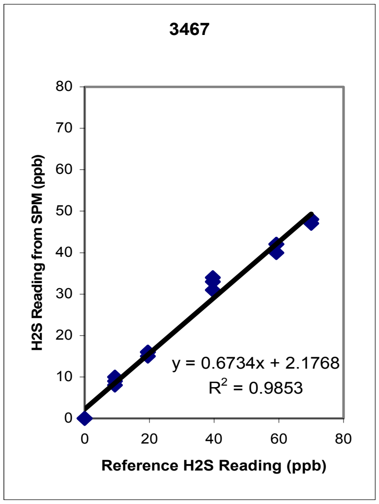
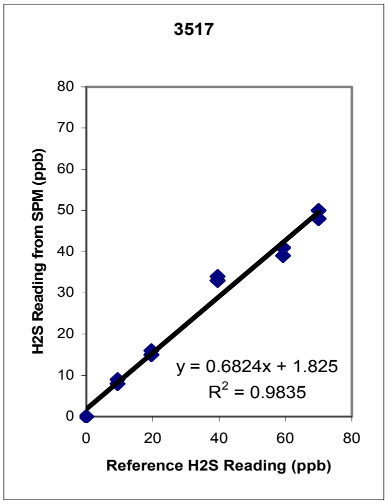
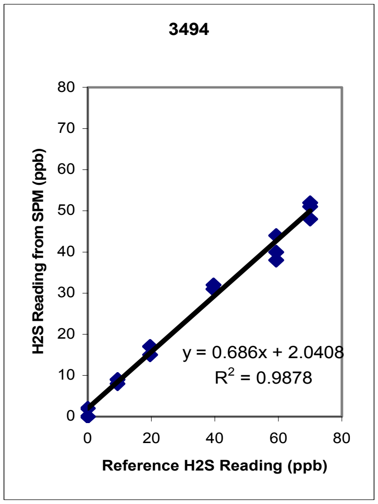
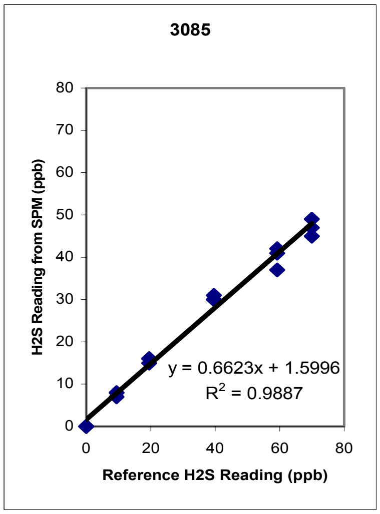
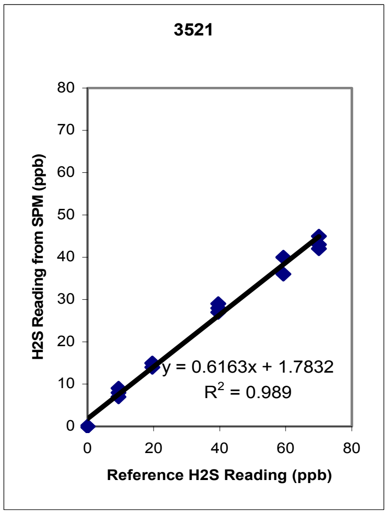
Appendix I. Calibration equations of H_2S measurement for individual SPM units (continued)

