

**On-Line Measurement of Nitrous Oxide from Combustion Sources  
by Automated Gas Chromatography**

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**Abstract**

The combustion of fossil fuels is suspected to contribute to the measured increases in the ambient concentrations of nitrous oxide ( $N_2O$ ). Characterization of  $N_2O$  emissions from fossil fuel combustion and associated pollution control systems has been hindered by a sampling artifact whereby  $N_2O$  may be generated from nitrogen oxides, sulfur dioxide, and moisture present in the sample vessel while these samples await analysis. To truly assess the  $N_2O$  emissions from fossil fuel combustion, a real-time or near real-time measurement technique is required. To accomplish this, a gas chromatograph equipped with an electron capture detector was configured and automated. This system is capable of detection levels below ambient concentrations and a practical quantifying range of 0.1 to 200 ppm. A pre-column backflushing system negates the effects of interferants present in fossil fuel combustion emissions. The automated system is capable of one on-line measurement every 8 minutes and has been used to evaluate  $N_2O$  emissions from a variety of combustion sources, fuels, and post-combustion pollution control techniques.

**Introduction**

Nitrous oxide ( $N_2O$ ) has been of concern to the combustion community largely because the combustion of fossil fuels has been proposed to be a contributor to the measured increases in the ambient concentrations of  $N_2O$  (Pierotti and Rasmussen, 1976; Weiss and Craig, 1976; Hao et al., 1987). This increase is significant because  $N_2O$  is considered to be a "greenhouse" gas due to its infrared radiation absorptive properties as well as an active participant in stratospheric ozone depletion kinetic mechanisms (Ramanathan et al., 1985).

N<sub>2</sub>O from combustion sources has been measured using a variety of methodologies including both grab (container) sampling and on-line monitoring techniques. Once collected, grab samples are often analyzed using gas chromatography (GC). On-line monitoring methods include non-dispersive infrared (NDIR), tunable diode infrared laser (TDIR), Fourier transform infrared (FTIR), and GC techniques. Each of these methods presents its own advantages and disadvantages.

Grab sampling methods are appealing from cost and convenience considerations. However, the integrity of samples taken in this manner has been demonstrated to be compromised under most common combustion sampling conditions (Muzio and Kramlich, 1988; Muzio et al., 1989; Linak et al., 1990). This sample artifact has been observed when nitrogen oxides (NO<sub>x</sub>), sulfur dioxide (SO<sub>2</sub>), and moisture, present in most combustion samples, react in the sampling containers to produce N<sub>2</sub>O. N<sub>2</sub>O generation in grab sample containers approaching 200 ppm has been observed (Linak et al., 1990). However, current research is evaluating the use of modified sample conditioning techniques that minimizes or negates N<sub>2</sub>O formation in contained samples.

On-line, real-time N<sub>2</sub>O analyzers are desirable; however, the commercial availability of these monitors is limited. Of those available, detection levels may be insufficient, and elaborate sample conditioning systems are routinely required. Additionally, these systems are largely research-oriented (Lanier and Robinson, 1986; Kramlich et al., 1988), requiring extensive operator attention and may not be designed for field use. Several continuous, real-time monitoring techniques based on infrared radiation absorption have been developed for N<sub>2</sub>O combustion source monitoring applications. A NDIR system, developed at the University of California's Irvine Combustion Laboratory, has been used to characterize the N<sub>2</sub>O emissions from several pulverized coal utility boilers (Montgomery et al., 1989). The NDIR system provides real-time measurement capabilities and is capable of monitoring N<sub>2</sub>O levels as low as several parts per million. However, the system is susceptible to interferences from other compounds present in combustion gases that absorb IR radiation at similar wavelengths as N<sub>2</sub>O. These interferences can often be minimized through the use of elaborate conditioning systems as well as electronic background correction.

TDIR spectrometry is another potential real-time monitoring technique. A TDIR analyzer has been developed by EPA's Air and Energy Engineering Research Laboratory (AEERL) to monitor N<sub>2</sub>O emissions from its fossil fuel combustion test facilities (Briden et al., 1991). TDIR systems offer excellent sensitivity, and are capable of detection levels in the parts per billion range. In addition, interferences from other IR radiation absorbing gases can be minimized by the TDIR's

ability to isolate appropriate N<sub>2</sub>O absorbing wavelengths with greater resolution. The main disadvantages of TDIR spectrometry are its complexity, high cost, short life span of laser diodes (1-2 years), and the necessity for cryogenic cooling.

FTIR spectrometry is yet another viable real-time N<sub>2</sub>O monitoring method. The FTIR offers excellent wavelength resolution and sensitivity. In addition, FTIR is capable of monitoring multiple wavelengths simultaneously, making the technique suitable for real-time, multi-component monitoring of combustion gases. The main disadvantages of FTIR systems are their complexity and high cost.

