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## **System Responses of Ammonia and Hydrogen Sulfide Measurement Equipment**

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**Abstract.** *System response analysis was performed on a chemiluminescence ammonia analyzer, a pulsed fluorescence hydrogen sulfide analyzer, and tubing used with flux chamber measurement. System responses were measured and evaluated using transfer functions. System responses must be taken into account so that data collected is not skewed up or down, causing measurements to be in error. By taking instrument response into account, an estimate of the true value may be obtained. This paper discusses an application of system response analysis to gaseous emission measurement equipment. The system responses for the analyzers were found to be first order with delay and dependent on the averaging time and gas input. The tubing response was found to be a first order response with delay.*

**Keywords.** Ammonia, Hydrogen Sulfide, instrument response, flux chamber, transfer functions

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## Introduction

Ammonia and hydrogen sulfide are two odorants that result from biological breakdown of manure from animal feeding operations. Ammonia is produced primarily from the breakdown of urine while hydrogen sulfide is a result of anaerobic breakdown of waste in a lagoon. Many methods exist for measuring ammonia and hydrogen sulfide. The chemiluminescence ammonia analyzer (Thermo Electron Corp. 17C, Franklin, MA) is one method used for measuring ammonia concentrations and the pulsed fluorescence analyzer (Thermo Electron Corp. 450C, Franklin, MA) is a method used to measure hydrogen sulfide concentrations. Understanding the dynamic response of a measurement system is necessary when measuring a dynamic emission rate or performing tests that involve a dynamic concentration.

Product data sheets often contain data regarding the dynamic response of the specific component. Using the information provided on each datasheet, the entire system response can be found. The datasheet however, may not provide a complete look at a specific complex component such as an analyzer. Different settings of the analyzer averaging times will provide different response times.

The goal of this paper is to understand the specific responses of the ammonia and hydrogen sulfide analyzers to a concentration input. A transfer function will be used to describe the system response using available mathematical transforms. Transfer functions for tubing connecting the analyzers will also be assessed using nitric oxide (NO) as the transport gas. A transfer function will be determined as a function of tubing length.

## Background

Finding a transfer function involves measuring the response of the specific instrument or component to a stimulus signal. The stimulus signal may take any form, but a sine wave, square wave (step function), or impulse function are most easily interpreted. Depending on the system involved, different stimulus signals are better suited to finding the response. For example, a first order system that is very slow would not show a response to an impulse function very well. This system would be better suited for a slow square wave.

Two transforms that control engineers often use are the Laplace transform and the Z-transform. The Laplace transform is used to identify systems on a continuous time basis. The Z-transform is used on discrete time systems. The transforms allow for easier system analysis. One of the properties of the transform is the ability to measure each components system response separately and combine the results by superposition to form the entire system response. This can be done easily by a simple multiplication of the individual transfer functions.

Two common signal responses found in signal processing are the first order response, and transport delay. The first order response is the response characterized by a continuously stirred tank reactor (CSTR) (Perry & Green, 1997). The transport delay is often characterized by a plug flow reactor (PFR) (Perry & Green, 1997). The responses to step functions are presented in Table 1.

**Table 1.** Step responses and transforms to common signal responses (Franklin, Powell, & Emami-Naeini, 2002)

Response type	Step Response (time domain)	Laplace Transform	Z-Transform
1 <sup>st</sup> order	$G(t) = 1 - e^{-at}$	$\frac{a}{s + a}$	$\frac{z}{z - e^{-aT}}$
Transport delay	$G(t) = G(t - T_d)$	$G(s) = e^{-T_d s}$	$z^{-k_0}$

When accounting for plug flow in a long tube with a compressible fluid, the density of the fluid must be taken into account. The time delay may be found by using the following equation:

$$T_d = \frac{A_{cs} L^2}{\dot{M} \int_0^L \frac{1}{\rho(x)} dx} \quad (1)$$

where:

$T_d$  = time delay [s]

$A_{cs}$  = cross sectional area of tube [cm<sup>2</sup>]

$L$  = length [cm]

