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## **Uncertainty in ammonia flux measurement systems**

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**Abstract.** *Uncertainty analysis was performed on an ammonia sampling and analyzing system by using the first order Taylor series techniques. The system included analyzers, mass flow controllers, calibration gases, and analog outputs. The uncertainty was found to be 9.4% when measuring a 40 ppm ammonia stream with a 50ppm span. Uncertainty analysis was performed with a higher purity gas and a higher quality (lower uncertainty) flow meter to determine the reduction in uncertainty of the system. The uncertainty of the higher quality gas and flow meter were reduced to 8.3% at 40 ppm with a 50 ppm span. The overall uncertainty reduction comes however with increased costs due to instrumentation and quality control.*

**Keywords.** Uncertainty, ammonia, flux chamber, sensitivity, equipment performance, air quality, air pollution

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## Introduction

Scientists, engineers, and policy makers must understand the reliability of air quality data. In particular scientists and engineers use the reliability of data in the determining of emissions. The data must be reported with its uncertainty limits so that practitioners can understand and use what was learned from the study. Policy makers must understand the credibility of the data in order to make sound policy decisions.

One method of showing the reliability of data is by reporting the uncertainty. Uncertainty is defined as the interval about the measurement or result that contains the true value for a given confidence interval (ASME, 1998). Uncertainty arises as a result of random errors. Measurement uncertainty may be grouped into two main categories: those evaluated by statistical methods and those evaluated by other means. These groups are often referred to as type A and type B, respectively.

An error is defined as the difference between an individual result and the true value (Eurachem/Citac, 2000). Errors cannot be known exactly. A system may have a large uncertainty and a small random error value. For this reason, statistical distribution is often applied to a collection of errors. Three types of error are involved in measurement systems. Random errors arise from unpredictable variations in the quantity measured. These errors give rise to variations in repeated observations of a measurand. Systematic errors arise from factors that create a shift in the measured quantity from the actual quantity. Systematic errors are independent of the number of observations. Systematic errors may be constant over a range or vary in a predictable manner. The third type of error, spurious error, is an error which invalidates the measurement. This error arises from instrument malfunction or human error. Bias is different from uncertainty in that bias is a result of systematic error and can be corrected through calibration. A correction factor is often used to correct for biases.

Every engineering system has uncertainty associated with it. In gas sampling, uncertainty is often associated with instrumentation and flow. Current focus at the Center of Agricultural Air Quality Engineering and Science (CAAQES) at Texas A&M University is the development of an uncertainty budget for the gas sampling equipment. The uncertainty budget may be used to define areas of improvement in instrumentation. The objective of this paper is to perform an instrumentation uncertainty analysis of a sampling setup used to measure ammonia emissions. The paper does not provide system uncertainty which includes the uncertainty associated with removing bias from the chamber and lines used to convey the gas.

## Background

Flux chambers have been used by several researchers to determine gaseous emissions. Kienbusch developed a user's guide (1986) for the use of the chamber. The chamber is the form of a continuously stirred reactor. In CAAQES's ammonia ( $\text{NH}_3$ ) emission protocol, the flux chamber method involves pumping zero air into the chamber at a flow rate of 7 L/min. Zero air is a form of purified air such that no detectable ammonia is present in the incoming gas stream. The chamber is vented to the atmosphere with 2 L/min extracted by a Teflon vacuum pump to the sensor. Zero air is generated with a zero air generator (Model 737-12, AADCO Instruments, Village of Cleaves OH). A chemiluminescence analyzer (Model 17C, Thermo Corp., Franklin MA) is used to measure the concentration of ammonia in the chamber. The sampling setup is presented in figure 1.