N<sub>2</sub>O emissions in combustion gases are most commonly monitored using GC. GC techniques, coupled with electron capture detection (ECD), offer excellent sensitivity with detection levels less than ambient concentrations (approximately 300 ppb). Other detection methods such as thermal conductivity detection (TCD) and mass spectrometry (MS) have also been used successfully. An important limitation of GC methods is that they do not allow a continuous real-time measurement. Other disadvantages include analytical difficulties and detector de-sensitivity caused by other compounds present in the combustion gases. Conversely, in addition to excellent sensitivity, GC methods are typically easy to construct and operate, and relatively inexpensive. A GC analytical procedure suitable for N<sub>2</sub>O measurement from combustion gases has been documented (Ford, 1990).

Realizing that much of the N<sub>2</sub>O emissions data reported prior to the discovery of the sampling artifact were at best suspect, the EPA conducted a series of tests characterizing the N<sub>2</sub>O emissions from numerous pilot- and full-scale fossil fuel combustion facilities (Clayton et al., 1989; Linak et al., 1990). Due to the lack of available on-line analytical techniques, the EPA research group chose to develop a near real-time method based on GC/ECD. During the pilot- and full-scale tests, the limitations of the on-line GC/ECD system used were identified. These limitations included susceptibility to interferences present in the flue gases measured and memory effects from moisture and SO<sub>2</sub> resulting in detector baseline instability as well as operational difficulties. These effects had a direct impact on detector sensitivity, often raising detection levels to values above actual N<sub>2</sub>O concentrations present in the gas streams measured. However, regardless of these limitations and the fact that this technique would never yield real-time information, the GC/ECD system offered the advantages of being highly sensitive, relatively inexpensive, widely available, and fairly simple to operate. Therefore, since the development of a reliable on-line technique was important to the continued characterization of N<sub>2</sub>O emissions from fossil fuel combustion sources, EPA/AEERL set out to develop a GC/ECD analytical system and

procedure suitable for the on-line measurement of N<sub>2</sub>O from fossil fuel combustion sources. The development of the system required negating the effects of interferences present in combustion process emissions, configuring the instrument for automated operation, and improving the linear working range of N<sub>2</sub>O emission quantification.

## Experimental

The GC/ECD analytical system developed uses a precolumn backflush method to isolate the interfering flue gas components. The system is automated by using the timed event commands associated with the GC operation/data acquisition system to control and activate the sampling/valving hardware. N<sub>2</sub>O is quantified by relating integrated peak areas to a least squares linear regression of logarithm transformed calibration variables (peak area and N<sub>2</sub>O concentration). The system requires that a particulate free, moisture conditioned, sample stream be delivered to the system under slight positive pressure. Figure 1 is a schematic diagram of the analytical system. The analytical conditions of the GC/ECD system are presented in Table 1.

Table 1. GC/ECD analytical system equipment and conditions.

Gas Chromatograph	Hewlett-Packard Model 5890A
Integrator	Hewlett-Packard Model 3392A
Timed Sample Event Controller	Hewlett-Packard Model 19505A
Detector	<sup>63</sup> Ni constant current cell electron capture detector maintained at 300°C
GC Oven Temperature	Isothermal, 50°C
Carrier Gas	5 or 10% methane in argon (P5, P10)
Precolumn	6 ft (1.8 m) x 0.125 in. (0.32 cm) O.D. stainless steel, packed with HayeSep D - 100/120 mesh support.
Precolumn Carrier Flow	30 cm <sup>3</sup> /min (head pressure ~30 psig, 308.2 kPa)
Analytical Column	12 ft (3.7 m) x 0.125 in. (0.32 cm) O.D. stainless steel, packed with Porapak Super Q - 80/100 mesh support
Analytical Column Carrier Flow	30 cm <sup>3</sup> /min (head pressure ~40 psig, 377.1 kPa)

## Backflush Method

The backflushing method uses a single 10-port valve to divert/direct the flow of carrier gas and sample gas streams through the chromatograph system. A schematic diagram of a 10-port valve is presented in Figure 2. The 10-port valve can be operated in two positions or modes. In the "off" or backflush position (Figure 2a), the precolumn is backflushed by carrier 2 to a vent

(ports 10, 9, 6, and 8 consecutively). The analytical column, supplied by carrier 1 (ports 5 and 7 consecutively), is connected to the ECD. A 1 cm<sup>3</sup> sample loop, bridging ports 3 and 4, can be charged with the sample stream (ports 1 and 2 consecutively). In the "on" or analyze position (Figure 2b), the valve is aligned so that carrier 1 purges the sample loop onto the precolumn (ports 5, 3, 4, and 6 consecutively). The effluent of the precolumn is routed to the analytical column and on to the detector (ports 9 and 7 consecutively). Carrier 2 is vented via ports 10 and 8. The sample stream is vented via ports 1 and 2. Once the analyte of interest (N<sub>2</sub>O) has eluted from the precolumn onto the analytical column, the valve is returned to the backflush position: the flow through the precolumn is reversed and the interfering sample components are purged from the precolumn.

