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## Performance of Single Point Monitors for Measuring Aerial Ammonia and Hydrogen Sulfide

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**Abstract.** Performance of 43-44 Single Point Monitors (SPMs) was evaluated for measuring aerial ammonia ( $\text{NH}_3$ , 0-30 ppm) and hydrogen sulfide ( $\text{H}_2\text{S}$ , 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  $\text{NH}_3$  and pulsed-fluorescence analyzer for  $\text{H}_2\text{S}$ . Linear relationships were observed between readings of the SPMs and those of the respective reference analyzer, which were influenced by moisture content or  $t_{dp}$  of the calibration or sample air. Specifically, average  $\text{H}_2\text{S}$  readings by the SPMs were, respectively, 66%, 80%, 87% and 97% of those by the reference analyzer for calibration gas at  $t_{dp}$  of -22 (dry), 9, 13 and 16 °C. In comparison, average  $\text{NH}_3$  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 °C respectively. Coefficient of variation of “as-is” readings among the tested SPMs was up to 15% for  $\text{H}_2\text{S}$  and up to 25% for  $\text{NH}_3$ . 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  $\text{H}_2\text{S}$  readings; however, such equations were not as effective in predicting or correcting  $\text{NH}_3$  readings by the SPMs.

**Keywords.** Animal feeding operation, air quality monitoring, single point monitor, moisture interference

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## Introduction

Air pollutants, such as ammonia (NH<sub>3</sub>), nitrous oxide (N<sub>2</sub>O), methane (CH<sub>4</sub>), hydrogen sulfide (H<sub>2</sub>S), carbon dioxide (CO<sub>2</sub>) and particulate matter (PM), are generally associated with animal feeding operations (AFOs). Ammonia and H<sub>2</sub>S have received particular attention due to their health effects on humans. As the need to determine gas concentrations and emission rates increases, various measurement methods and instruments have evolved. Gas detection tubes have been used to measure NH<sub>3</sub> concentrations from various swine, dairy and broiler facilities (Chung et al., 1996; Zhu et al., 2000; Stowell et al., 2002). Jerome<sup>®</sup> H<sub>2</sub>S analyzers have been used to measure H<sub>2</sub>S concentration in swine, dairy and broiler facilities (Zhu et al., 2000; Stowell et al., 2002) and in beef cattle feedlots (Rhoades et al., 2003). Chemiluminescence NH<sub>3</sub>/nitric oxide (NO) analyzers have been used to measure NH<sub>3</sub> concentrations in both UK and US livestock buildings (Wathes et al., 1997; Demmers et al., 1999; Jacobson et al., 2003). Concentrations of NH<sub>3</sub>, CH<sub>4</sub> and N<sub>2</sub>O in exhaust air from manure storage have been measured with a photoacoustic multi-gas monitor (Hansen et al., 2003) and evaluated with gas detector tubes. A Fourier transform infrared analyzer (FTIR) has also been used to measure emissions of NH<sub>3</sub>, N<sub>2</sub>O and CH<sub>4</sub> from dairy housing (Amon et al., 2001). Hinz and Linke (1998) measured NH<sub>3</sub> concentrations from various livestock buildings with both photoacoustic multi-gas monitor and FTIR spectrometer as a comparison. The authors concluded that deviations in measured NH<sub>3</sub> levels (4-8 ppm range) between the two different devices were negligible ( $r^2 = 0.9287$ ).

Single Point Monitors (SPMs) (Model 7100, Zellweger Analytics, Inc., Lincolnshire, IL) have been used to monitor NH<sub>3</sub> and H<sub>2</sub>S levels in or around 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 a SPM include its relatively low cost (~\$7,000), portability for field application, and ability to detect relatively low gas concentrations. The major drawbacks and concerns about 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 also is largely unknown. Nonetheless, SPMs have 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<sub>2</sub>S by the Minnesota Pollution Control Agency (MPCA).

The objective of this study was to evaluate and characterize operational performance of SPMs with regard to measurement uncertainty, repeatability, interference with moisture and interchangeability in measuring aerial NH<sub>3</sub> and H<sub>2</sub>S under laboratory and field conditions. Potential effect of ambient temperature on H<sub>2</sub>S readings was also checked.