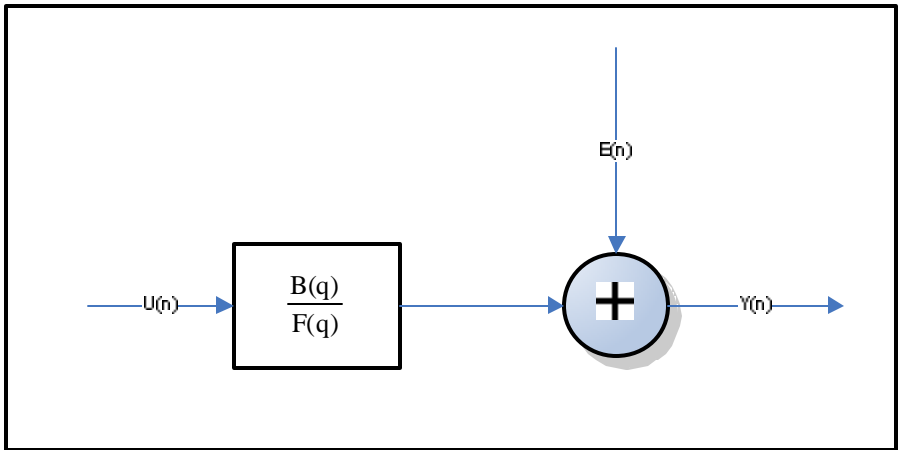
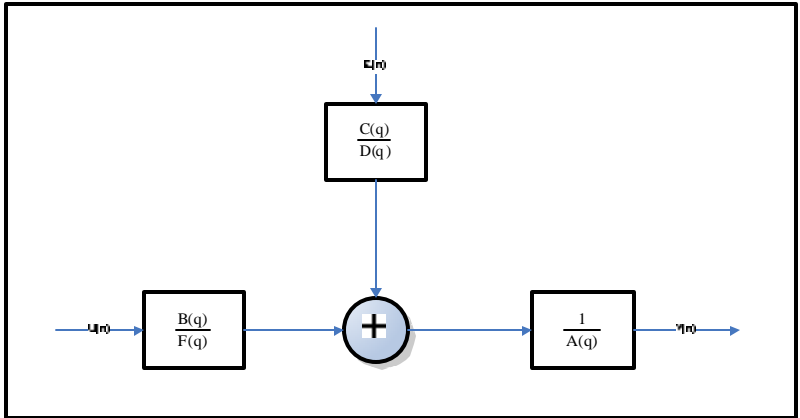
$\dot{M}$  = mass flow rate [g/s]

$\rho(x)$  = density as a function of length [g/cm<sup>3</sup>]

The density of the fluid may be found using the Peng-Robinson Equation of state (Perry & Green, 1997). The equation corrects for non ideal gas conditions that occur at high pressure.

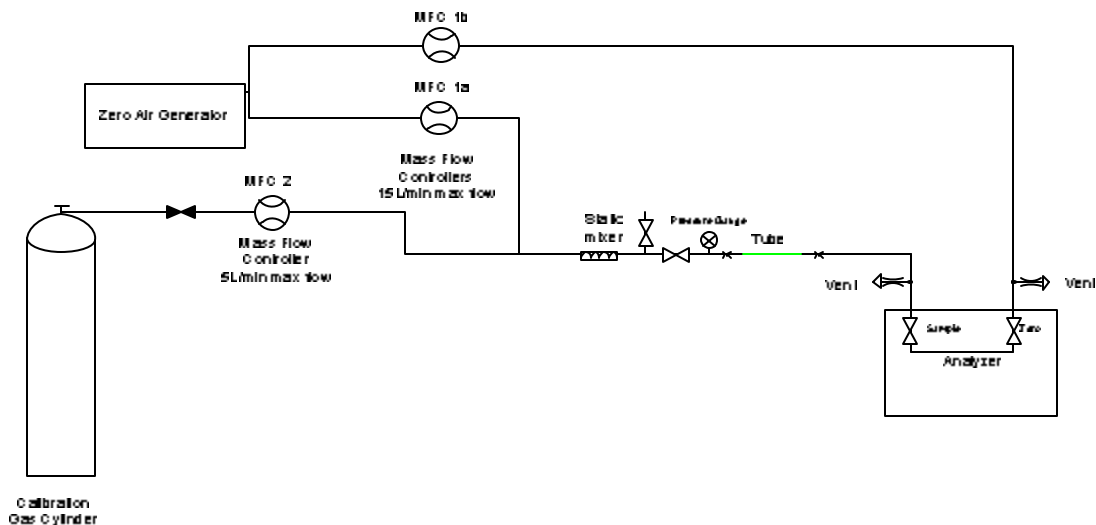
Several tools are available for measuring the system response of a component. One tool used for identifying the system response is the System Identification Toolkit of LabVIEW 7.1 (National Instruments, Austin, TX). The toolkit is able to input a stimulus and response signal and return the transfer function of the system response.

