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DEVELOPMENT OF SAMPLING
AND ANALYTICAL METHODS FOR THE
MEASUREMENT OF NITROUS OXIDE
FROM FOSSIL FUEL COMBUSTION SOURCES

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DEVELOPMENT OF SAMPLING AND ANALYTICAL METHODS FOR THE MEASUREMENT OF NITROUS OXIDE FROM FOSSIL FUEL COMBUSTION SOURCES

PROJECT REPORT

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ABSTRACT

The combustion of fossil fuels is suspected to contribute to measured increases in ambient concentrations of nitrous oxide (N_2O). Accurate and reliable measurement techniques are needed to assess the relative contribution of fossil fuel combustion N_2O emissions to the increase in ambient concentrations. The characterization of N_2O emissions from fossil fuel combustion sources has been hindered by the lack of suitable and acceptable grab sampling and on-line monitoring methodologies. Grab samples have been shown to be compromised by a sampling artifact where N_2O is actually generated in the sample container in the presence of sulfur dioxide (SO_2), nitrogen oxides (NO_x), and moisture. On-line monitoring techniques are limited and of those available, instrument costs are often prohibitive, detection levels are often insufficient, and the techniques are often susceptible to interferences present in combustion process effluents. The report documents the technical approach and results achieved while developing a grab sampling method and an automated, on-line gas chromatography method suitable to characterize N_2O emissions from fossil fuel combustion sources. The two methods developed were ultimately documented in the form of the U.S. Environmental Protection Agency (EPA) Air and Energy Engineering Research Laboratory (AEERL) Recommended Operating Procedures (ROPs).

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SECTION 1

INTRODUCTION

1.1 BACKGROUND

Nitrous oxide (N_2O) has been of concern to the combustion community largely because fossil fuel combustion has been proposed as a potential contributor to the measured increases in ambient N_2O concentrations.[1,2,3] Currently, atmospheric N_2O concentrations are increasing at nearly 1 ppbv annually from a present level of 303 ppbv.[2,3,4] This increase is of concern because N_2O is considered a "greenhouse" gas owing to its infrared (IR) radiation absorptive properties as well as a contributor to stratospheric ozone depletion.[5] To further substantiate the supposition that increases in atmospheric N_2O concentrations are associated with the combustion of fossil fuels, studies tracking atmospheric increases of carbon dioxide (CO_2) over time reveal that the increase of N_2O and CO_2 occur similarly.[6] The increase of both anthropogenic pollutants correlate well with increases in industrial activity.

Early efforts to characterize N_2O emissions from fossil fuel combustion sources focused on identifying a relationship between nitrogen oxides (NO_x) and N_2O emissions. Data were nominally collected in a "piggy back" manner, where N_2O grab samples were collected during NO_x performance tests. Considerable data exist comparing NO_x emissions to N_2O emissions from diverse combustion sources and techniques firing on various fossil fuels.[2,7,8,9,10] As a result of increasing concern over rising atmospheric N_2O concentrations, the first of a series of workshops specifically designed to address this issue was conducted in 1986. The U.S. Environmental Protection Agency's (EPA's) Air and Energy Engineering Research Laboratory (AEERL) sponsored this workshop designed to assist

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EPA in identifying critical issues related to fossil fuel combustion emission of N_2O that would guide

EPA in developing an N_2O research program plan.[8] Additional EPA/AEERL-sponsored workshops

were conducted that continued to evaluate the role of fossil fuel combustion and N_2O emissions. At

the 1988 workshop, the N_2O grab sampling artifact was presented.[10]

The grab sampling artifact is a situation in which the presence of NO_x, sulfur dioxide (SO_2),

and moisture, N_2O is actually generated in grab sample containers through a chemical reaction/series

of chemical reactions.[11,12] N_2O generation approaching 200 ppm in grab sample containers has been

observed.[13] Much of the data reported on N_2O measurements from fossil fuel combustion sources

were obtained using grab sampling methods conducive to the sampling artifact.[10,13] For EPA/AEERL

to continue conducting research characterizing N_2O emissions from fossil fuel combustion sources,

sampling and monitoring methods that provided representative measurements were required.