## Materials and Methods

### *Laboratory Evaluation System*

A laboratory evaluation and verification system was set up to evaluate SPMs for the anticipated measurement ranges of NH<sub>3</sub> and H<sub>2</sub>S (figure 1). Range span for these SPMs is set by inserting a "chem-key", which adjusts measurement time and interval according to a factory-set algorithm. The range of chem-keys for NH<sub>3</sub> 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<sub>2</sub>S 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<sub>3</sub> and H<sub>2</sub>S, respectively. Calibration gases at various known concentrations were simultaneously introduced to the SPMs and the respective reference analyzer.

A chemiluminescence NH<sub>3</sub>/NO analyzer (Model 17C, Thermo Environmental Instruments, Franklin, MA) and a pulsed-fluorescence H<sub>2</sub>S/SO<sub>2</sub> analyzer (Model 450TCL, TEI) were used as the reference analyzers, with their measurement ranges set at 0-30 ppm NH<sub>3</sub> and 0-100 ppb H<sub>2</sub>S, respectively. The NH<sub>3</sub>/NO analyzer uses an external vacuum pump to create a sample flow rate of 0.6

LPM. The H<sub>2</sub>S/SO<sub>2</sub> 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).

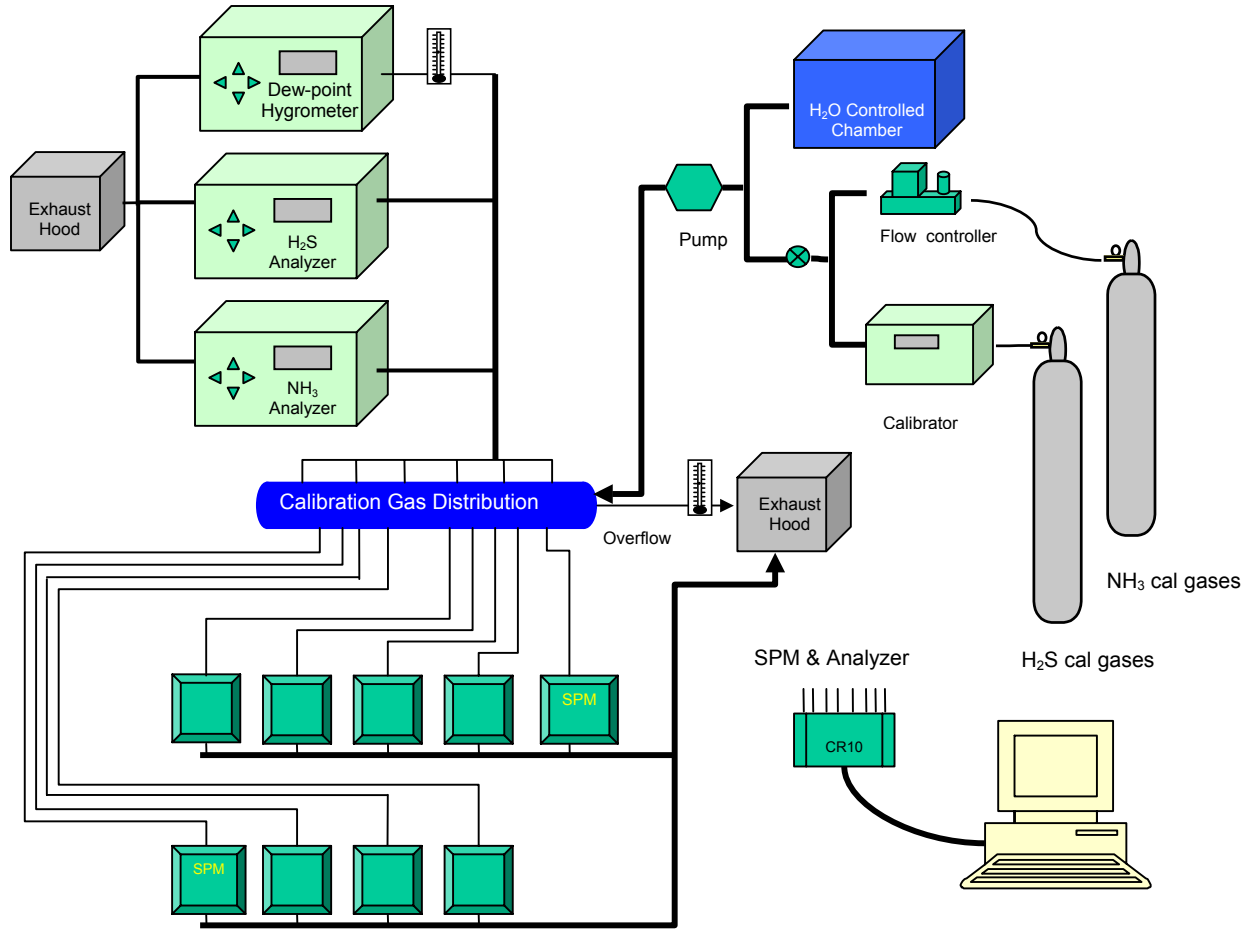


Figure 1. A schematic representation of the lab system setup for Single Point Monitor (SPM) evaluation.