A signal is made up of two components, the deterministic portion and the stochastic portion. The stochastic portion of the signal results from uncertainty of the system. The deterministic portion is the system response. Depending on the origin of the stochastic portion of the signal, different models may be used to identify the system. The general linear model as described in the System Identification Toolkit User Manual (National Instruments, 2004) may be described as in Figure 1.



## Materials and Methods

The system setup is shown in Figure 3 with flowrate set points for each component. The laboratory setup consisted of one analyzer, mass flow controllers (Aalborg, model GFC17-15L/m and model GFC17-5L/m, Orangeburg, NY), zero air generator (Aadco Instruments, Inc., Model 737, Village of Cleves, OH), and PFA grade 3.2 mm (1/8 in.) inside diameter tubing. Several solenoid valves were additionally used to control flow to specific components.



**Figure 3.** Laboratory system setup for determination of System Response

System response was measured for the analyzers by performing the following steps:

- *Calibrate the instrumentation*- the instrumentation was calibrated using the appropriate calibration gas according to manufacturer's guidelines. Ultra High Purity gases were mixed with at least 25% purified air.
- *Measure the system response*- The system response was measured by switching the analyzer zero/span/sample valve option. The sample stream into the analyzer was set so that a specific concentration of calibration gas was allowed to vent. At the same time purified air was sent to the zero stream of the analyzer. The analyzer was switched from zero stream to the sample stream. The response to the switch was logged on a 1 second interval using LabVIEW software communicating via the RS232 port. Data is saved for further analysis in a spreadsheet file. The system response for the  $\text{NH}_3$  analyzer was measured for manual mode  $\text{N}_1$  and auto mode with 40 ppm  $\text{NO}$ , 40 ppm  $\text{NH}_3$ , and 2.5ppm  $\text{NH}_3$ . The averaging times for the  $\text{NH}_3$  analyzer were set to 1s in manual mode and 10s in auto mode. The  $\text{H}_2\text{S}$  analyzer was measured for manual mode CS and auto mode with 4ppm  $\text{H}_2\text{S}$  and 4ppm  $\text{SO}_2$ . The averaging times for the  $\text{H}_2\text{S}$  analyzer were set to 10s in manual mode and 60s in auto mode. The resulting system response is the response to a step function.
- *Analyze system response*- System response is analyzed by first noting and removing the transport delay from the data. A z-transform is applied to the data using the LabVIEW System Identification Toolkit. The discrete transfer function is converted to a continuous transfer function by using the forward algorithm to calculate the Laplace transform. The forward algorithm is shown below as

$$z \rightarrow 1 + sT \quad (2)$$



System response to the tube was performed by using the NH<sub>3</sub> analyzer set to N<sub>t</sub> mode with an averaging time of 1s. The following steps were performed to determine the system response to tubing.

- *Calibrate the instrumentation*
- *Measure the system response*- The system response was measured with 6 lengths of tubing (36.6m, 82.3m, 128.0m, 173.7m, 219.5m, 265.2m) for 40 ppm of NO. The system response included both the analyzer response and the response of the tubing to a step function.
- *Analyze system response*- System response is analyzed by first noting and removing the transport delay from the data. The transfer function of the analyzer is used to separate the response of the analyzer and tubing. A z-transform is applied to the data using the LabVIEW System Identification Toolkit. The discrete transfer function is converted to a continuous transfer function by using the forward algorithm to calculate the Laplace transform.

## Results and Discussion

The NH<sub>3</sub> analyzer system responses are presented in Table 2.