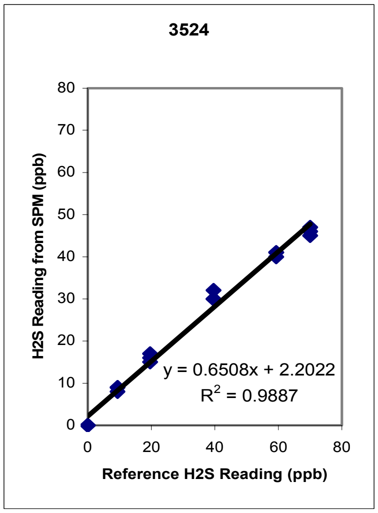


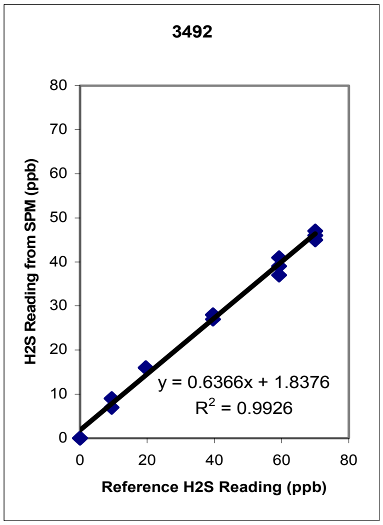


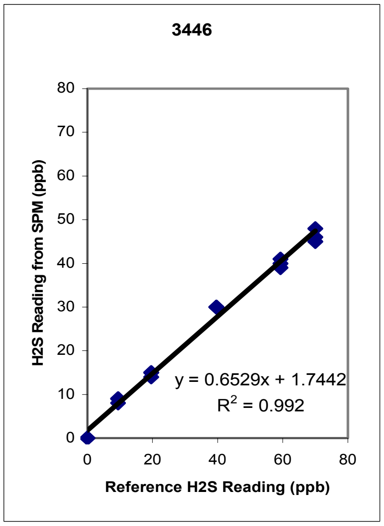


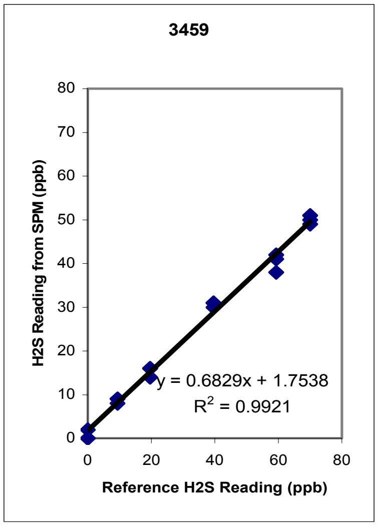




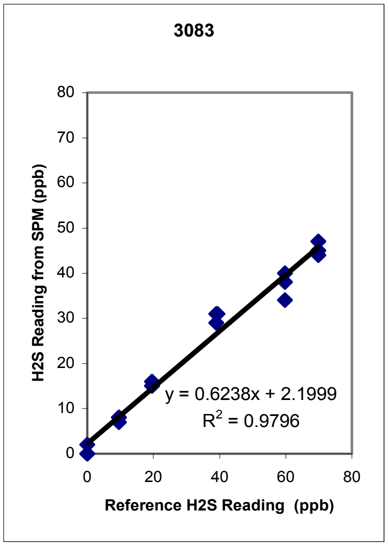


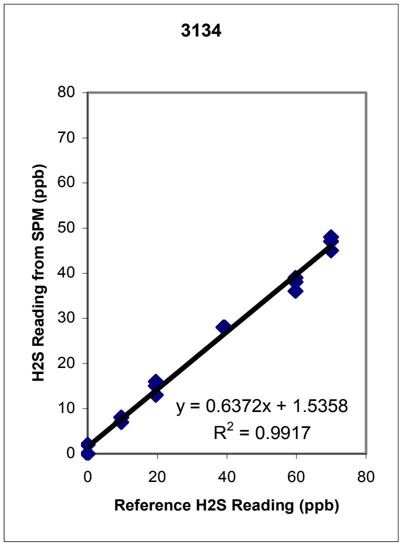


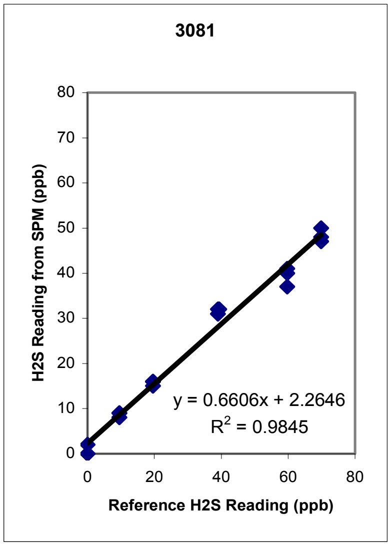


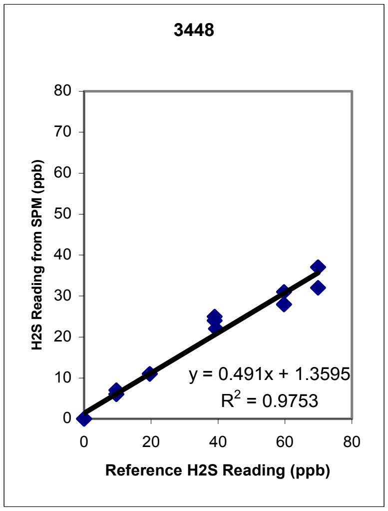


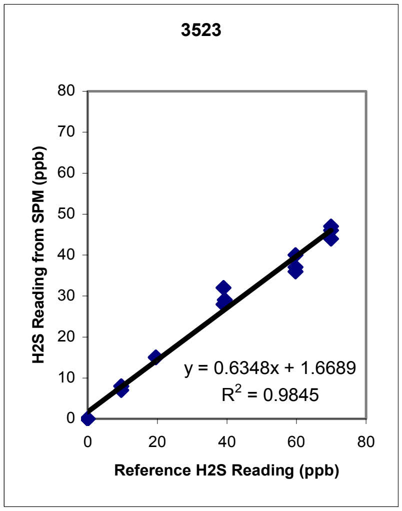
Appendix I. Calibration equations of H_2S measurement for individual SPM units (continued)