The calibration gas distribution system consisted of a Teflon<sup>®</sup> 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<sup>®</sup> 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.

Analog outputs from the SPMs (4–20 mA) and the analyzers (0–1 VDC) were sampled at 2-s intervals and stored as either 1-min averages (H<sub>2</sub>S test) or 3-s averages (NH<sub>3</sub> 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<sub>2</sub>S (+N<sub>2</sub> balance, ± 2% accuracy) and 233 ppm NH<sub>3</sub> (+air balance, ± 2% accuracy) (Matheson Tri-Gas Inc., La Porte, TX) were used to generate various gas concentrations used for the lab evaluation.

### *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 ( $t_{dp}=-22^{\circ}\text{C}$ ) H<sub>2</sub>S calibration gas at nominal concentrations of 0, 10, 20, 40, 60 or 70 ppb. Selection of a concentration was randomized in the testing sequence.

Because the dynamic diluting calibrator was unable to dilute 233 ppm NH<sub>3</sub> 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<sub>3</sub> calibration gas cylinder to control the desired NH<sub>3</sub> gas flow rate, while the dynamic diluting calibrator was used to generate dry zero air. The NH<sub>3</sub> gas and dry zero air were mixed to achieve the concentrations of 0, 5, 10, 15, 20 or 25 ppm. Selection of a 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<sub>2</sub>S gas at concentrations up to 90 ppb. Four updates were collected for each H<sub>2</sub>S level, with the first update discarded in data analysis. For the dry H<sub>2</sub>S calibration air evaluation, each group of tests took 6 hours, and the 44 units were tested in five days. According to the manufacturer, the H<sub>2</sub>S chemcassette tape expires in 30 days once the sealed package has been 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 °C storage room.

The SPMs updated readings every 15 seconds when monitoring NH<sub>3</sub> 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 six concentrations, completed in one hour, before switching to the next group. The NH<sub>3</sub> chemcassette tape expires 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.

### *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 °C (48, 55 or 61°F). Nominal concentrations of 0, 12, 35 or 70 ppb H<sub>2</sub>S and 0, 5, 15 or 25 ppm NH<sub>3</sub> were chosen for the tests.

The desired gas concentration levels were achieved by proportionally mixing the dry calibration gas with the relatively constant  $t_{dp}$  fresh air drawn from 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 2°C for NH<sub>3</sub> and 0.5°C for H<sub>2</sub>S. As with the dry gas evaluation, SPMs were tested in five groups, with the H<sub>2</sub>S test finished in 10 days and the NH<sub>3</sub> test finished in 4 days.

### *Lab Evaluation - Temperature Effect*

The SPMs have a factory-recommended operating temperature range of 0 to 40°C. 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 30°C ambient temperature. Dry H<sub>2</sub>S calibration gas ( $t_{dp}=-22^{\circ}\text{C}$ ) at nominal levels of 0, 10 or 70 ppb was used in the evaluation that was completed in two days.

## Field Evaluation

Eight SPMs were randomly selected to monitor NH<sub>3</sub> gas at a poultry production site on October 17<sup>th</sup>, 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 quit 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 4°C cold room and were re-used in the subsequent test.

Six SPMs were then used to monitor NH<sub>3</sub> 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 a restriction in available flow rate, SPMs in groups of three units were appended to an existing air quality sampling/monitoring system for this study. 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<sub>2</sub>S concentration near the swine facility between November 19 and Dec 5, 2003. Air sampled 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-min intervals using the same CR10 module as used in the lab tests.

## Data Analysis

Two potential factors contribute to the discrepancy between the SPM reading and the reference analyzer reading, i.e., the inherent resolution 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:

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

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

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

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

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

Statistical analysis was performed using the SAS GLM procedure to detect 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<sub>2</sub>S, the pairs were formed at 15-minute intervals. Three recordings from the reference analyzer during the 15-min sampling interval immediately prior to the corresponding SPM 15-min update were selected and averaged as the corresponding reference reading. For NH<sub>3</sub>, 15-s data were averaged into 1-min data before being 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.