N_2O measurement from combustion sources has been performed using a variety of

methodologies including grab sampling and on-line monitoring techniques. Grab samples collected are

normally analyzed using gas chromatography (GC) methods. On-line monitoring techniques include

GC, nondispersive infrared (NDIR), Fourier-transform infrared (FTIR), and tuneable diode laser

infrared (TDLIR) real-time analyzers.[9,14,15,16,17] Each method has its own advantages and more often

than not, disadvantages. Grab sampling methods are appealing from a cost and convenience stand

point; however, the sample integrity has been demonstrated to be compromised under most common

sampling conditions.[10,11,12,13] On-line, real-time analyzers are desirable for obvious reasons although

instrument costs are often prohibitive, detection levels are often insufficient, elaborate conditioning

systems are routinely required, and overall operation is often complex. Realizing that accurate and

reliable N_2O measurements were essential to emissions characterization research, the Combustion

Research Branch (CRB) of EPA's AEERL initiated a program to concurrently develop grab sampling

and on-line monitoring methodologies suitable for characterizing N_2O emissions from various

combustion sources and processes. As a result of this program, two AEERL Recommended Operating

Procedures (ROPs) were generated. ROP No. 45, "Analysis of Nitrous Oxide from Combustion Sources," details a gas chromatography/electron capture detector (GC/ECD) method suitable for grab sample analysis as well as on-line monitoring purposes.[14] ROP No. 56, "Collection of Gaseous Grab Samples from Combustion Sources for Nitrous Oxide Measurement," details a grab sampling method suitable for collection of gaseous grab samples from combustion sources for the screening of N_2O emissions.[18] This report documents the approach and results obtained by Acurex Environmental while developing these procedures.

1.2 AEERL RESEARCH EFFORTS

The CRB of EPA's AEERL has been active in evaluating N_2O emissions from a variety of fossil fuel combustion sources and equipment. Early research efforts used grab sampling techniques where the sampling artifact was later confirmed to be present. Following sampling artifact identification, research efforts focused on developing reliable sampling and monitoring techniques to re-evaluate these same combustion processes. Direct comparisons of on-line measurements to grab sampling measurements were performed on in-house combustion facilities firing on varied fossil fuels.[13] These tests demonstrated the vast difference between the on-line and grab sampling measurements. On-line N_2O concentrations less than 2 ppm were common, whereas measurements from the grab samples often yielded concentrations approaching 200 ppm.[13] Actual N_2O generation within the sample container was found to vary with respect to initial (stack) SO_2, NO_x, and moisture concentration. With this in mind, several tests were performed evaluating methods of moisture removal and the subsequent artifact. Similarly, tests were also performed in which crude attempts at SO_2 removal were evaluated. To further understand the reactions occurring within the sample container, measurements over time of N_2O, SO_2, and NO/NO_2 were made using GC methods.

Having demonstrated that N_2O measurements from pilot-scale fossil fuel combustion sources in which grab sampling techniques were used could bias reported emissions by as much as several orders of magnitude,[13] the AEERL/CRB conducted a field study to evaluate the emissions from full-

scale utility fossil fuel combustion equipment[19] This study also demonstrated the large disparity between on-line and aged grab sample measured concentrations. The low on-line or actual concentrations supported the tenet that the direct emission of N_2O from fossil fuel combustion was not a significant contributor to the increase in observed atmospheric N_2O concentrations. On-line and grab sample measurements were performed on 12 coal-fired utility commercial boilers of varied firing configurations and thermal load.[19] On-line measurements revealed direct emission concentrations nominally less than 5 ppm, whereas grab sample measurements often yielded N_2O concentrations in excess of 100 ppm.

During the course of the pilot-scale and full-scale field fossil fuel combustion emission evaluations, the problem areas of AEERL/CRB's N_2O measurement methodologies were identified. The on-line GC method was susceptible to interferences present in flue gases measured. Memory effects from moisture and SO_2 resulted in detector baseline instability as well as chromatography difficulties.[19] These effects had a direct impact on detector sensitivity, often reducing detection levels to values above actual N_2O concentrations present in measured gas streams. Identical problems were encountered when analyzing a large number of grab samples.