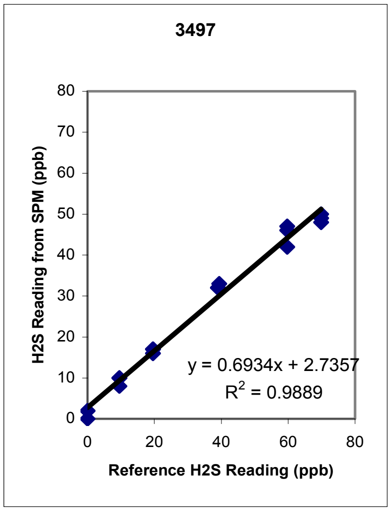


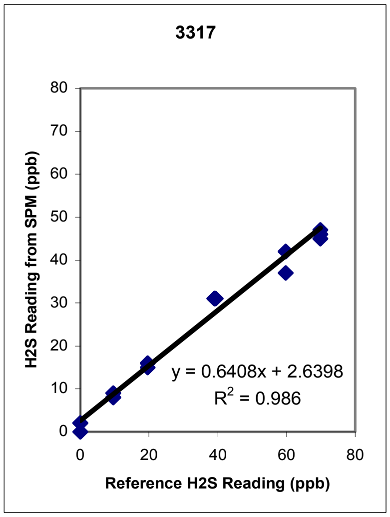


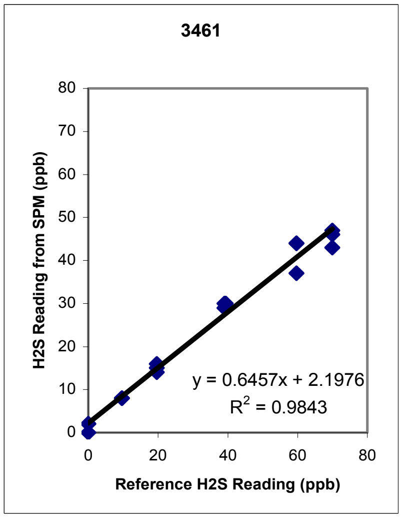




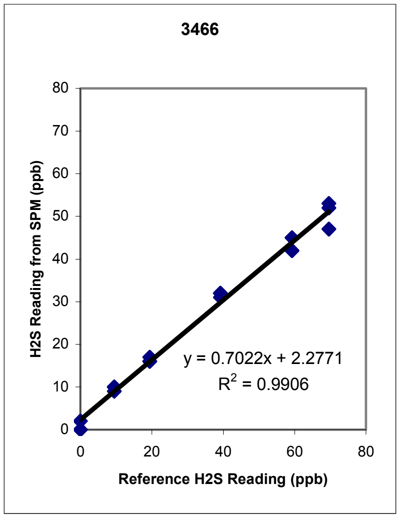


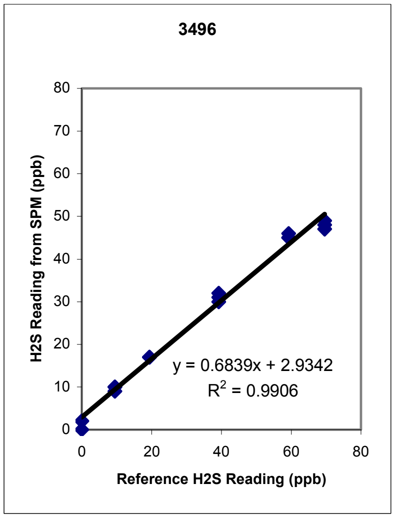


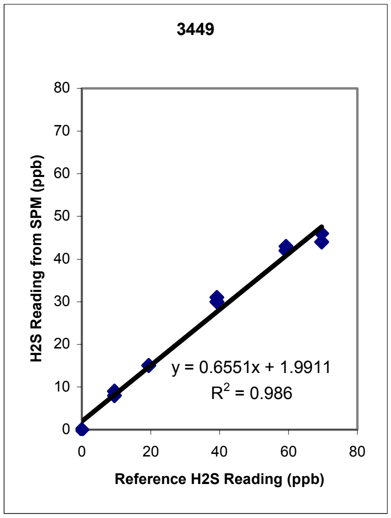


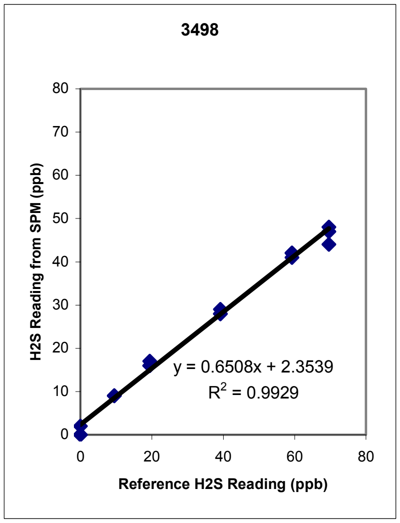


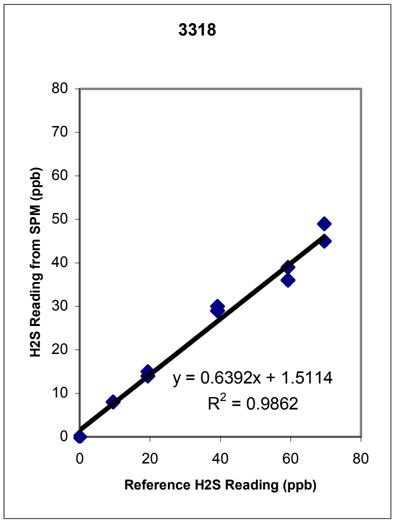
Appendix I. Calibration equations of H_2S measurement for individual SPM units (continued)

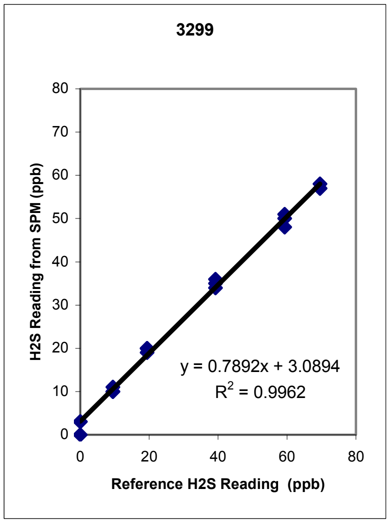


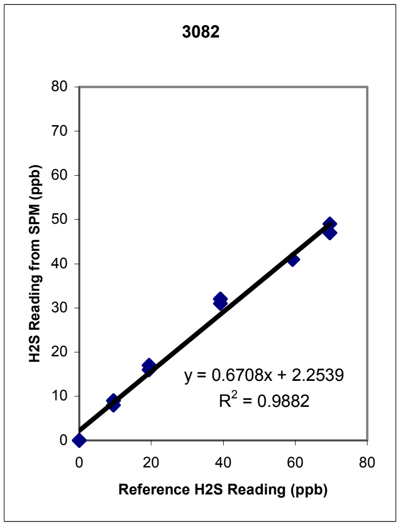


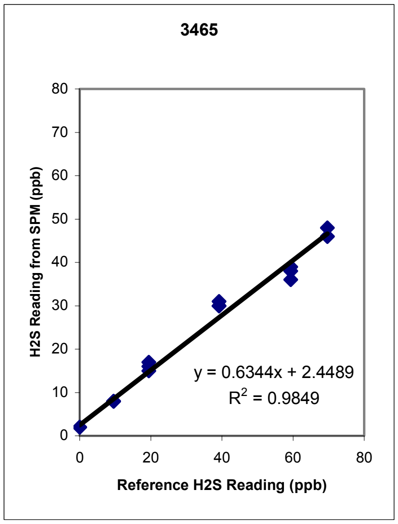


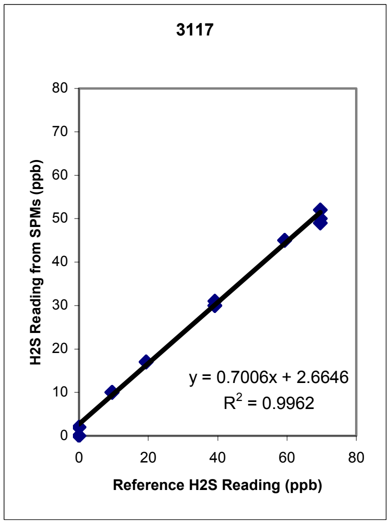




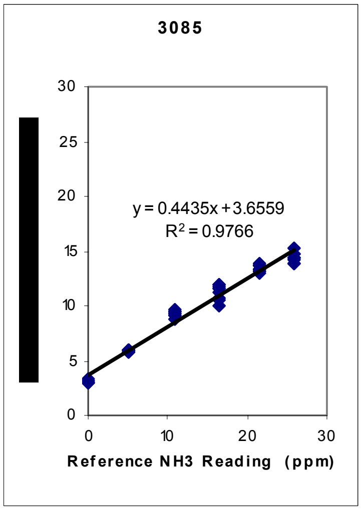


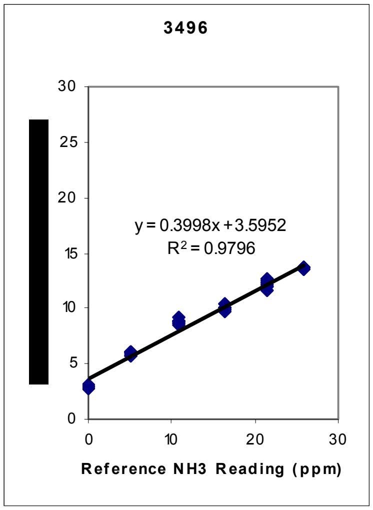


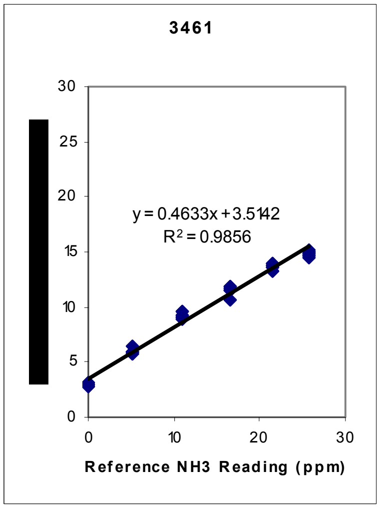


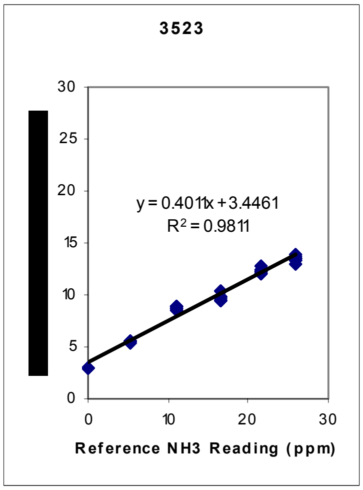


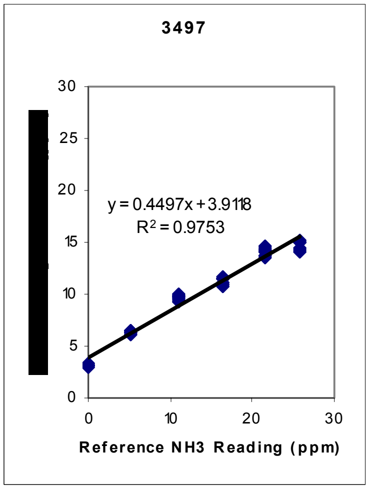
Appendix II. Calibration equations of NH$_3$ measurement for individual SPM units (44)