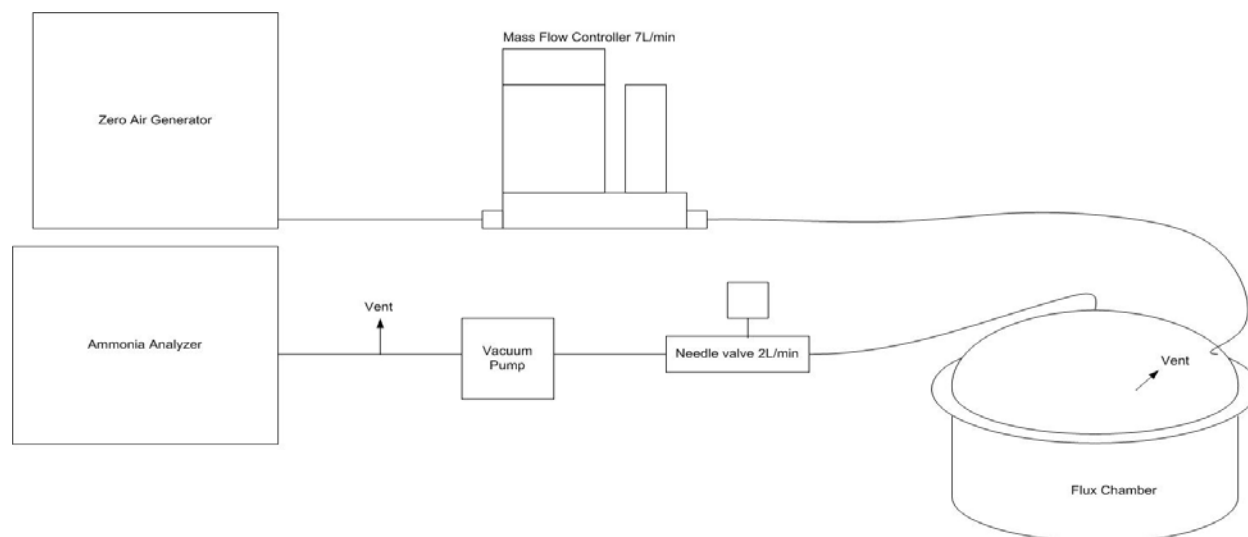


Figure 1. Ammonia analyzer setup

The chemiluminescence analyzer measures the luminescence produced by reacting nitric oxide (NO) with ozone (O<sub>3</sub>). The reaction produces light which is directly proportional to the concentration of NO.



Nitrogen oxides (NO<sub>x</sub>) are converted to nitric oxide in a molybdenum converter heated to approximately 325°C. Total nitrogen (N<sub>t</sub>) is converted to nitric oxide in a stainless steel converter heated to approximately 750°C. The concentration for NO, NO<sub>x</sub>, and N<sub>t</sub> are multiplexed within the analyzer to obtain the concentrations of NH<sub>3</sub> and nitrogen dioxide (NO<sub>2</sub>). To obtain the NH<sub>3</sub> concentration, the NO<sub>x</sub> concentration is subtracted from the N<sub>t</sub> concentration. To obtain the NO<sub>2</sub> concentration, the NO concentration is subtracted from the NO<sub>x</sub> concentration. The analyzer sequentially measures the NO, NO<sub>x</sub>, and N<sub>t</sub> concentrations.

Calibration of the chemiluminescence analyzer is performed on a weekly basis. The Standard operating procedure used to calibrate is outlined in the 17C Instruction manual (Thermo, 2001). In the procedure, the zero point is calibrated first, followed by each of the individual calibration gases. Each calibration gas (NO, NO<sub>2</sub>, and NH<sub>3</sub>; Praxair, Los Angeles CA) has a concentration of approximately 50 ppm and an uncertainty of 2%. Each gas is balanced in nitrogen. When calibrating the chemiluminescence analyzer, several constants are set. The equations used by the analyzer are presented below. In each case, the analyzers are single point calibrated at 80% of the span (maximum set point) onsite with each piece of equipment running for at least 24 hours before calibration. Each calibration stage is run until the values have stabilized for more than 10 consecutive readings. At least 20% zero air is input into the analyzer when calibrating. This allows oxygen to enter the converters to allow the reactions to take place. Multipoint calibrations are completed before and after each sampling venue or once per month (whichever is less). The multipoint calibration is performed using concentrations of 20%, 40%, 60%, and 80% of the span.

$$NO = a_1 * x_{NO} - b_1 + \varepsilon_1 \quad (2)$$

$$NO_x = a_2 * x_{NO_x} - b_2 - a_7 * x_{NH_3} + \varepsilon_2 \quad (3)$$

$$N_t = a_5 * x_{N_t} - b_3 + \varepsilon_3 \quad (4)$$

$$NO_{2a} = a_3 * (NO_x - NO) \quad (5)$$

$$NO_{2b} = a_4 * (NO_x - NO) \quad (6)$$

$$NH_3 = a_6 * (N_t - NO - NO_{2b}) \quad (7)$$

where:

NO = concentration reading of NO {ppb}

NO<sub>x</sub> = concentration reading of NO<sub>x</sub> {ppb}

NO<sub>2a</sub> = concentration reading of NO<sub>2</sub> {ppb}

NO<sub>2b</sub> = concentration of NO<sub>2</sub> converted in SSconverter {ppb}

N<sub>t</sub> = concentration reading of N<sub>t</sub> {ppb}

NH<sub>3</sub> = concentration reading of NH<sub>3</sub> {ppb}

x<sub>n</sub> = measured concentration of input gas {ppb}

a<sub>n</sub> = span calibration

b<sub>n</sub> = Zero calibration

ε<sub>n</sub> = instrument measurement errors

System biases furthermore include system response and concentration biases in the chamber. Each of the biases is likely to have some uncertainty surrounding the correction factor. The concentration biases within the chamber and tubing include ammonia emission suppression, adsorption, and interferences. Results from Mukhtar et. al(2003) show that bias due to adsorption of ammonia on polymer tubing is negligible. Current work by Capareda et. al(2004) indicates that adsorption of ammonia on the chamber constitutes less than an 8% negative bias. The response time of the system is a bias that is minimized as the system reaches stability. Measurements taken in the stabilizing range must be corrected for the system response. The chamber and tubing represent a first order response. Therefore the ammonia concentration at a given time is defined as

$$C(t) = C_0 + C_\infty (1 - \exp(t / \tau)) \quad (8)$$

Where:

C(t) = concentration at time t

C<sub>0</sub> = concentration at time t = 0

C<sub>∞</sub> = Concentration after system reaches stability

t = time

τ = time constant

## Methodology

The calibration setup for the analyzer consists of 2 mass flow controllers (Model GFC 17, Aalborg, Orangeburg NY) that control the zero air and calibration gas flow rates. A static mixing tube (Model ½-80-PFA-12-2, Koflo, Cary IL) is used to insure that the calibration and zero air were well mixed. Figure 2 shows the calibration setup for an analyzer.

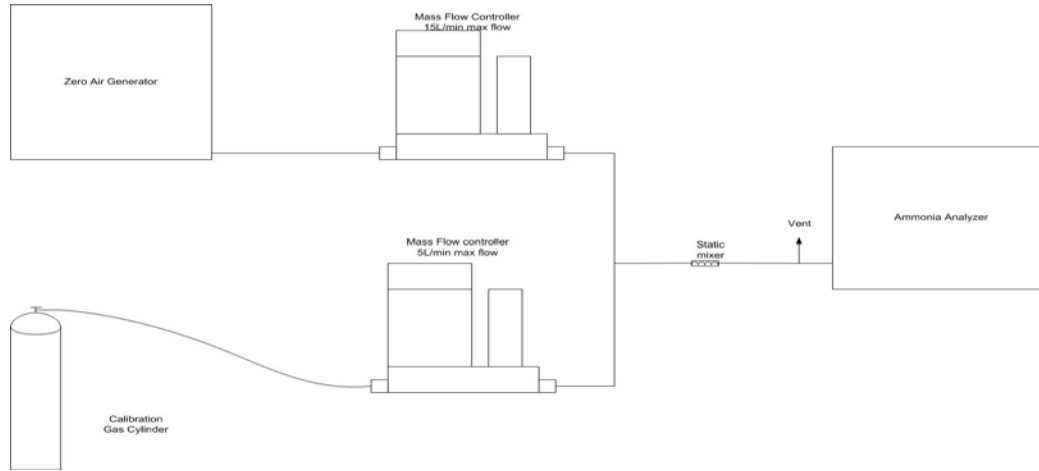


Figure 2. Calibration setup for ammonia analyzer

Uncertainty of the instrument was performed using the law of propagation of uncertainty (type B analysis). The law of propagation of uncertainty is based upon the first order Taylor series approximation of the measurand 'y' as determined to be a function of 'n' other quantities (Taylor & Kuyatt, 1994). The law of propagation of uncertainty allows individual standard uncertainties to be collected to determine the combined standard uncertainty of the system. Equation 8 below shows how the combined standard uncertainty is obtained. All uncertainties placed in equation 8 must be standard uncertainties, expressed as the standard deviation (EURACHEM/CITAC, 2000). By using a first order Taylor series, each error is assumed to be independent. This is likely not true in the analyzer. Thus the first order Taylor series will over estimate the uncertainty.

$$u_c(y(x_1, x_2, \dots)) = \sqrt{\sum_{i=1}^n c_i^2 u(x_i)^2} \quad (9)$$

where:

$u_c$  = combined uncertainty

$y(x_1, x_2, \dots)$  = function with several input variables  $x_n$

$c_i$  = sensitivity coefficient

$u(x_i)$  = uncertainty of input variable

The sensitivity coefficient is obtained by evaluating the partial differential of  $y$  with respect to  $x_i$  as shown in equation 9.

$$c_i = \frac{\delta y}{\delta x_i} \quad (10)$$

## Results & Discussion

Both biases and uncertainties exist within the sampling and analyzing system. These biases and uncertainties can be part of the entire system or just the instrumentation. Often uncertainty analysis is performed solely on the instrumentation. Instrumentation biases include analyzer constants and analyzer response. Uncertainties from the system arise from instrumentation, calibration gases, data analysis and processing, presentation and interpretation of results, and uncertainty in correction factors.

The uncertainty due to instrumentation for the system is generated from three major components: the analyzer, analog inputs and outputs, and flow meters. Each component's data sheet contains the necessary information to estimate the instrument uncertainty. Table 1 below shows the uncertainty levels for each of the components. Additionally, the uncertainty levels for the calibration gasses are each 2% of the reported concentration.

Table 1. Uncertainty Levels for Instrumentation

Manufacturer	Component	Model	Uncertainty type	Reported uncertainty	Uncertainty distribution	Standard Uncertainty	Notes
National Instruments	Field point module	FP-AO-210	Gain	0.40%	normal	0.20%	a
			Offset	14mV	normal	7mV	
Aalborg	Mass flow controller	GFC-17	Accuracy	0.5% FS	normal	0.25% FS	b
			Repeatability	1.5% FS	normal	0.75% FS	
Thermo	Ammonia analyzer	17C	Linearity	1% FS	normal	0.5% FS	c
			Span drift	1%FS	normal	0.5% FS	
			Zero drift	1 ppb	normal	0.5 ppb	
			Zero noise	0.5 ppb	normal	0.25 ppb	
			Lower detectable limit	1 ppb	normal	0.5 ppb	
a. (National Instruments, 2004)							
b. (Aalborg, 2002)							
c. (Thermo, 2001)							

The uncertainty of the ammonia analyzer presented in Table 1 is the uncertainty of the sensor. Since the analyzer multiplexes to obtain the ammonia and  $\text{NO}_x$  readings by difference, the total uncertainty must be taken into account. Each uncertainty was assumed to be normally distributed. The reported uncertainty was assumed to represent a 95% confidence interval. This corresponds to the range of values two standard deviations from the mean. The standard uncertainty for a normal distribution is one half of the reported uncertainty (Eurachem/CITAC, 2000). The standard uncertainty represents the range of values one standard deviation from the mean.

The results of the uncertainty analysis are presented in table 2. The table presents the uncertainty of the instrument based on a 50 ppm full scale setting. The analyzer has approximately a 9.4% uncertainty when measuring 40 ppm with a 50 ppm full scale setting. This nine percent uncertainty is acceptable for most cases. Since only a first order Taylor series is used, the uncertainty of the analyzer is likely to be overestimated. Further work to determine a better estimate sensitivity of the uncertainties is required. The detailed uncertainty analysis is presented in Appendix A.

Table 2. Instrument uncertainty for 50 ppm full scale range.

Concentration [ppm]	Uncertainty	
	[ppm]	% of reading
0	3.12	
5	3.13	62.7%
10	3.17	31.7%
20	3.30	16.5%
30	3.50	11.7%
40	3.78	9.4%
50	4.10	8.2%

If 9.4% is unacceptable, one or more of the components may be replaced with a component with less uncertainty. Each component was analyzed based on cost to replace and the uncertainty reduction. After examining the components, the mass flow controller is likely to decrease uncertainty the most for the least cost since replacement of the analyzer is cost prohibitive. By changing to a flow meter that has a 0.5% uncertainty, the system uncertainty is reduced to 8.7% for 40 ppm on a 50 ppm full scale range. Another area of improvement is a higher quality calibration gas. By changing to 1% uncertainty calibration gases, the system uncertainty is reduced to 9.1% (40 ppm @ 50 ppm full scale). By changing both the flow meter and the gas, the system uncertainty may be reduced to 8.3% (40 ppm @ 50 ppm full scale). The slight uncertainty reduction is met with a considerable cost and must be taken into account when budgeting for system uncertainty.