## Results and Discussion

### 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<sub>2</sub>S. Means and standard deviations (S.D.) of H<sub>2</sub>S readings by the SPMs and the reference analyzer are shown 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.

Table 1. Summary of Single Point Monitor (SPM) readings for various calibration H<sub>2</sub>S concentrations and dew-point temperatures in laboratory conditions.

Dew-point Temperature (°C)	Reference Concentration (ppb)	H <sub>2</sub> S Readings by SPM and Statistics				
		Mean (ppb)	Within Units		Among Units	
			S.D.	C.V. (%)	S.D.	C.V. (%)
-22	0.00	0.97	0.99	101.88	0.74	76.26
	9.52	8.52	0.50	5.84	1.03	12.07
	19.54	15.73	0.62	3.93	1.84	11.67
	39.33	30.82	0.81	2.62	3.21	10.42
	59.58	40.34	1.76	4.36	4.24	10.50
	69.88	47.23	1.47	3.11	4.38	9.27
9	0.35	1.07	0.17	15.90	1.34	125.3
	11.59	11.02	0.36	3.31	1.49	13.55
	35.87	29.49	0.91	3.08	4.22	14.31
	66.8	54.80	1.69	3.09	7.25	13.23
13	0.37	0.00	0.00	N/A	0.00	N/A
	11.48	11.56	0.37	3.22	1.35	11.72
	35.24	31.59	0.91	2.89	3.78	11.96
16	65.26	57.33	1.59	2.77	6.76	11.79
	0.36	0.12	0.21	177	0.26	214.58
	11.28	12.48	0.52	4.20	1.77	14.15
	34.77	35.18	1.11	3.15	5.42	15.40
	64.71	63.24	2.00	3.16	7.34	11.61`

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

Comparisons in H<sub>2</sub>S readings by the SPMs and the reference analyzer at the tested t<sub>dp</sub> are shown in figure 2. Generally, SPM readings were lower 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<sub>2</sub>S readings at each t<sub>dp</sub> level were of the following forms:

$$\text{For } t_{dp} = -22^{\circ}\text{C}, [\text{H}_2\text{S, ppb}]_{\text{SPM}} = 0.655[\text{H}_2\text{S, ppb}]_{\text{Ref}} + 2.36 \quad (R^2 = 0.9931) \quad [5]$$

$$\text{For } t_{dp} = 9^{\circ}\text{C}, [\text{H}_2\text{S, ppb}]_{\text{SPM}} = 0.802[\text{H}_2\text{S, ppb}]_{\text{Ref}} + 1.11 \quad (R^2 = 0.9996) \quad [6]$$

$$\text{For } t_{dp} = 13^{\circ}\text{C}, [\text{H}_2\text{S, ppb}]_{\text{SPM}} = 0.8739[\text{H}_2\text{S, ppb}]_{\text{Ref}} + 0.57 \quad (R^2 = 0.9990) \quad [7]$$

$$\text{For } t_{dp} = 16^{\circ}\text{C}, [\text{H}_2\text{S, ppb}]_{\text{SPM}} = 0.9734[\text{H}_2\text{S, ppb}]_{\text{Ref}} + 0.72 \quad (R^2 = 0.9991) \quad [8]$$

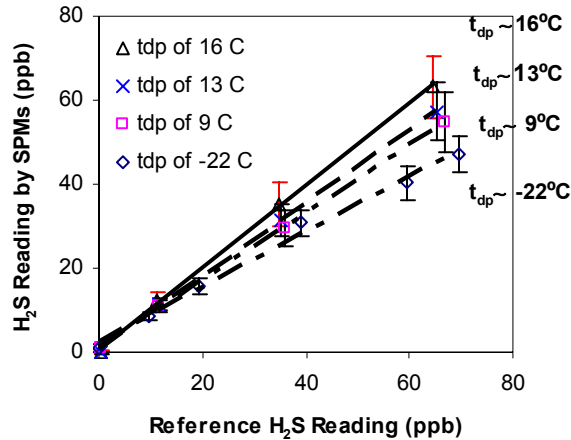


Figure 2. Comparison of H<sub>2</sub>S measurements by SPMs (43 units) and the reference analyzer for the selected concentrations of calibration gas at dew-point temperature ( $t_{dp}$ ) of -22 °C, 9 °C, 13 °C and 16 °C. The vertical bars of the data points represent standard deviation.