1.3 OBJECTIVES

Having taken the position that the direct emission of N_2O from fossil fuel combustion was not a significant contributor to measured increases in atmospheric N_2O concentrations, the AEERL/CRB was interested in developing an economical method for screening various fossil fuel combustion sources to further support this tenet as well as identify potentially high N_2O emitting sources. The most cost-effective method for meeting this objective was to develop a grab sampling method suitable for this purpose. AEERL/CRB researchers also realized that developing a grab sampling technique that completely eliminated the generation artifact would be difficult and that developing a grab sampling technique that consistently minimized the artifact to acceptable levels for screening purposes would be more practical. If the grab sampling method were to minimize the N_2O generation artifact

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to less than 10 ppm over a 1-2 week period following sample collection, the resulting measurements would be acceptable for direct comparison of previously reported data as well as identifying potentially large emission sources. The intent was that if a potentially large emission source was identified through grab sample screening, then that source could be further evaluated using on-line monitoring techniques; on-line measurements provide the most accurate means for assessing actual direct N_2O emissions.

This would necessitate the development of an on-line monitoring method suitable for combustion source application. The interfering effects of SO_2 and moisture would need to be eliminated if a gas chromatographic method were to be used. In addition, an automated monitoring system would make the monitoring process more efficient, allowing for unattended operation. Using this approach, AEERL/CRB implemented a series of tasks to develop sampling and analytical capabilities to meet these objectives. Specifically, these objectives were to:

- Improve the existing GC/ECD instrumentation so that potential interferences present in combustion process emissions do not effect continuous N_2O measurements

- Develop a method to automate the GC/ECD system for near continuous on-line monitoring purposes

- Configure the GC/ECD system so that it could be used for grab sample analyses as well as on-line monitoring purposes

- Develop a grab sampling method that minimizes N_2O generation in grab sample containers to less than 10 ppm over a 1-2 week period

This project was performed under an AEERL-approved Category IV Quality Assurance Project Plan (QTRAK No. 89014). This report documents the approach and results obtained while meeting these objectives.

SECTION 2

DEVELOPMENT OF ANALYTICAL PROCEDURES

2.1 DEVELOPMENT OF INITIAL ANALYTICAL METHOD

Acurex Environmental's initial work for AEERL/CRB investigated suitable methods of grab sampling analysis by GC/ECD. Because of the relatively recent need for combustion source grab sample measurements, the number of analytical methods available were limited. In 1986, Dr. R. Weiss proposed an analytical configuration at the first EPA workshop on N_2O emissions from fossil fuel combustion.[8] This configuration is similar to the system used by Dr. Weiss for ambient applications.[20] The Energy and Environmental Research Corporation further adapted Weiss' proposed method (see Appendix A). Another analytical approach was developed by Radian (see Appendix B). The initial procedure, developed by Acurex Environmental, incorporated elements from both of these procedures. The initial procedure was ultimately adopted as an AEERL ROP and presented in 1988 at the third N_2O workshop held in France.[10] The original ROP, since modified, is contained in Appendix C. The appended ROP details the analytical apparatus and methodology and will not be reiterated here.

During the initial development of the analytical method, a number of experimental concerns were investigated. The non-linearity of the ECD was characterized over varied N_2O concentrations as well as carrier gases. The detector was found to have a more pronounced non-linearity at concentrations less than 20 ppmv. For quantitative purposes, the linearity problem was accommodated by increasing the number of calibration points and breaking up the overall analytical quantitative range

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into smaller, calibrated ranges. It was also found that the ECD-suitable carrier gases evaluated had no significant effect on detector linearity. The detector sensitivity was slightly enhanced by the 5 percent methane/95 percent argon (P5) carrier relative to the nitrogen carrier. CO_2 was evaluated as a potential analytical interference. Reportedly, CO_2 could positively bias the ECD response to N_2O if the two analytes were to coelute.[9] To evaluate this possibility, a test was performed that compared the detector response to N_2O from an N_2O and CO_2-containing calibration standard where the CO_2 component was eluted both before and after N_2O using different chromatographic columns. No significant difference in N_2O ECD response was observed.[13] Lastly, concern over detector desensitizing from repetitive oxygen exposure was evaluated. A standard gas mix containing nominal combustion effluent oxygen and CO_2 concentrations was analyzed continually over a 7-h period with no discernable loss in detector sensitivity.