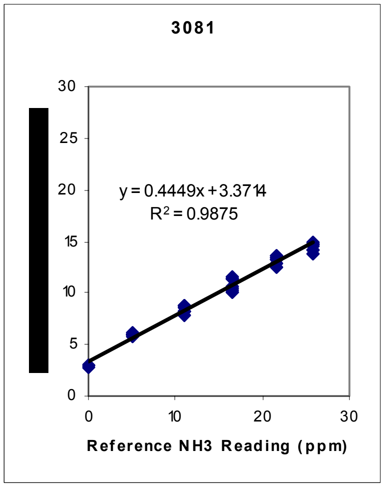


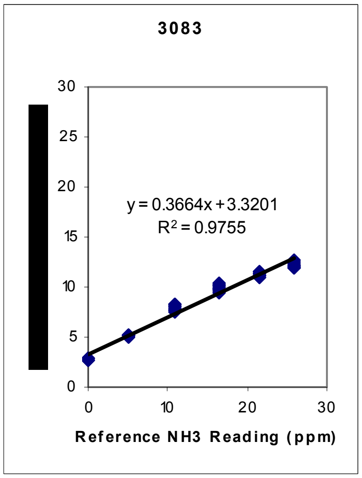


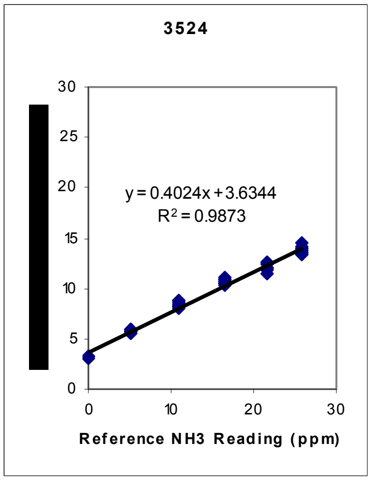


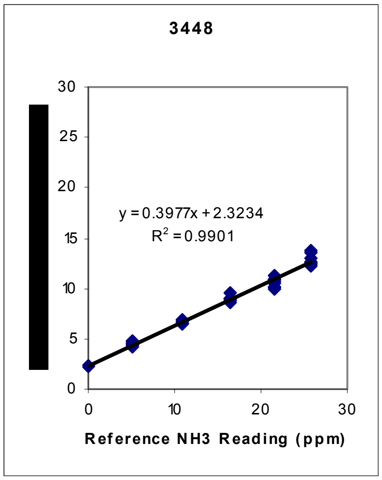




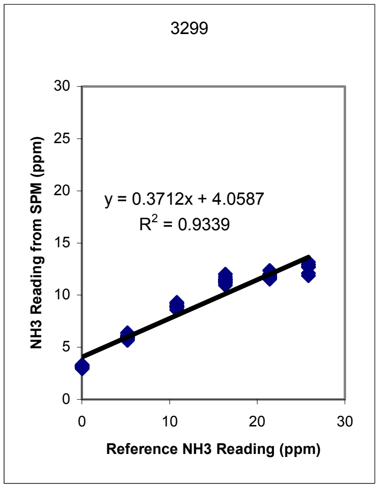


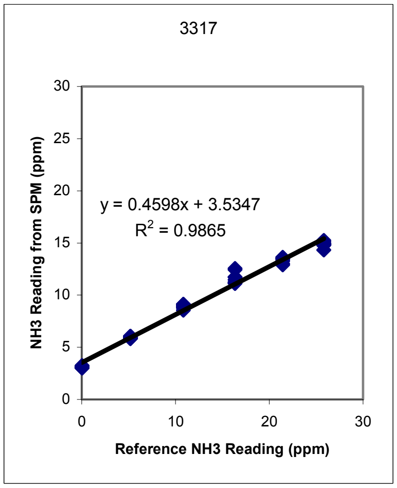


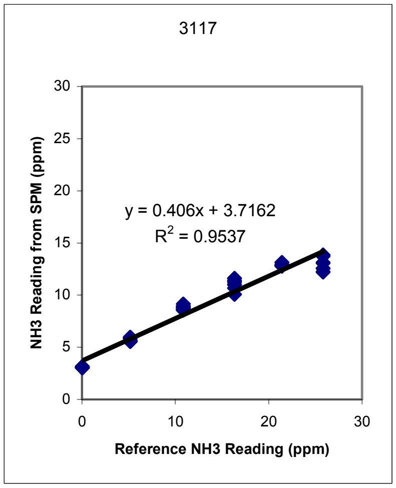


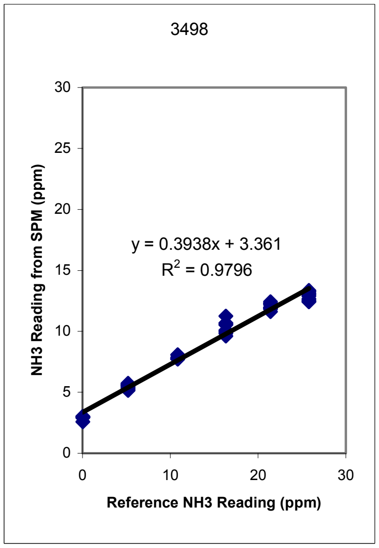


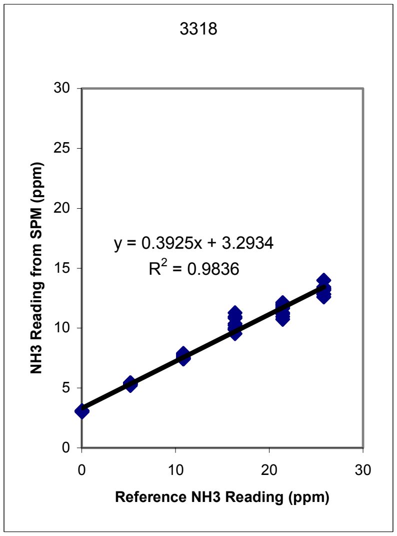
Appendix II. Calibration equations of NH_3 measurement for individual SPM units (continued)