## Conclusions

An essential item in an engineer or scientist's toolbox is uncertainty analysis, which allows an uncertainty interval to be placed on the results of a study. When information is transferred to the scientific community, uncertainty intervals allow the reader to assess the quality of data taken. In air pollution engineering, results of a study are often used to make policy decisions. Reporting the uncertainty with the results allows the policymakers to make sound decisions regarding emissions. The proper ranges must be used with the instrumentation to ensure a reasonable uncertainty. Results from this study suggest a 9.4% uncertainty at a concentration of 40ppm on a 50ppm span. This uncertainty represents the range obtained using a first order Taylor series. This range is likely over estimated because errors are not independent within the analyzer.

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## **Appendix A**

Detailed uncertainty budget

NH3									
set	40000	ppb							
span	50000	ppb							
C_cyl	98100	ppb							
NO2									
span	50000	ppb							
NOx									
C_cyl	49700	ppb							
set	40324.54	ppb							
NO									
set	40000	ppb							
span	50000	ppb							
C_cyl	49300	ppb							
Flow									
set	7	L/min							
Concentration			95% CI	3775.484	ppb	9.439%			
NH3-->a6*(Nt-NO-NO2b)									
ε	1887.742	ppb							
		error (1sd)	sensitivity		sensitivity	%error (1SD)	setpoint	full scale	actual error
	a6	0	40000		Nt-NO-NO2b	0.00%	1		0
	Nt	1500.177965	1		a6		40000		1500.178
	NO	353.5541861	1		a6		0		354
	NO2b	1089.969948	1		a6		0		1089.9699
Nt-->a5*(x_NH3+x_NOx)-b3+e_lin3+e_xd3+e_zn3+e_sd3									
ε	1500.178	ppb							
		error (1sd)	sensitivity		sensitivity	%error (1SD)	setpoint	full scale	actual error
	a5	0	80324.54		x_Nt	0.00%	1		-
	e_sd3	750	1			0.5%	0	150000	750
	x_NH3	750	1		a5		40000		750
	x_NoX	750.3554912	1		a5		40324.54		750.355
	b3	0.5	1				0		0.5
	e_lin3	750	1			0.5%	0	150000	750
	e_xd3	0.25	1				0		0.25
	e_zn3	0.5	1				0		0.5
NO2b-->a4*(NOx-NO)									
ε	1089.97	ppb							
		error (1sd)	sensitivity		sensitivity	%error (1SD)	setpoint	full scale	actual error
	a4	0	324.5436		NOx-NO	0.00%	1		-
	NOx	1031.035366	1		a4		40324.54		1031
	NO	353.5541861	1		a4		40000		354
NO2a-->a3*(NOx-NO)									
ε	1089.97	ppb							
		error (1sd)	sensitivity		sensitivity	%error (1SD)	setpoint	full scale	actual error
	a3	0	324.5436		NOx-NO	0.00%	1		0
	NOx	1031.035366	1		a3		40324.54		1031.0354
	NO	353.5541861	1		a3		40000		354
NOx--> a2*x_NOx-b2-a7*x_NH3+e_lin2+e_xd2+e_zn2+e_sd2									
ε	1031	ppb							
		error (1sd)	sensitivity		sensitivity	%error (1SD)	setpoint	full scale	actual error
	a2	0	40324.54		Q_cyl/(Qcyl+Q_zero)		1		-
	x_NOx	750.3554912	1		a2		40324.54	100000	750.35549
	b2	0.5	1				0		0.5
	a7	0	40000				0		-
	x_NH3	16682.44607	0		x_NH3		40000		16682.446
	e_lin2	500	1		a7		0	100000	500
	e_xd2	0.25	1			0.5%	0		0.25
	e_zn2	0.5	1				0		0.5
	e_sd	500	1			0.5%	0		500
NO--> a1*x_NO-b1+e_lin1+e_xd1+e_zn1+e_sd1									
ε	354	ppb							
		error (1sd)	sensitivity		sensitivity	%error (1SD)	setpoint	full scale	actual error
	a1	0	40000		x_NO	0.0%	1		0
	x_NO	0	1		a1+e_sd1		40000		0
	b1	0.5	1				0		0.5
	e_sd1	250	1			0.5%	0	50000	250
	e_zn1	0.25	1				0		0.25
	e_zd1	0.5	1				0		0.5
	e_lin1	250	1			0.5%	0	50000	250

[illegible]