Under the original Acurex Environmental analytical configuration, grab samples were introduced to the analytical system via a vacuum evacuation apparatus (refer to Appendix C). The GC gas sample loop was brought down to near absolute vacuum (~5 mm Hg), and a valve located between the sample loop and grab sample container was opened allowing the gaseous sample to fill the sample loop. An absolute manometer was used to determine the absolute pressure within the sample loop to correct the sample volume. This system had a number of limitations, the majority of which were leak-related. In addition, the grab sample containers (bombs) provided were of insufficient volume to perform reliable replicate analyses. Ultimately, the vacuum evacuation apparatus was abandoned and the analytical system and sample containers were configured for syringe injections.

Shortly before the European N_2O workshop in June 1988, AEERL researchers became aware of the N_2O sampling artifact. Based on this information, AEERL initiated efforts to characterize, by on-line means, the direct N_2O emissions from fossil combustion.

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2.2 INITIAL ON-LINE ANALYTICAL EFFORTS

As a result of the grab sampling container N_2O generation artifact discovery, the need for the development of on-line measurement/monitoring techniques became more imperative. Real-time monitoring capabilities were essential to establishing "true" N_2O emissions from fossil fuel combustion and developing reliable grab sampling methodologies. Realizing this, AEERL/CRB initiated a series of in-house tests to compare on-line measurements from pilot-scale fossil combustors to aged grab samples collected at the time of on-line measurement. N_2O measurements were made from the grab samples over progressive, elapsed periods of time to illustrate the extent of the sampling artifact. These data are reported in detail elsewhere.[13] Similarly, AEERL/CRB initiated a field study, also conducted by Acurex Environmental, that performed similar tests on full-scale, coal-fired utility boilers. These data are also described in detail elsewhere.[13,19]

These studies were conducted using GC/ECD systems configured as described in the associated references. In summary, the GCs used were equipped with ^{63}Ni ECDs nominally maintained at 330 °C. N_2O was chromatographically separated from flue gas components with a 0.125-in (0.32-cm) OD by 12-ft (3.66-m) stainless steel column packed with Porapak Super Q, 80/100 mesh (Alltech Associates Inc), using P5 as the carrier at 20 cc/min. The analyses were performed isothermally at 35 °C. A 0.25-in (0.64-cm) OD by 1.5-in (3.8-cm) section of Teflon tubing filled with indicating P_2O_5 (AquaSorb, Mallinckrodt Inc.) was used as a precolumn for moisture removal. Gaseous samples were introduced on column via a 6-port switching valve with a 1-cc sample loop. Flue gas samples were obtained from a sample delivery system configured for use with continuous emission monitors (CEMs). A portion of the sample stream, conditioned for moisture (refrigeration condenser only) and particulate removal, was diverted under positive pressure to the gas sampling valve.

During these studies, various fossil fuels and combustion configurations were evaluated. As a result, a fairly representative cross section of combustion process effluents was encountered, both in

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composition and concentration. Also during these tests, the presence of high SO_2 concentrations in post-combustion gas streams was discovered to present analytical problems. Once on the analytical column, the SO_2 component ultimately eluted from the column. Under the analytical conditions employed, SO_2 eluted from the column nearly 1 h after sample injection. In addition, because of the low-column temperature, the peak shape was very broad (several minutes), resulting in an upset of the baseline conditions and chromatographic difficulties. Similarly, coelution of the N_2O and SO_2 components caused a reduction in detector sensitivity to N_2O. During the field study, this problem was minimized through the use of dual detector GCs.[19]

2.3 ANALYTICAL METHOD IMPROVEMENT REQUIREMENTS

Realizing that the majority of reported fossil fuel combustion N_2O emissions data were suspect because of the discovery of the grab sampling artifact, AEERL/CRB researchers felt that although the relative direct emissions of N_2O emissions from fossil fuel combustion were probably much less than previously reported, it was still necessary to characterize the actual direct N_2O emissions from fossil fuel combustion. AEERL/CRB believed this could be accomplished through a combination of grab sampling and on-line monitoring campaigns where the grab sampling approach could be a mechanism for screening potentially large N_2O-emitting sources, which subsequently could be characterized in detail through on-line monitoring efforts. However, substantial improvements would be required to the analytical procedure to make it suitable for efficient, reliable, on-line monitoring applications. In addition, an on-line monitoring method would be essential to the development of a grab sampling method. Initial N_2O concentrations would have to be established to evaluate the performance of the grab sampling method.