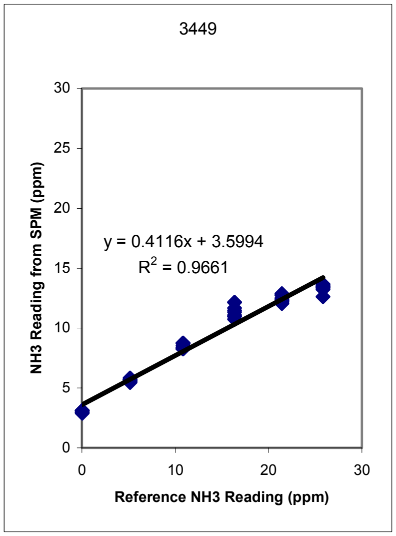


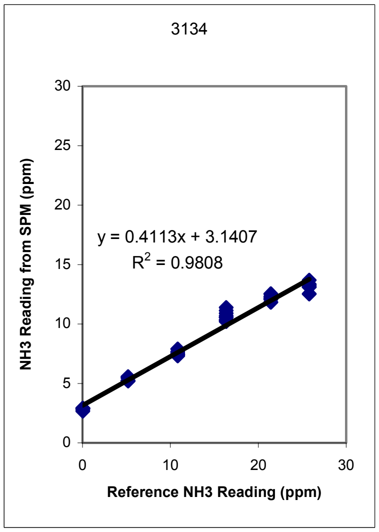


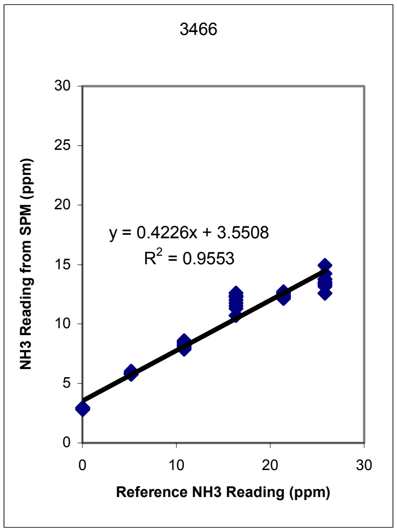




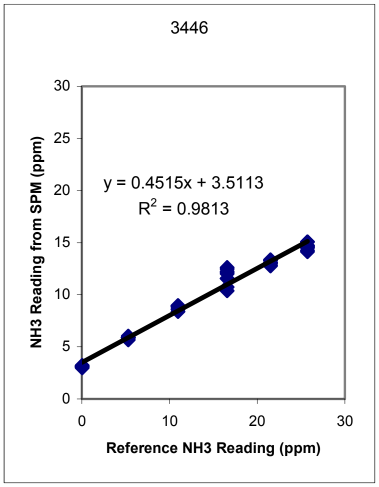


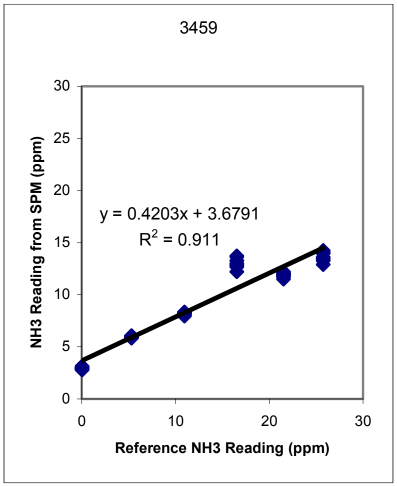


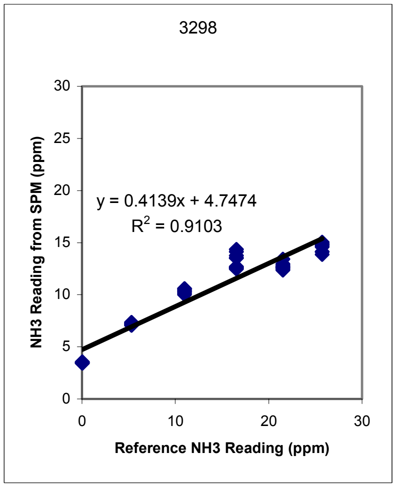


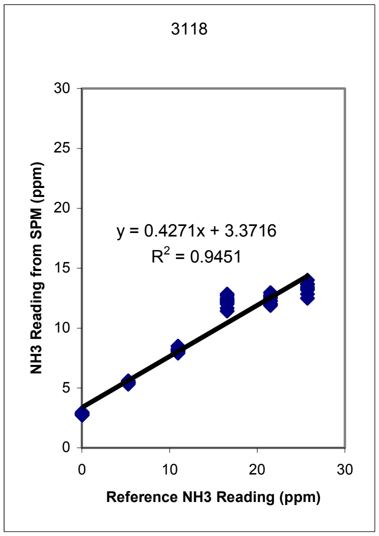


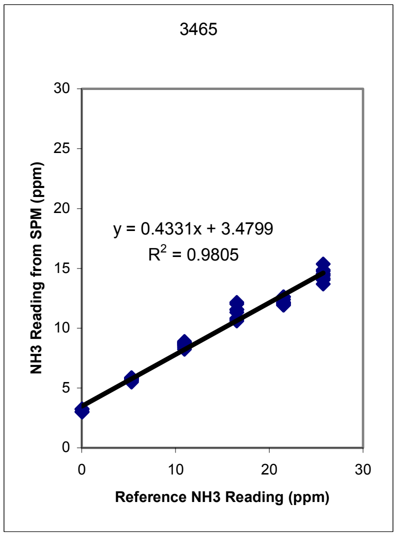
Appendix II. Calibration equations of NH_3 measurement for individual SPM units (continued)