An electronically controlled air actuator was used to automate valve switching. The valving system was controlled by interfacing the GC and integrator to a timed event control module that converted digital commands from the integrator to time controlled electrical switches. To further aid in analytical system automation, a solenoid valve, installed upstream of the 10-port valve sample loop, allows continuous purging of the sample loop with sample gas until the time of analysis. The valve was controlled so that, just prior to analysis, the solenoid valve was closed, sample flow was stopped, and the sample loop was equilibrated to atmospheric pressure. At the time of backflushing, the 10-port valve was returned to the off position and the solenoid valve opened, restoring flow to the sample loop. The system was also configured for unattended, continuous operation by incorporating the programmed timed events into a separate program capable of automatically re-initiating the sequence of timed events.

### **Calibration and Linearity**

The linearity of the GC/ECD system was evaluated with varied concentration N<sub>2</sub>O in nitrogen span gases ranging from 0.514 to 128 ppmv (Figure 3a). The detector response to N<sub>2</sub>O (area counts/ppm N<sub>2</sub>O) exhibited decreasing sensitivity with increasing concentration. This effect tends to limit the linear working range of quantitation. The linearity of the detector was evaluated using two mathematical approaches: a least squares linear regression of the calibration variables, concentrations, and peak areas; and a least squares linear regression based on transformed (natural logarithmic) calibration variables. A comparison of these two approaches is presented in Table 2 and Figure 3. The approaches are compared by back-calculating the concentration of each calibration standard and determining the percent bias from the known value.

Table 2. Two mathematical approaches to evaluate detector linearity.<sup>a</sup>

N <sub>2</sub> O (known)	Linear Regression			ln Transformed Linear Regression			
	Peak area	N <sub>2</sub> O (calc.)	Bias %	ln(N <sub>2</sub> O) known	ln(Peak area)	N <sub>2</sub> O (calc.)	Bias %
0.514	6858	-3.11	-705.1	-0.66553	8.833171	0.47	-8.6
0.97	13153	-2.13	-319.6	-0.03045	9.484405	0.99	2.1
1.99	24199	-0.40	-120.1	0.688134	10.09406	2.02	1.5
5.03	56075	4.58	-8.9	1.615419	10.92444	5.36	6.6
9.85	99278	11.35	15.2	2.287471	11.50567	10.41	5.7
19.4	174880	23.18	19.5	2.965273	12.07185	20.11	3.7
40.4	318970	45.74	13.2	3.698829	12.67285	40.45	0.1
80.1	559344	83.36	4.1	4.383275	13.23451	77.74	-2.9
128	816984	123.68	-3.4	4.852030	13.61337	120.79	-5.6

<sup>a</sup>N<sub>2</sub>O concentrations in ppmv.

The linear regression of the transformed calibration variables was effective in minimizing the relative error of calculated concentrations. Less than 10 percent bias was observed over the entire range. By calibrating in a narrower concentration range, more specific to anticipated emission concentrations, the relative error can be further reduced.

### System Performance

The automated, on-line GC/ECD system was evaluated extensively on a number of diverse fossil fuel combustion test facilities. The system was used to monitor N<sub>2</sub>O emissions from the combustion of various coals during parametric SO<sub>2</sub> removal testing. N<sub>2</sub>O concentrations measured ranged from 0.5 to 10 ppm.

The on-line GC/ECD system was also used extensively during a series of selective non-catalytic NO<sub>x</sub> reduction (SNCR) tests. During these tests, additives such as ammonia and urea were injected into the combustion test facility to reduce NO<sub>x</sub> emissions. The on-line measurements were used to compare N<sub>2</sub>O emissions with and without NO<sub>x</sub> control. The N<sub>2</sub>O concentrations measured ranged from 0.5 to 35 ppm, and compared well with measurements taken by a tunable diode laser. Similarly, the on-line GC/ECD system was used to characterize the N<sub>2</sub>O emissions from a selective catalytic NO<sub>x</sub> reduction (SCR) pilot-scale test facility. N<sub>2</sub>O concentrations were

measured both before and after the catalyst evaluated. Measured concentrations ranged from 0.5 to 3 ppm.