Hence, when using SPMs to measure the *change* in H<sub>2</sub>S concentration under dry air condition ( $t_{dp} = -22^{\circ}\text{C}$ ), the result will be about 66% of that measured using the reference analyzer. Under moist air conditions with  $t_{dp}$  of 9, 13 and 16°C, the result will be about 80%, 87% and 97%, respectively, of the reference values.

### Lab Evaluation - Ammonia

A total of 45 units were evaluated for NH<sub>3</sub> 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 test conditions with this gas.

Comparisons in NH<sub>3</sub> 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<sub>3</sub> measurement by the SPMs and the reference analyzer under each humidity or  $t_{dp}$  level had the following forms:

$$\text{For } t_{dp} = -22^{\circ}\text{C}, [\text{NH}_3, \text{ppm}]_{\text{SPM}} = 0.4182[\text{NH}_3, \text{ppm}]_{\text{Ref}} + 3.46 \quad (R^2 = 0.9866) \quad [9]$$

$$\text{For } t_{dp} \approx 9^{\circ}\text{C}, [\text{NH}_3, \text{ppm}]_{\text{SPM}} = 0.8559[\text{NH}_3, \text{ppm}]_{\text{Ref}} + 2.01 \quad (R^2 = 0.9494) \quad [10]$$

$$\text{For } t_{dp} \approx 13^{\circ}\text{C}, [\text{NH}_3, \text{ppm}]_{\text{SPM}} = 1.0186[\text{NH}_3, \text{ppm}]_{\text{Ref}} + 3.72 \quad (R^2 = 0.8749) \quad [11]$$

$$\text{For } t_{dp} \approx 16^{\circ}\text{C}, [\text{NH}_3, \text{ppm}]_{\text{SPM}} = 1.7818[\text{NH}_3, \text{ppm}]_{\text{Ref}} + 2.37 \quad (R^2 = 0.9222) \quad [12]$$

Hence when using SPMs to measure the *change* in NH<sub>3</sub> concentration under  $t_{dp}$  of -22 (dry air), 9, 13 and 16°C, the result will be, respectively, 42%, 86%, 102% and 178% of the reference values.

Table 2. Summary of Single Point Monitor (SPM) readings for various calibration NH<sub>3</sub> concentrations and dew-point temperatures in laboratory conditions.

Dew-point Temperature (°C)	Reference Concentration (ppm)	NH <sub>3</sub> Readings by SPM and Statistics				
		Mean (ppm)	Within units		Among units	
			S.D.	C.V. (%)	S.D.	C.V. (%)
-22	0.03	2.96	0.08	2.70	0.24	8.16
	5.24	5.73	0.13	2.19	0.48	8.41
	10.93	8.32	0.21	2.55	0.70	8.42
	16.50	11.08	0.46	4.11	0.92	8.34
	21.48	12.39	0.29	2.34	0.83	6.73
	25.81	13.75	0.40	2.88	0.72	5.25
8.5-10	0.00	0.02	0.00	0.00	0.06	396
	5.53	8.31	0.33	3.97	1.52	18.28
	13.84	15.77	1.22	7.71	1.47	9.31
	23.71	20.81	1.59	7.64	2.72	13.06
12.6-14	-0.02	0.01	0.00	6.84	0.07	958
	5.68	12.30	0.5	4.06	2.10	17.06
	13.83	21.69	1.00	4.61	2.86	13.18
	23.25	24.41	1.15	4.73	2.30	9.41
16-17	0.03	0.09	0.02	22.90	0.42	453
	5.49	14.70	0.66	4.51	2.47	16.81
	9.54	22.01	1.00	4.57	3.53	16.05
	13.62	23.77	1.08	4.53	5.91	24.85

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

The seemingly quadratic relationships between the SPM and the reference readings of NH<sub>3</sub> under moist conditions as shown in figures 3b-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<sub>3</sub> concentration required relatively larger proportion of the dry calibration gas, which resulted in somewhat less humidity or a 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 3b-d were collected under progressively declining  $t_{dp}$  of the sample air (10.2–8.6°C in figure 3b; 14.4–12.6°C in figure 3c; 17.6–16.7°C in figure 3d). The linear relationship between the SPM and the reference readings at dry conditions is shown in figure 3a. The actual  $t_{dp}$  values were used in subsequent analysis of moisture interference on NH<sub>3</sub> readings of SPMs (discussed later).