**Table 2.** System responses of NH<sub>3</sub> analyzer for various inputs

Mode	Input	Transfer function (including delay)	Delay [s]
N <sub>t</sub> (1s averaging time)	40 ppm NO	$\frac{0.95e^{-3s}}{0.95 + s}$	3
	40 ppm NH <sub>3</sub>	$\frac{0.47e^{-3s}}{0.47 + s}$	3
	2.5 ppm NH <sub>3</sub>	$\frac{0.16e^{-3s}}{0.16 + s}$	3
Auto (10 s averaging time)	40 ppm NO	$\frac{0.10e^{-4s}}{0.10 + s}$	4
	40 ppm NH <sub>3</sub>	$\frac{0.098e^{-28s}}{0.098 + s}$	26
	2.5 ppm NH <sub>3</sub>	$\frac{0.093e^{-23s}}{0.093 + s}$	23

In  $N_1$  mode, the transfer function is a function of the gas being input into the analyzer. On reason for this is that ammonia must be converted to NO before being measured. Although the reaction rate is fast, the reaction does add some time to the system response. In Auto mode, the responses are essentially the same but the delays are much different for the gases input. The response when in the auto mode is much slower than that of the manual  $N_1$  mode.

**Table 3.** System responses of H<sub>2</sub>S analyzer for various inputs

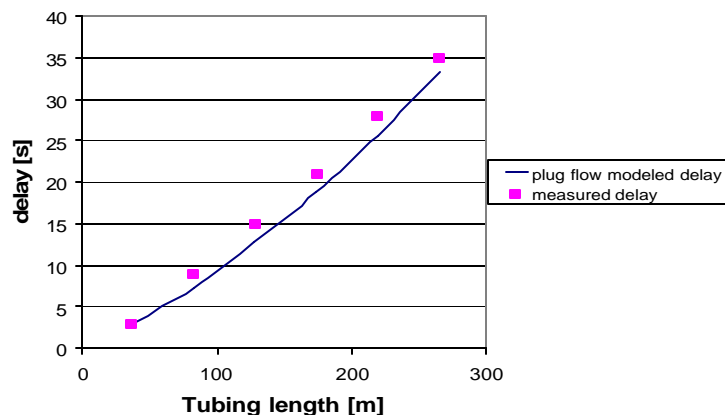
Mode	Input	Transfer function (including delay)	Delay
cS (10s averaging time)	4 ppm SO <sub>2</sub>	$\frac{0.077e^{-7s}}{0.077 + s}$	7
	4 ppm H <sub>2</sub> S	$\frac{0.071e^{-7s}}{0.071 + s}$	7
Auto (60 s averaging time)	4 ppm SO <sub>2</sub>	$\frac{0.064e^{-98s}}{0.064 + s}$	98
	4 ppm H <sub>2</sub> S	$\frac{0.063e^{-96s}}{0.063 + s}$	96

In cS mode the H<sub>2</sub>S and SO<sub>2</sub> have slightly different response times. The H<sub>2</sub>S has a slightly slower response time but must be converted in the converter. In the auto mode, the responses are much slower than in the manual mode. The responses for the two gases in auto mode are almost identical.

The transfer function for the tubing is shown in equation 3

$$\frac{0.95e^{-T_d s}}{0.95 + s} \quad (3)$$

where the time delay,  $T_d$  is a function of the length of tube. Figure 4 shows the measured and modeled time delay. The delay was found to follow equation 1 closely. A small amount of dispersion occurs in the tube as shown by the first order portion of the transfer function.



**Figure 4.** A plug flow reactor transfer function was found to model the time delay in the tubing.

When using the  $\text{NH}_3$  and  $\text{H}_2\text{S}$  analyzers with a flux chamber, the response is much faster than the chamber response. A correction for the response is not necessary. However, when measuring  $\text{NH}_3$  and  $\text{H}_2\text{S}$  of a source such as a fan from a layer facility, the response must be taken into account. The analyzer shows a delayed response that is first order. The importance of obtaining accurate data from a dynamically responding source increases when multiple sample streams are multiplexed. The tubing that connects the sample port and the analyzer not only effects the sample time but may have a significant response due to adsorption of ammonia. This effect increases the amount of air that must be sampled before a measured result accurately depicts an actual concentration sampled.

## Conclusion

Several conclusions can be drawn from the work presented:

- The transfer function for the 17C is a function of the gas input. The transfer function is slower for the ammonia than for the nitric oxide since ammonia must be converted to nitric oxide before being measured in the analyzer.
- In averaging mode the analyzer response is much slower than in the manual mode. This is primarily due to the minimum averaging times being less in the manual mode.
- The transfer function for the tubing was found to follow a first order with delay. The delay transfer function was found to follow the modeled time delay for a compressible fluid.

Understanding system response for air quality measurement systems is important when measuring dynamic systems. The system response must be taken into account so that accurate results may be obtained from dynamically changing measurements.

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