Calibration and Performance of a Thermal Converter in Continuous Atmospheric Monitoring of Ammonia

Sir: The important nitrogen-containing compounds in the atmosphere are N_2O, NO, NO_2, and NH_3, and salts of NO_2^-, NO_3^-, and NH_4^+. The oxides of nitrogen (NO_x), namely, nitric oxide (NO) and nitrogen dioxide (NO_2), are significant atmospheric pollutants. Although primarily emitted by natural sources, ammonia (NH_3) from anthropogenic emissions contributes significantly to local concentrations.

Atmospheric NH_3 results naturally from biological decay at the Earth's surface. The following processes account for the fate of NH_3 in the atmosphere (*1*): (1) Absorption on wet surfaces to form NH_4^+, (2) Reaction with acidic material in either gaseous or condensed phases to form NH_4^+, and (3) Oxidation to NO_3^-. Routes 1 and 2 account for the fate of approximately 75% of the NH_3, and Route 3 for the remaining 25% (1).

Wet chemical methods for determination of ammonia (e.g., Nesslerization) are tedious and not easily adapted to on-line monitoring of emissions. The efficiency of ammonia uptake

Table I. NH_3 Permeation Rates for Permeation Tubes at 30.0 ± 0.5 °C[a]

low permeation device	19.8 ± 1.5 ng/min
2-cm std permeation tube	656.2 ± 27.4 ng/min
4-cm std permeation tube	1299.0 ± 72.4 ng/min

[a] Statistical analysis based on 95% confidence interval.

in the liquid phase for concentrations <20 μg/L (NH_3-nitrogen) is also unreliable (2). Current chromatographic methods require a high NH_3 concentration (>500 ppm). Other instrumental methods (e.g., electrochemical) are either too slow in response time to be applicable to real-time monitoring or else very expensive.

METHODS

Known concentrations of ammonia were obtained from permeation tubes (*3*). The NH_3 Dynacal permeation tubes (commercially prepared) were calibrated at 30.0 °C by the weight loss technique. A stable temperature (±0.5 °C) was maintained with a constant temperature water bath. The system adapted for this purpose was as recommended by the manufacturer (*4*). Gaseous nitrogen, from a cylinder, was used to flush ammonia from around the permeation tubes. Statistical analyses on the weight loss vs. time data were performed with a computer routine and the pemeation rates ascertained on a 95% confidence limit.

Different NH_3 permeation tubes were used to generate various levels of NH_3. Table I gives a comparison of the permeation rates. The gas flow meters (rotameters) were calibrated prior to the commencement of the experiment with a soap bubble method.

The heart of the NH_3 converter is a coil constructed from 1.829 m of Type 316 stainless steel tubing (0.318-cm o.d., 0.071-cm wall thickness). The tubing is coiled to approximately 5 cm in diameter, sheathed in Refrasil tubing, and wrapped with heat-resistant tape. Stainless fittings are attached to each end of the coil, and a Chromel–Alumel thermocouple (0–1000 °C) is attached to the midpoint of the coil. The coil is then placed in a metal container which is insulated with aluminum foil and Fiberfran. The coil is electrically insulated from the container by Teflon spacers. Heat radiators are attached to the ends of the coil protruding from the container to dissipate axial heat generated within the coil and to provide for electrical connection with a transformer.

The converter transformer takes the line voltage, usually 115 volts ac, and drops it to approximately 5 volts ac. This low voltage, high current source provides the heating power to maintain the temperature within the coil. The converter temperature controller is an on–off type (Thermo Electron AP1 Model 232). It is connected to the primary (115 V) voltage of the transformer and maintains the set point temperature to approximately ±2 °C. It is equipped with a fail-safe mechanism that turns off the power if the thermocouple is damaged.