The GC/ECD system was also evaluated under ambient conditions. The system was used to assess the N<sub>2</sub>O mass emissions resulting from the open hearth combustion of Chinese coal. In China, the open hearth combustion of coal comprises a significant portion of all coal burned. These ambient measurements were used to assess the magnitude of the mass contribution of N<sub>2</sub>O to the environment from this combustion source. The N<sub>2</sub>O concentrations measured were only slightly above ambient concentrations. However, the GC/ECD analytical system was sensitive enough to resolve this 100 - 200 ppb relative increase.

During on-line analyses, span or performance checks were conducted on a routine basis. These checks, used to evaluate method accuracy and precision, were conducted at various times during the measurement process. Figures 4 and 5 present results of span checks conducted during representative ambient and source monitoring activities. Overall, the accuracy and precision levels achieved during various on-line monitoring requirements were consistent. The type of combustion source monitored did not appear to affect method performance. Accuracy of span checks, expressed as percent bias, was consistently less than 15 percent. The precision of replicate span checks, expressed as percent relative standard deviation (RSD), was consistently less than 10 percent.

## Summary

The GC/ECD backflush method developed was found to be suitable for the measurement of N<sub>2</sub>O from a variety of combustion sources and applications. In addition, the method was found to be equally suitable for on-line monitoring or grab sample analysis. Analytical interferences, present in combustion process effluents, were negated through the use of a backflushing technique. Common flue gas components such as NO<sub>x</sub>, SO<sub>2</sub>, oxygen, carbon monoxide, carbon dioxide, moisture, unburned hydrocarbons, and ammonia were not found to interfere with the analytical procedure. Method accuracy (percent bias) and precision (percent RSD) were determined to be less than 15 and 10 percent, respectively. The method was found to be suitable for the quantitation of N<sub>2</sub>O concentrations ranging from 0.100 to 200 ppm. Ultimately, the procedure was approved as an AEERL Recommended Operating Procedure (ROP) (Ford, 1990).

Using this method for on-line monitoring purposes allows a semi-continuous measurement approximately once every 8 minutes. The system can be easily incorporated into most continuous

emission monitoring sample delivery/conditioning systems, the only requirements being the removal of particulate and moisture from the sample stream by a refrigeration condenser. The sample stream should be diverted to the analytical system prior to further moisture conditioning by a desiccant.

The non-linear response of the detector to  $N_2O$  at low concentrations was minimized through use of a logarithmic transformation of the calibration variables. The transformed data are used to derive a least-squares linear regression.