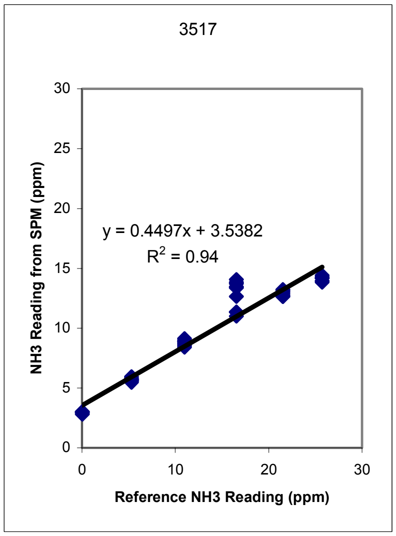


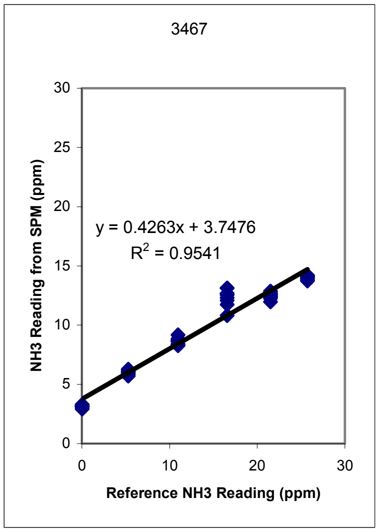


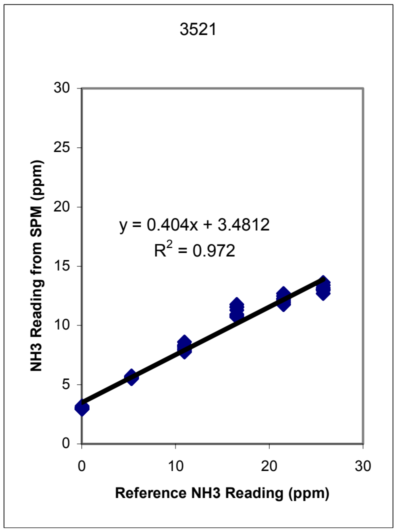


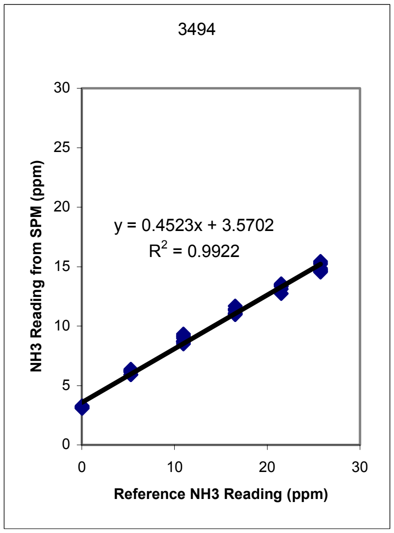




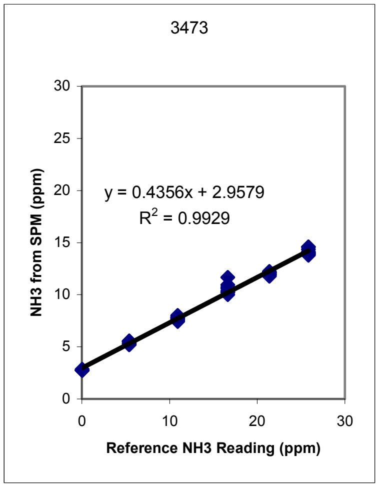


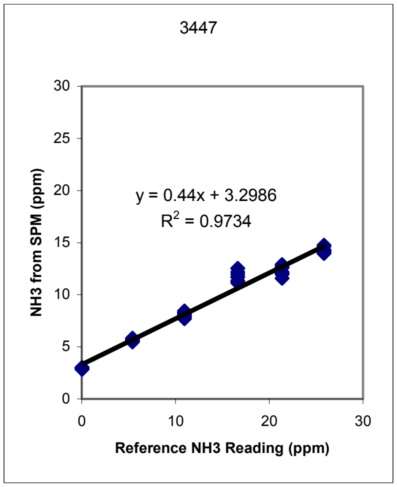


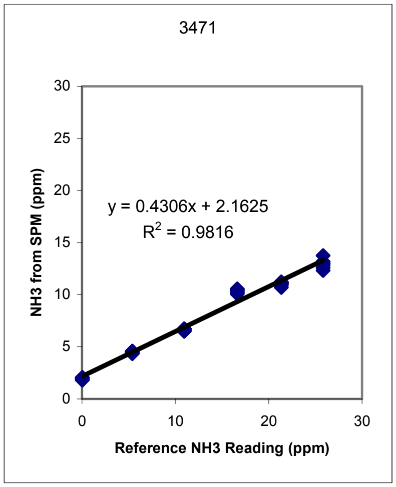


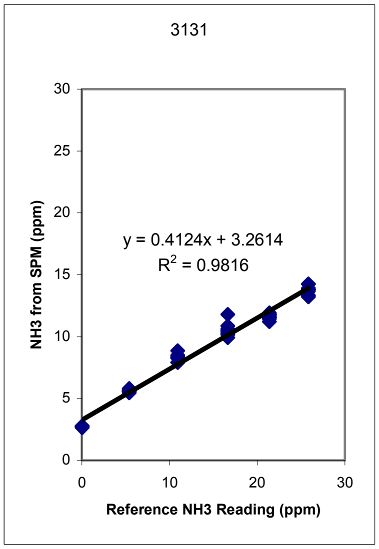


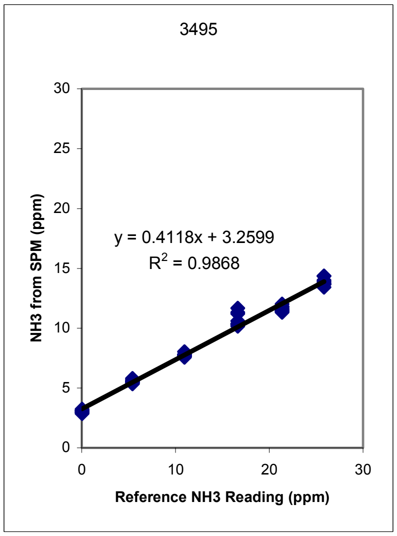
Appendix II. Calibration equations of NH_3 measurement for individual SPM units (continued)