EXPERIMENTAL

A flow diagram for the NH_3 converter calibration system is shown in Figure 1. Nitrogen picks up the NH_3 emitted from a permeation tube at 30.0 °C, and the combined gases are mixed with a stream of purified dry air. Since the air flow is in large excess relative to the nitrogen flow, the gaseous composition approximates that in the atmosphere. With this gas dilution system, it was possible, with the lowest permeation device, to generate concentrations of 1 ppb with a precision of 10%. The gases are injected into the ammonia converter where the NH_3 is catalytically converted to NO at temperatures in excess of 800 °C on the stainless steel converter. The gases then enter a chemiluminescent nitrogen oxides analyzer. Pure dry air, for cleaning the NH_3 converter, can be injected via a three-port valve interrupting the ammonia flow.

To minimize adsorption effects, the gases come into contact with only Teflon and Pyrex surfaces until they enter the analyzer. The gas flow rates are monitored by rotameters, and temperatures are measured by mercury-in-glass thermometers.

The thermal converter oxidizes NH_3 to NO by the following reaction (*5–8*):

$$4NH_3 + 5O_2 \xrightarrow[Fe_2O_3,\ CrO_3]{\Delta} 4NO + 6H_2O \qquad (1)$$

As pointed out by Sigsby et al. (*7*), NH_3 response can be segregated from the NO_x response by a subtractive method.

RESULTS AND DISCUSSION

The ammonia converter was calibrated at 700, 800, and 900 °C for a fixed sample flow rate of 400 mL/min, and the calibration curves are presented in Figures 2 and 3. These curves indicate that above 800 °C, the conversion of NH_3 to NO is the same at both 800 °C and 900 °C (Figure 2). The efficiency of the converter at 800 °C is greater than that at 700 °C, as seen from the slopes in Figure 3. Sigsby et al. (*7*)