### **Acknowledgments/Disclaimer**

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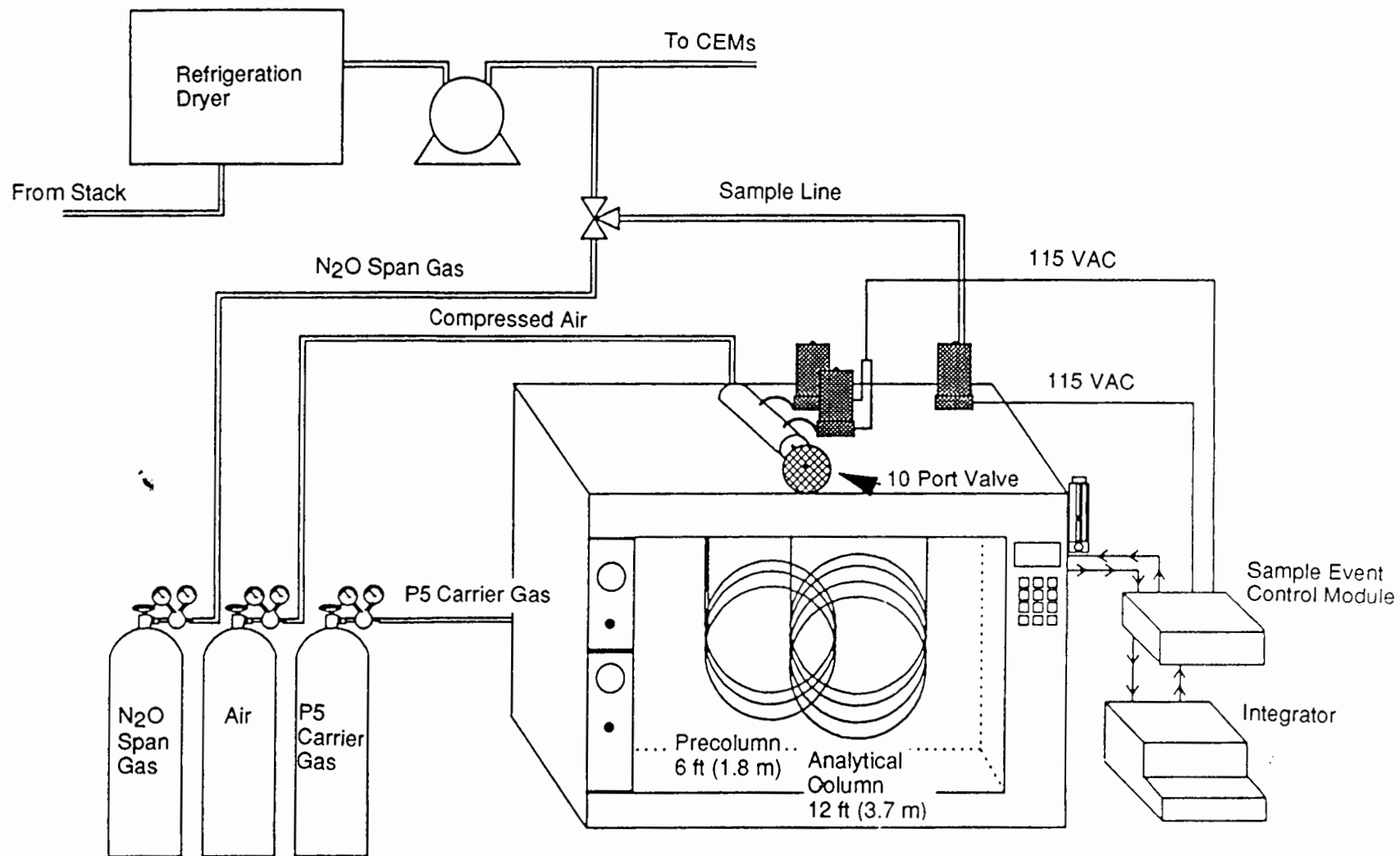
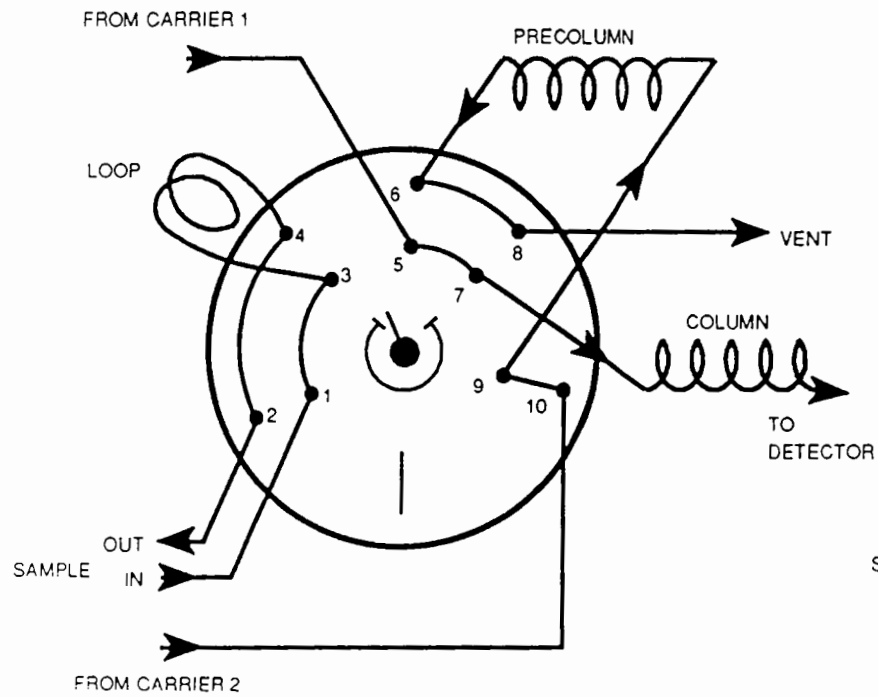


Figure 1. Automated on-line GC/ECD N<sub>2</sub>O monitoring system.