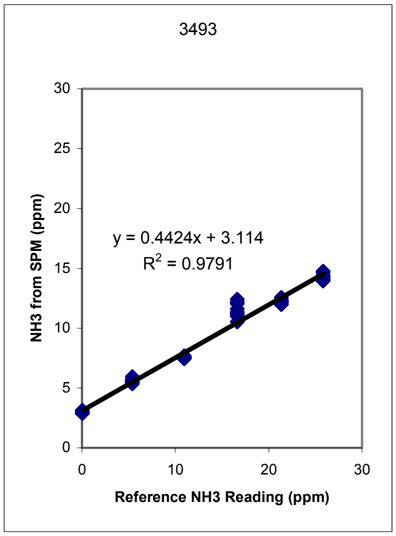


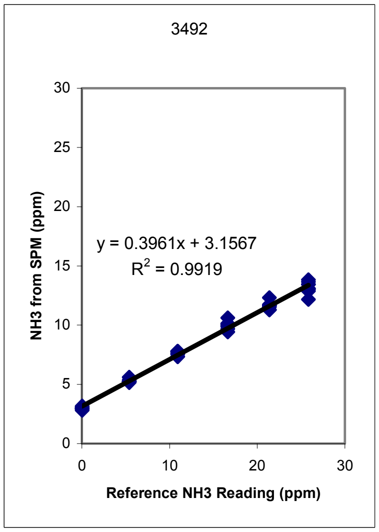


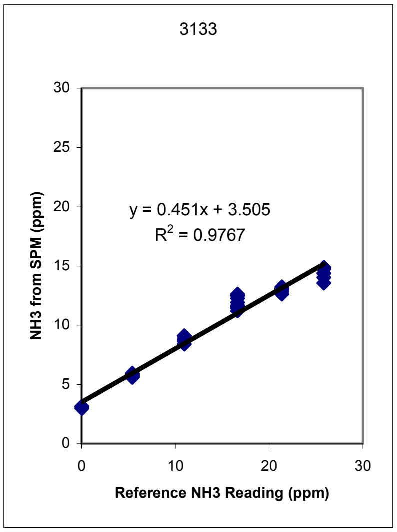


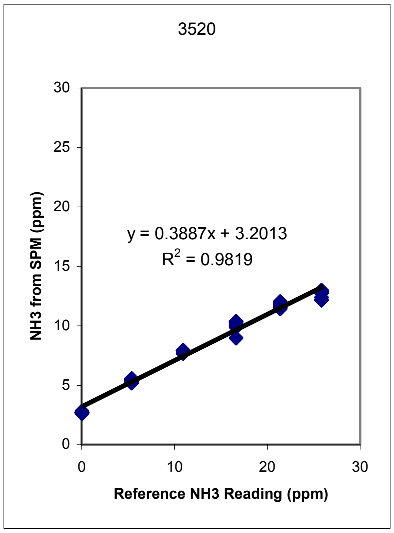




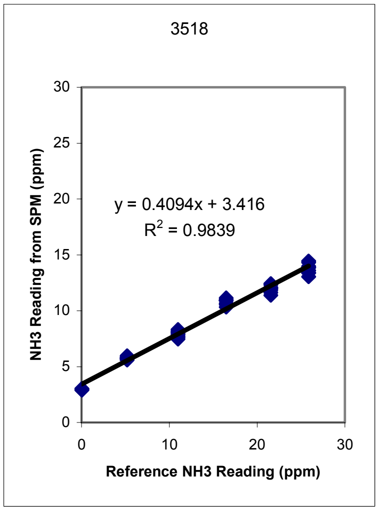








Appendix II. Calibration equations of NH_3 measurement for individual SPM units (continued)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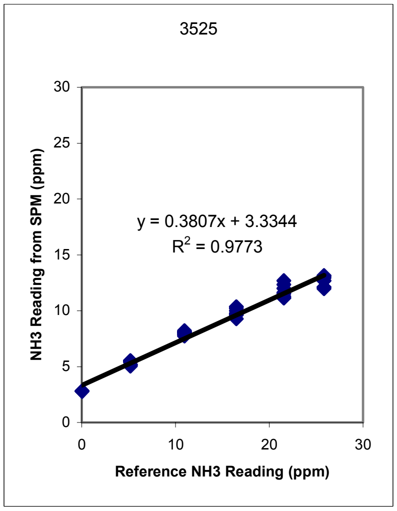
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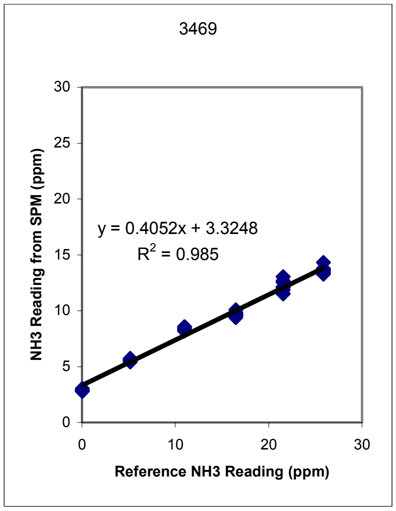
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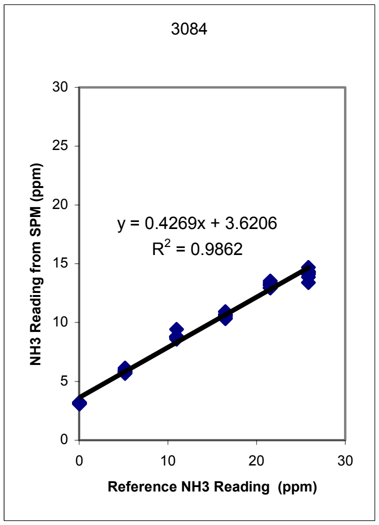
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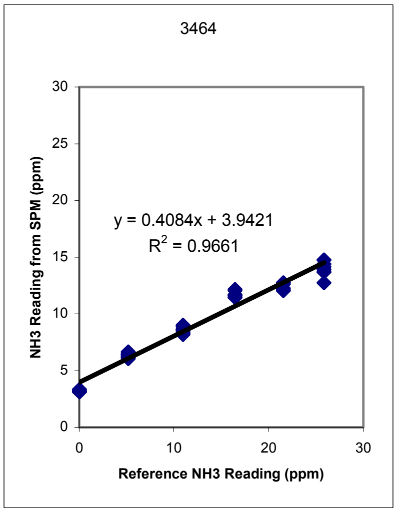
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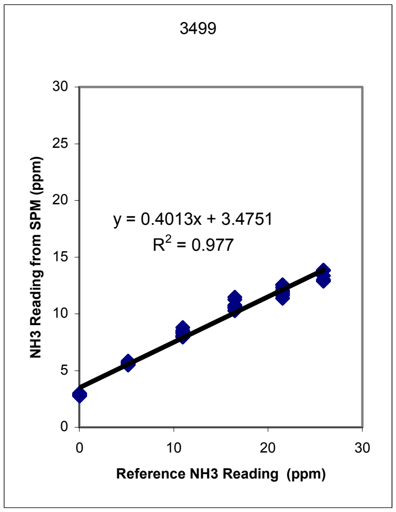
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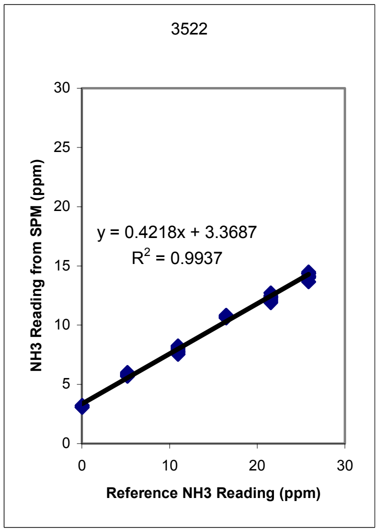
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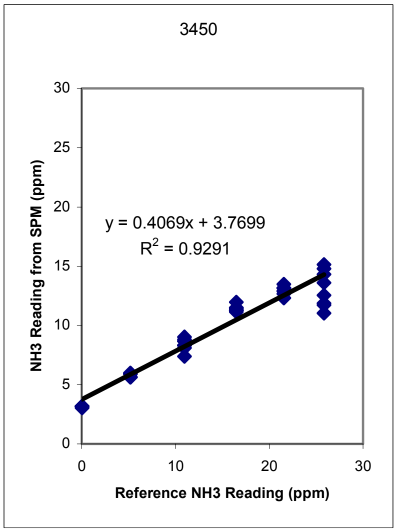
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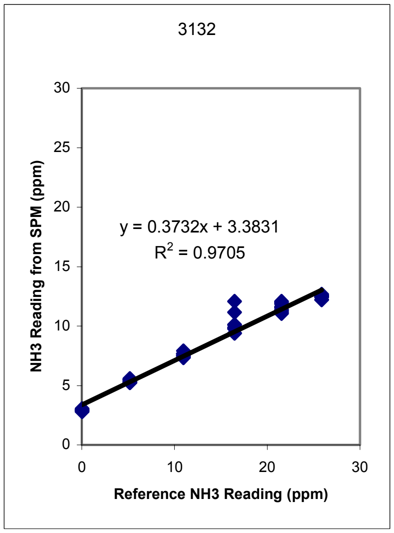
3132