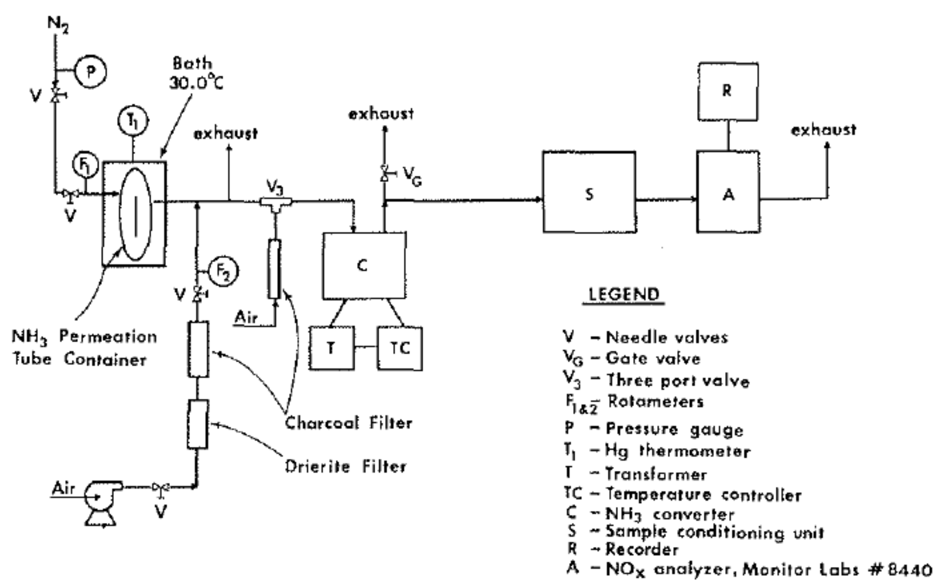

Figure 1. Ammonia converter calibration system

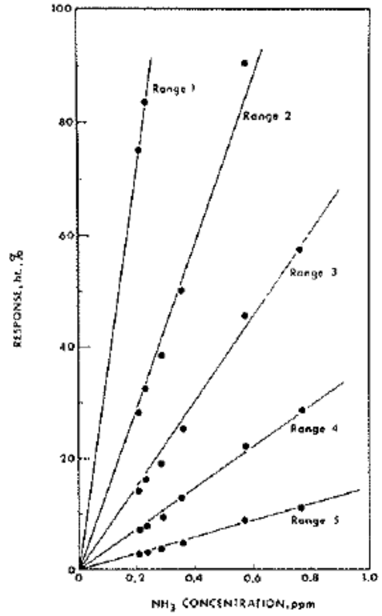

Figure 2. Ammonia converter calibration at 800 °C and 900 °C

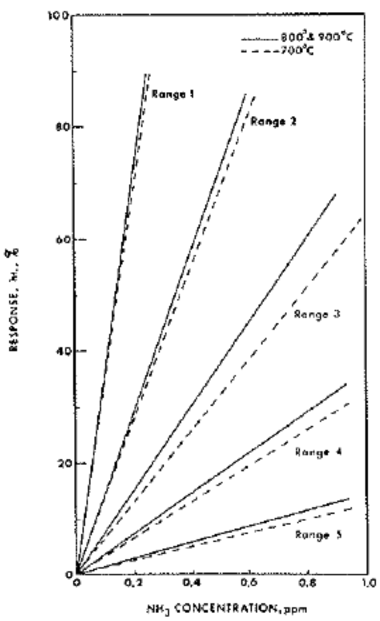

Figure 3. Comparison of ammonia converter calibration at 700, 800, and 900 °C

reached similar conclusions, pointing out that depending upon sample flow, when a 1.829-m converter tube is utilized, temperatures between 750 and 900 °C are required.

The source of zero air was ambient air filtered by activated carbon and dried by Drierite (Figure 1). The zero line was established with this air. The zero line was checked before, after, and periodically during the experiment. The activated carbon and Drierite were changed periodically (~6 h of operation).

The efficiency of conversion of NH_3 to NO of the NH_3 converter at 800 °C was determined with a known source of NO. Within the precision of the technique, it was found to be 100%. The NO concentration was determined before the efficiency measurement by standard techniques. The source of NO was a high purity cylinder gas (Matheson Gas Products).

The NH_3 source was a calibrated NH_3 permeation tube. Table II gives analyses for NH_3 converter efficiency measurements.

This method permits continuous monitoring of NH_3 over a range of concentrations (>5 ppb). The response is linear. The response time is less than 2 min and is primarily a function of the conditioning of the converter with NH_3; here a period of 12 h was used. The system described provides a convenient, steady, and rapid analysis of NH_3 in the gas phase at heretofore impossibly low concentrations. It is important to recognize that NO and NO_2 as well as other nitrogeneous compounds such as amines, etc., are potential interferences, requiring that NH_3 be obtained by a subtractive technique in such instances. This instrumentation functioned well in studying NH_3 uptake by selected plant species (*9*).

Table II. NH_3 Converter Efficiency Measurement at 800 °C

permeation rate of NH_3 = 1299 ng/min at 30.0 ± 0.5 °C permeation tube

analysis of NO (in N_2) gas cylinder (performed by Research Triangle Institute, RTP, N.C.): NO 50.1 ppm, NO_2 1.7 ppm

temperature of NH_3 converter: 800 °C

	NH_3			NO		
sample no.	range of analyzer	concn to analyzer, ppm	response ht, %	concn to analyzer, ppm	response ht, %	efficiency (%) [95% C.I.]
1	4	0.55	20	0.55	19	105 ± 5
2	4	1.6	56	1.6	56	100 ± 5

ACKNOWLEDGMENT

We thank R. E. Baumgardner, F. M. Black, H. E. Jeffries, and J. E. Sickles for their valuable suggestions and comments.

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RECEIVED for review May 18, 1978. Accepted July 20, 1978. Research support was provided by: General Research Support

(Dean's Office), School of Public Health, University of North Carolina at Chapel Hill; and Specific Cooperative Research Agreement (12-14-7001-122), Science and Education Administration, U.S. Department of Agriculture and Botany Department, North Carolina State University at Raleigh.

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