(a) "off" or backflush position



(b) "on" or analyze position

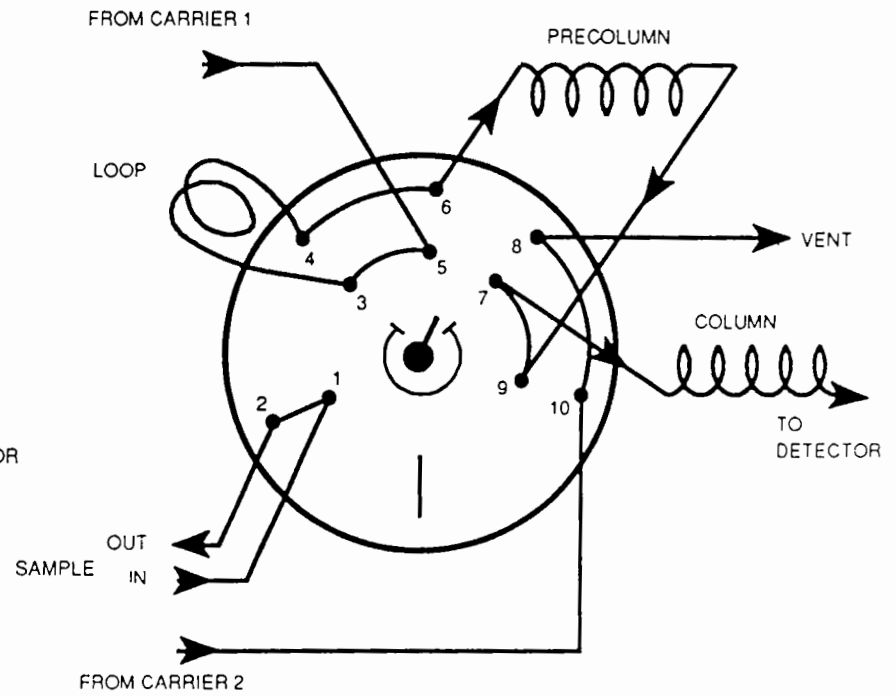


Figure 2. 10-port sampling valve.

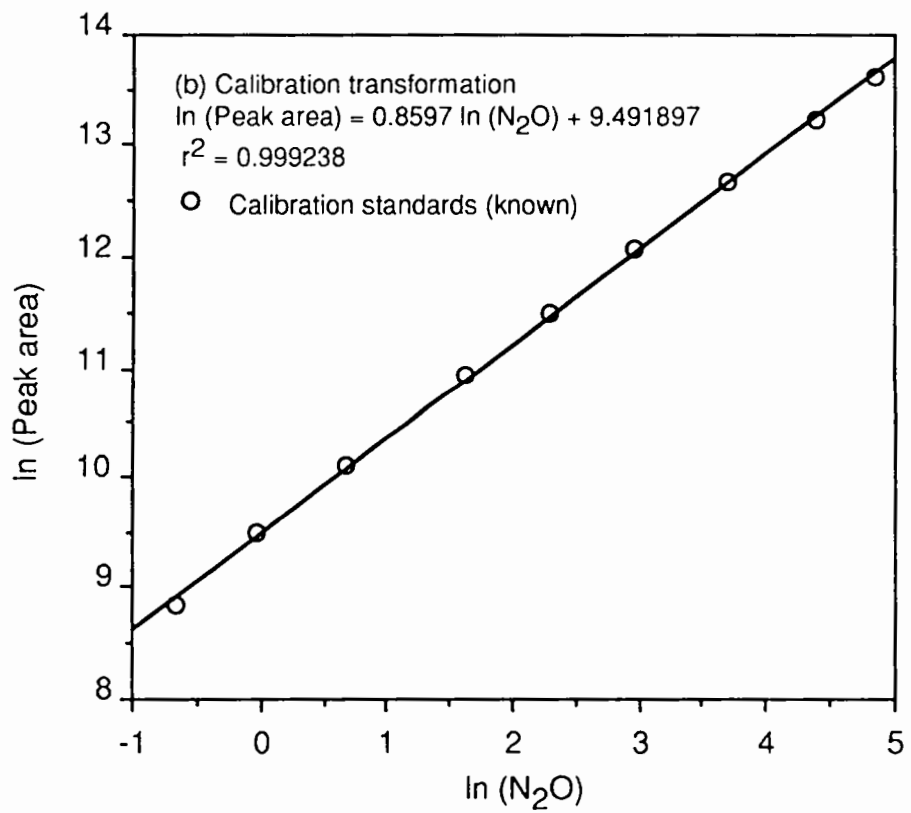
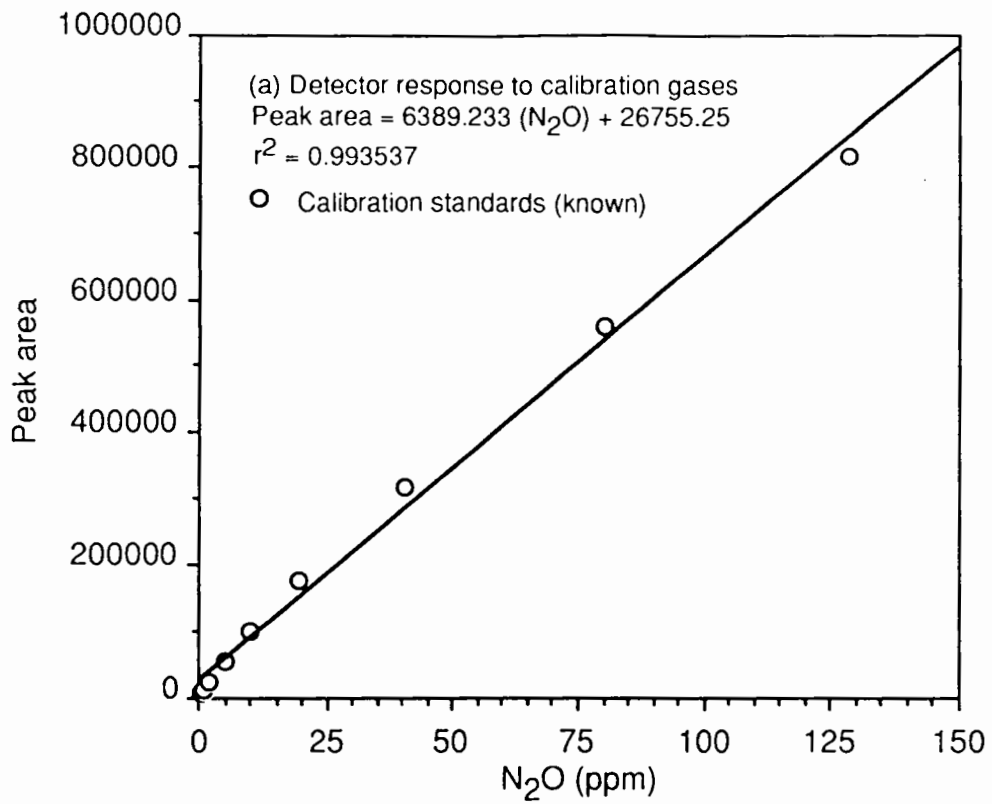