Less than 43 data points were involved in calculating the average readings for the last two points of figure 3c-d. Specifically, when  $t_{dp}$  was about 13°C (figure 3c), 20% of the SPMs displayed the “30<sup>+</sup>” out of range error at a reference value of 24 ppm NH<sub>3</sub>. When  $t_{dp}$  was about 16°C (figure 3d), the “30<sup>+</sup>” out of range error occurred to 90% of the SPMs at >14 ppm NH<sub>3</sub>, thereby resulting in a shorter curve.



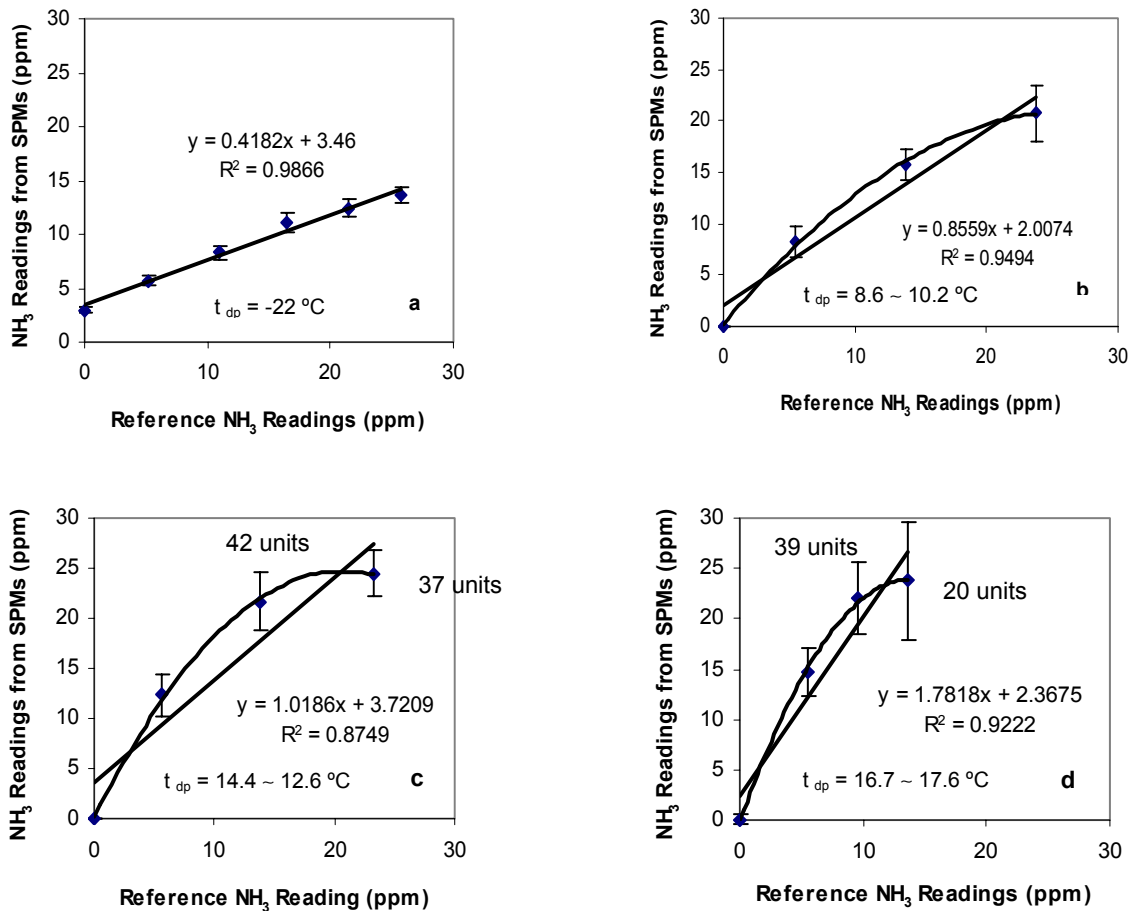


Figure 3. Comparison of NH<sub>3</sub> measurements by SPM units and reference analyzer at selected concentrations of calibration gas and dew-point temperature ( $t_{dp}$ ) of a)  $-22\text{ }^{\circ}\text{C}$ ; b) 10.2, 9.9, 9.3, 8.6  $^{\circ}\text{C}$  progressively; c) 14.4, 14.0, 13.5, 12.6  $^{\circ}\text{C}$  progressively; and d) 17.6, 17.3, 17.0, 16.7  $^{\circ}\text{C}$  progressively. The vertical bars represent standard deviation. Values were averaged from 45 units unless otherwise labeled.