Appendix III Parameters of regression equations used to compensate for the effect of moisture on H_2S readings by Single Point Monitors. The change caused by moisture is expressed as following:

$$\Delta C_{SPM} = a + b \cdot \Delta t_{dp} + c \cdot C_{SPM\_as-is} + d \cdot \Delta t_{dp} \cdot C_{SPM\_as-is}$$

SN	a	b	c	d	R^2
3081	-1.341	-0.022	-0.338	0.0175	0.967
3082	3.992	-0.165	-0.162	0.0138	0.987
3083	3.327	-0.159	-0.307	0.0154	0.938
3085	3.946	-0.153	-0.380	0.0192	0.979
3117	6.906	-0.262	-0.552	0.0230	0.933
3118	0.659	-0.085	-0.724	0.0282	0.973
3131	5.788	-0.222	-0.667	0.0270	0.968
3132	-4.488	0.059	-0.225	0.0129	0.919
3133	7.867	-0.309	-0.668	0.0274	0.961
3134	3.399	-0.137	-0.381	0.0177	0.952
3298	0.560	-0.164	-0.476	0.0244	0.982
3299	2.323	-0.137	-0.070	0.0103	0.969
3317	1.549	-0.105	0.227	0.0028	0.986
3318	9.852	-0.303	-0.890	0.0323	0.980
3446	-1.796	-0.002	-0.375	0.0184	0.940
3447	-6.564	0.088	-0.122	0.0126	0.979
3449	0.296	-0.049	-0.414	0.0171	0.917
3450	-0.769	-0.029	-0.666	0.0269	0.979
3459	-5.209	0.091	-0.115	0.0122	0.970
3461	-1.353	-0.014	-0.418	0.0202	0.974
3464	-5.291	0.065	-0.221	0.0151	0.978
3465	-1.883	0.003	-0.260	0.0152	0.938
3466	8.064	-0.276	-0.454	0.0188	0.870
3467	1.404	-0.109	-0.016	0.0101	0.987
3469	-3.655	0.049	-0.126	0.0117	0.965
3471	5.345	-0.190	-0.588	0.0239	0.924
3473	2.536	-0.131	-1.172	0.0394	0.942
3492	-0.915	-0.027	-0.675	0.0239	0.899
3493	-1.503	-0.029	-0.227	0.0140	0.926
3494	10.616	-0.367	-0.945	0.0346	0.961
3495	3.792	-0.128	-0.172	0.0125	0.927
3496	-0.124	-0.064	-0.359	0.0168	0.934
3497	0.047	-0.064	-0.122	0.0120	0.964
3498	-4.269	0.063	-0.163	0.0116	0.951
3499	-1.494	-0.010	-0.487	0.0209	0.959
3517	-6.382	0.111	-0.233	0.0152	0.949
3518	-3.678	0.036	-0.471	0.0207	0.937
3520	-0.783	-0.053	-0.754	0.0307	0.984
3521	-1.125	-0.031	-0.514	0.0228	0.976
3522	10.238	-0.333	-1.169	0.0386	0.927
3523	-6.199	0.129	-0.061	0.0094	0.959
3524	-2.159	-0.005	-0.711	0.0272	0.967
3525	-2.971	0.001	-0.578	0.0250	0.973

Appendix IV. Parameters of regression equations used to compensate for the effect of moisture on NH_3 readings by Single Point Monitors. The change caused by moisture is expressed as following:

$$\Delta C_{SPM} = a + b \cdot \Delta t_{dp} + c \cdot C_{SPM\_as-is} + d \cdot \Delta t_{dp} \cdot C_{SPM\_as-is}$$

SN	a	b	c	d	R^2
3081	2.886	-0.157	-0.512	0.0336	0.982
3082			Not usable for NH_3 monitor		
3083	1.124	-0.110	-0.614	0.0358	0.989
3084	2.474	-0.152	-0.555	0.0346	0.986
3085	0.060	-0.093	-0.515	0.0337	0.992
3117	-0.495	-0.081	-0.381	0.0308	0.991
3118	2.019	-0.136	-0.882	0.0436	0.989
3131	1.978	-0.134	-0.604	0.0366	0.965
3132	2.402	-0.147	-0.635	0.0371	0.991
3133	4.588	-0.203	-0.825	0.0410	0.982
3134	2.914	-0.153	-0.730	0.0393	0.989
3298			Not usable for NH_3 monitor		
3299	1.254	-0.122	-0.375	0.0316	0.996
3317	2.989	-0.164	-0.671	0.0377	0.993
3318	2.590	-0.148	-0.734	0.0387	0.985
3446	1.559	-0.122	-0.713	0.0379	0.990
3447	1.944	-0.127	-0.867	0.0420	0.979
3448	2.136	-0.110	-0.762	0.0386	0.981
3449	1.947	-0.135	-0.550	0.0344	0.983
3450	-2.107	-0.036	-0.069	0.0235	0.997
3459	0.596	-0.106	-0.519	0.0342	0.995
3461	2.103	-0.143	-0.788	0.0416	0.984
3464	1.481	-0.134	-0.566	0.0357	0.993
3465	-1.367	-0.050	-0.385	0.0305	0.993
3466	-0.038	-0.087	-0.337	0.0290	0.996
3467	0.485	-0.108	-0.559	0.0359	0.991
3469	1.338	-0.117	-0.749	0.0402	0.993
3471	5.039	-0.187	-1.334	0.0534	0.983
3473	2.527	-0.136	-0.680	0.0374	0.979
3492	-2.042	-0.009	-0.095	0.0210	0.964
3493	4.457	-0.192	-0.830	0.0403	0.979
3494	-0.222	-0.079	-0.592	0.0359	0.989
3495	2.606	-0.144	-0.493	0.0321	0.982
3496	1.694	-0.131	-0.600	0.0358	0.989
3497	2.598	-0.162	-0.770	0.040	0.985
3498	0.982	-0.108	-0.748	0.041	0.990
3499	1.789	-0.132	-0.918	0.0442	0.995
3517	0.322	-0.097	-0.647	0.0384	0.990
3518	-1.179	-0.055	-0.396	0.0318	0.993
3520	-2.672	-0.014	-0.458	0.0329	0.975
3521	2.286	-0.149	-0.853	0.0426	0.956
3522	2.831	-0.154	-0.746	0.0389	0.987
3523	-3.063	-0.002	-0.375	0.0306	0.978
3524	3.121	-0.169	-1.019	0.0477	0.987
3525	2.722	-0.154	-0.555	0.0354	0.987