Figure 3. ECD response to N<sub>2</sub>O calibration gases.

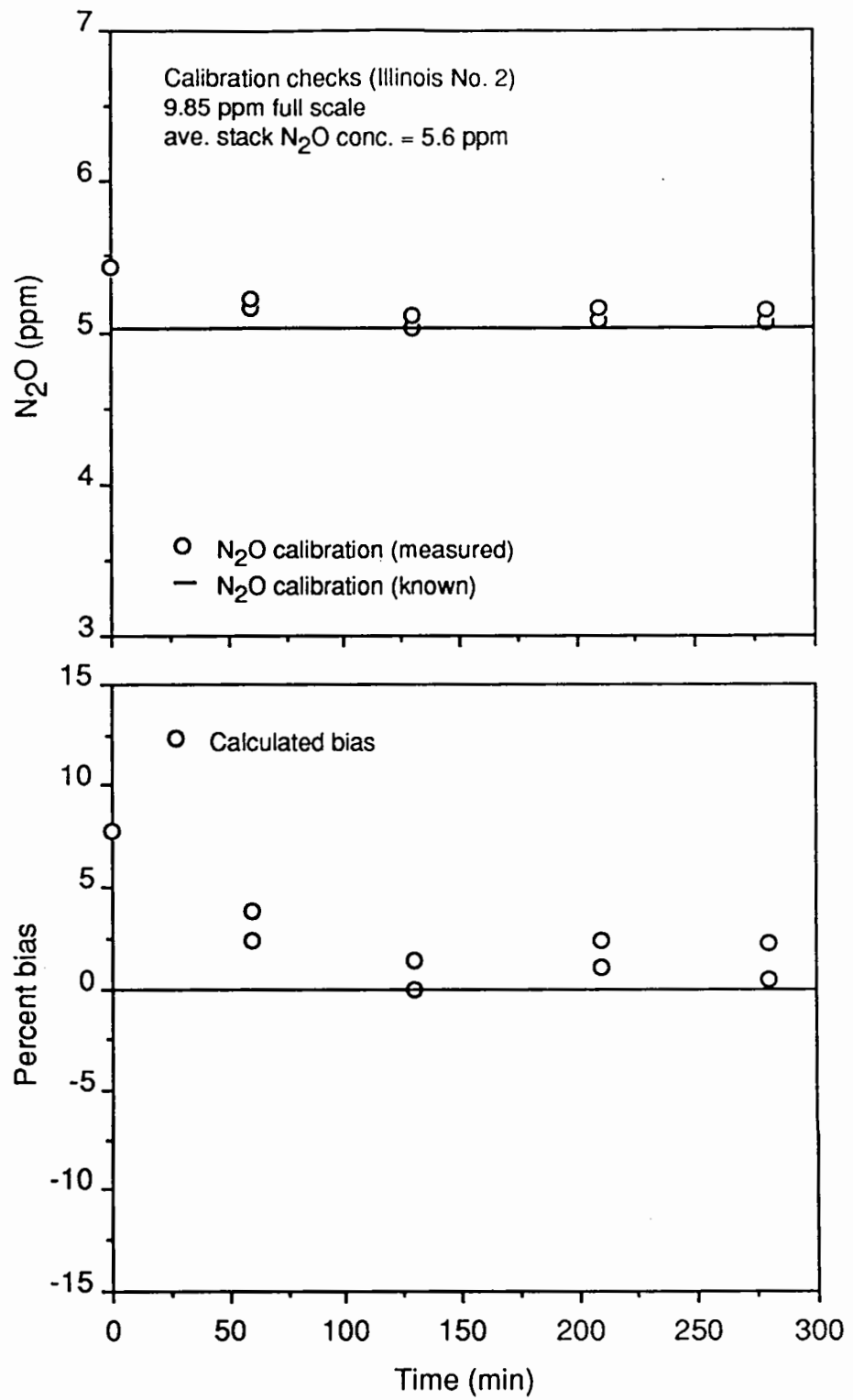


Figure 4. Illinois No. 2 coal calibration checks, downfired