### Temperature Effect

Hydrogen sulfide concentrations measured by four SPMs at ambient temperatures of 10, 20 and 30  $^{\circ}\text{C}$  are presented in table 3. Significant differences were observed at zero ppb ( $P < 0.001$ ) but not at 10 or 70 ppb. However it was unclear whether the significant differences at zero air was caused by the temperature effect or a result of the inherent uncertainty of readings or detection at zero level.

### 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. Examples of comparative results before and after correction of the SPM readings under humid conditions ( $t_{dp} = 8 \sim 16\text{ }^{\circ}\text{C}$ ) are plotted in figure 4 (H<sub>2</sub>S) and figure 5 (NH<sub>3</sub>). The corrected H<sub>2</sub>S concentrations (from equation 5) generally showed a linear trend ( $R^2 > 0.99$ ), having a slope close to 1 and an intercept less than 1 (figure 4). In comparison, the corrected NH<sub>3</sub> concentrations had larger variability, as evidenced by the lower  $R^2$  value of 0.92 (vs. 0.99 for H<sub>2</sub>S).

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

H <sub>2</sub> S Concentration (ppb)	Ambient Temperature (°C)		
	10	20	30
0	0.1 ± 0.2 *	1.5 ± 0.6 *	2.4 ± 0.3 *
10	7.8 ± 0.2	8.1 ± 0.3	7.9 ± 0.3
70	38.9 ± 1.2	38.0 ± 0.4	38.4 ± 2.8

\*Significant at P<0.001

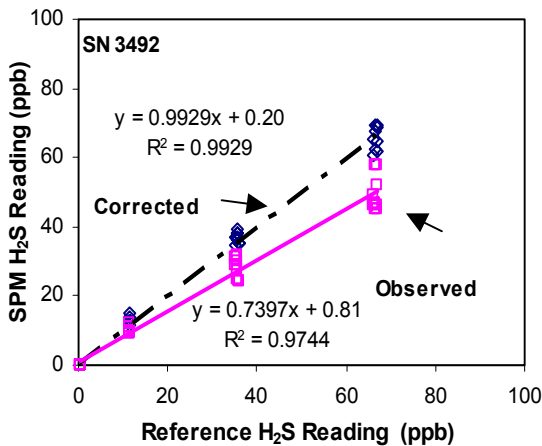


Figure 4. Comparison of H<sub>2</sub>S concentrations (SN 3492) before and after correction for moisture content in the sample air.

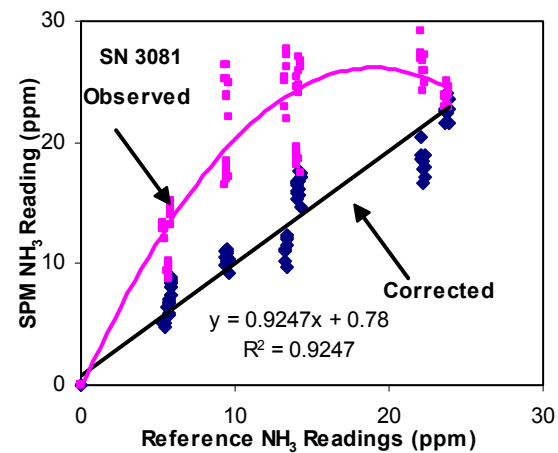


Figure 5. Comparison of NH<sub>3</sub> concentrations (SN 3081) before and after correction for moisture content in the sample air.

### Interchangeability and Overall Regression for Hydrogen Sulfide

Interchangeability among the SPMs was examined under the dry air testing conditions for H<sub>2</sub>S gas. Because the usefulness of individual regressions for NH<sub>3</sub> gas was marginal, unit interchangeability was not investigated. Since readings by all SPMs exhibited linear relationships with 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 of 0.6–0.7, 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<sub>2</sub>S 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,

$$\Delta\text{SPM}_{\text{H}_2\text{S}} = 0.701 - 0.0824 \cdot \Delta t_{\text{dp}} - 0.374 \cdot \text{SPM}_{\text{H}_2\text{S}} + 0.0185 \cdot \Delta t_{\text{dp}} \cdot \text{SPM}_{\text{H}_2\text{S}} \quad (R^2 = 0.9036) \quad [13]$$

The H<sub>2</sub>S concentrations predicted with the *overall* equation and with the *individual* regression equations were compared against the reference values and are plotted in figure 6. The *individual* correctional regression equations gave appreciably better prediction results than the *overall* equation.