furnace/stack sampling.

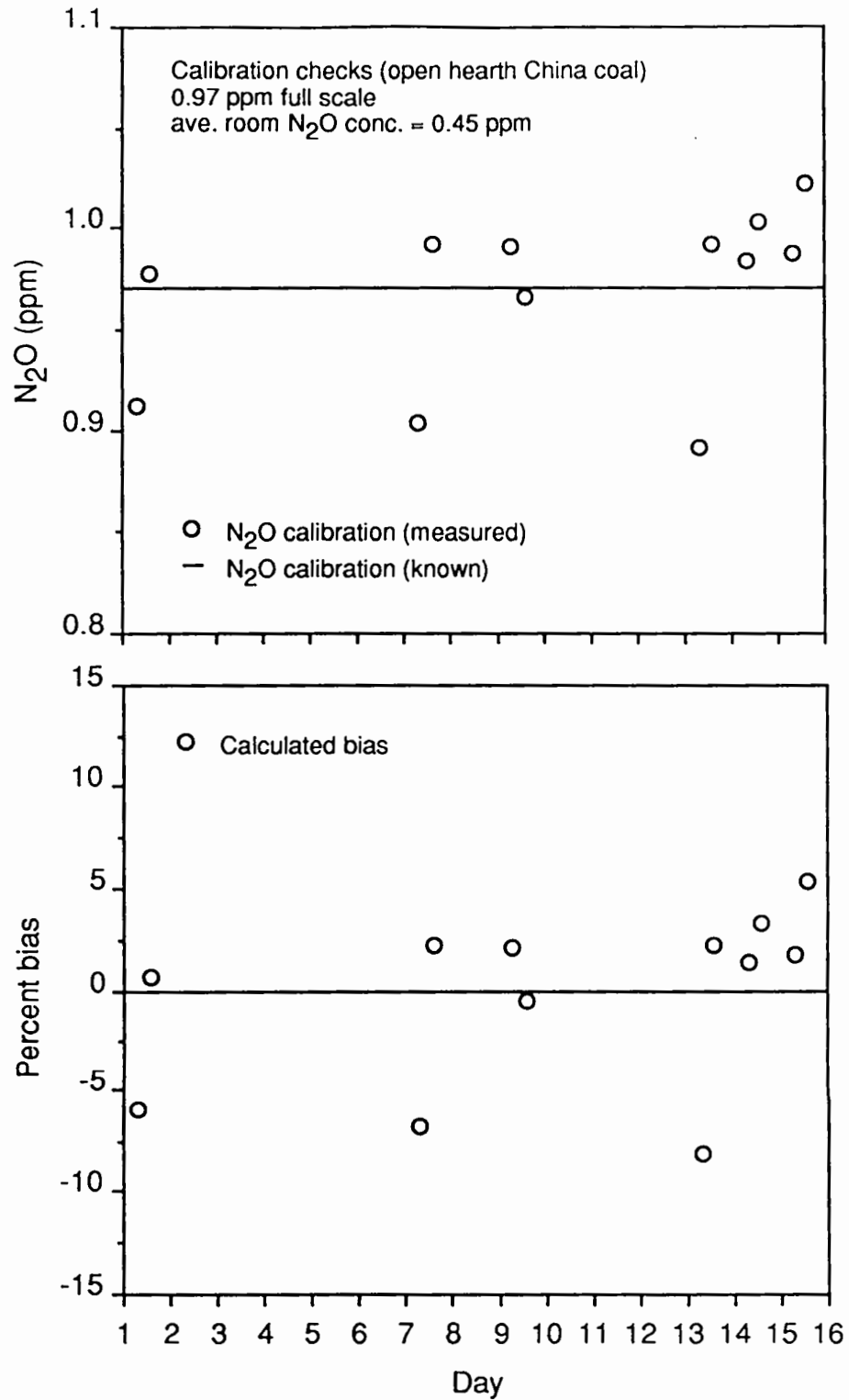


Figure 5. China coal calibration checks, open hearth combustion/ambient air sampling.