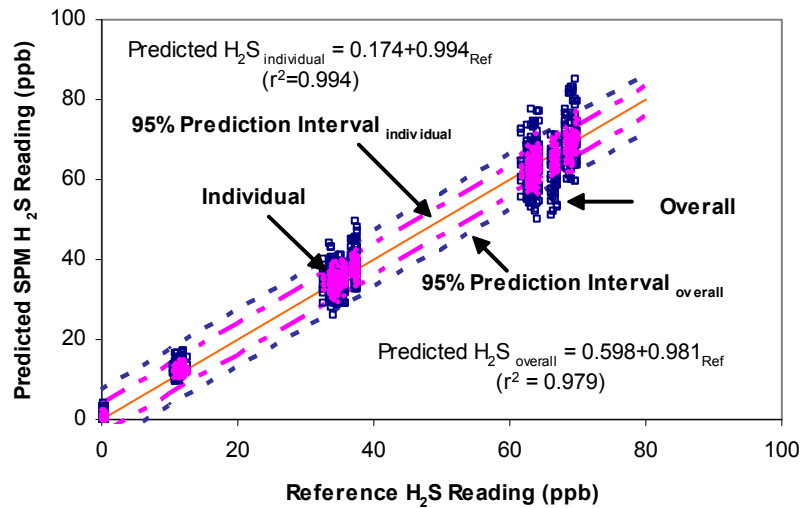


Figure 6. Corrected H<sub>2</sub>S readings with *overall* regression equation vs. *individual* regression equations, and the respective 95% prediction intervals.

### Field Evaluation

#### Hydrogen Sulfide

More than 4000 observations were collected at  $t_{dp}$  of -10 to 8 °C, with median dew-point temperature around zero. Most (68%) of the measured H<sub>2</sub>S 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 SPMs' H<sub>2</sub>S readings 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<sub>2</sub>S readings to reference values during 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 <sup>2</sup>	Slope	R <sup>2</sup>	Slope	R <sup>2</sup>
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	<b>0.697</b>	0.980	<b>0.995</b>	0.949	<b>0.973</b>	0.954
Standard Deviation	<b>0.032</b>	0.002	<b>0.079</b>	0.008	<b>0.050</b>	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 ( $\pm 0.079$  S.D.,  $R^2=0.95$ ) of the reference values, and the overall corrected readings were 0.973 ( $\pm 0.050$  S.D.,  $R^2=0.95$ ) of the reference values. Hence, results in table 4 show that H<sub>2</sub>S readings by SPMs can be corrected with the overall regression equation derived from lab evaluation to achieve > 90% agreement with the reference values.

### 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<sub>3</sub> concentrations from five 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	<b>4.0</b>	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	<b>4.0</b>	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	<b>3.8</b>	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	<b>3.9</b>	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	<b>3.9</b>	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	<b>4.0</b>	4.7	3.0	5.0	4.0	5.2	4.5	5.0	3.5			5.3	4.0
18:18	<b>3.9</b>	4.6	2.8	4.9	3.7	5.1	4.3	4.9	3.4			5.1	3.7
19:18	<b>3.9</b>	4.8	3.0	5.1	3.9	5.2	4.3	5.0	3.5			5.8	4.5
Mean	<b>3.9</b>	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  $P < 0.05$

Table 6. Field evaluation of SPM readings for NH<sub>3</sub> measurement at a swine production site

Serial Number	Hours of operation	Concentration range (ppm)	$t_{dp}$ range (°C)	As-is		Corrected	
				Slope	R <sup>2</sup>	Slope	R <sup>2</sup>
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 can be established; DC = duty cycle; Slope is between SPM and reference readings

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<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub> measurement, or the chem-cassette tape had partially lost sensitivity due to aging.

## Conclusions

Operational performance of Single Point Monitors (SPMs) for measuring aerial NH<sub>3</sub> and H<sub>2</sub>S levels was evaluated under laboratory and some field conditions. The following conclusions were drawn.

- SPMs show weak interchangeability, especially for NH<sub>3</sub>. Hence individual calibration and correction is recommended.
- Moisture content in the sample air elevates gas concentration readings by the SPM units. 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 H<sub>2</sub>S gas, achieving 97% agreement with the reference value. In comparison, such compensation was less effective for NH<sub>3</sub> measurement.

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