Based on past results, the required analytical method improvements were fairly well defined. The chromatographic interferences present in combustion process emissions would need to isolated from the analytical system. The GC/ECD system would need to be automated to increase method efficiency. An improved quantitative approach, compensating for the non-linearity of the detector,

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would be desirable. Lastly, the system should also be suitable for grab sample analyses. Based on these requirements, improvements to the analytical method/system were initiated.

2.4 CONFIGURATION OF THE ANALYTICAL SYSTEM

2.4.1 Precolumn Selection

The interfering flue gas components, believed to be the cause of chromatographic/analytical difficulties, were isolated through a chromatographic backflushing procedure. This technique uses a precolumn to isolate the analyte of interest from slower eluting, undesirable constituents. Once the analyte of interest has eluted from the precolumn to the secondary analytical column, the carrier gas flow through the precolumn is reversed, flushing the undesirable components from the precolumn.

The primary combustion process flue gas components of concern were moisture (H_2O) and SO_2, both of which have moderate response to the ECD. The relative retention times of these components as well as N_2O, CO_2, and O_2 were compared, and an elution order was determined for a variety of potential chromatographic columns. The ideal precolumn would have adequate separation of analytes at greater than ambient temperature, and the interferants (SO_2 and H_2O) would both elute after N_2O. In addition, the length of the precolumn should be minimized to avoid excessive back pressure of the carrier gas within the chromatographic system. Based on these criteria, precolumn candidates were evaluated. Realizing that any change in elution order of the CO_2 and N_2O components would probably complicate the analyses, columns where the elution did not change narrowed the selection. Of the remaining candidate precolumns, relative separation of N_2O and H_2O was used to further isolate precolumn suitability. Using this selection technique, the precolumn packing materials were narrowed to basically two choices: Poropak Q, the same packing material contained in the analytical column, and HayeSep D 100/120 mesh (Alltech Associates Inc), a packing similar in properties to the Poropak Q but apparently more efficient at separating identical compounds at comparable temperatures. Several HayeSep D columns of varied length were obtained for evaluation.

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2.4.2 Description of the Backflush Method

The backflushing method uses a single, 10-port valve to divert/direct the flow of carrier and sample gas streams through the chromatographic system. A schematic diagram of the 10-port valve system is presented in Figure 2-1. The 10-port valve can be operated in two positions or modes. In the off or backflush position (diagram 2-1a), 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 interfaced to the detector. A 1-cc sample loop, bridged by ports 3 and 4, can be charged with the sample stream (ports 1 and 2, consecutively). In the on or analyze position (diagram 2-1b), the valve is switched to align the carrier gas flow so that the sample loop, precolumn, and analytical column are routed in series (consecutively) to the detector. Once the valve is switched, 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 has eluted from the precolumn onto the analytical column, the valve is returned to the backflush position, the flow through the precolumn reversed, and the undesirable sample components is purged from the precolumn. The N_2O GC/ECD analytical system was configured using this approach.

All previous analytical work was performed using either rented or borrowed Varian GCs or CRB's Shimadzu GC. The Shimadzu GC had a number of hardware limitations that made changes in plumbing more complicated than necessary. Similarly, the addition of a 10-port valve, required for precolumn backflushing, could not be easily incorporated into the Shimadzu system. As a result, the Shimadzu GC was not considered for backflushing configuration. A Hewlett-Packard (HP) 5890 GC was made available for the backflushing configuration. An ECD was installed on the GC, and a 10-port valve was incorporated into the analytical system. This required installation of separate carrier mass flow controllers.

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FROM CARRIER 1

PRECOLUMN

LOOP

4

6

8

VENT

3

5

7

COLUMN

2

1

9

10

TO
DETECTOR

OUT

SAMPLE   IN

FROM CARRIER 2

2-1a. Off position.

FROM CARRIER 1

PRECOLUMN

LOOP

4

6

8

VENT

3

5

7

COLUMN

2

1

9

10

TO
DETECTOR

OUT

SAMPLE   IN

FROM CARRIER 2
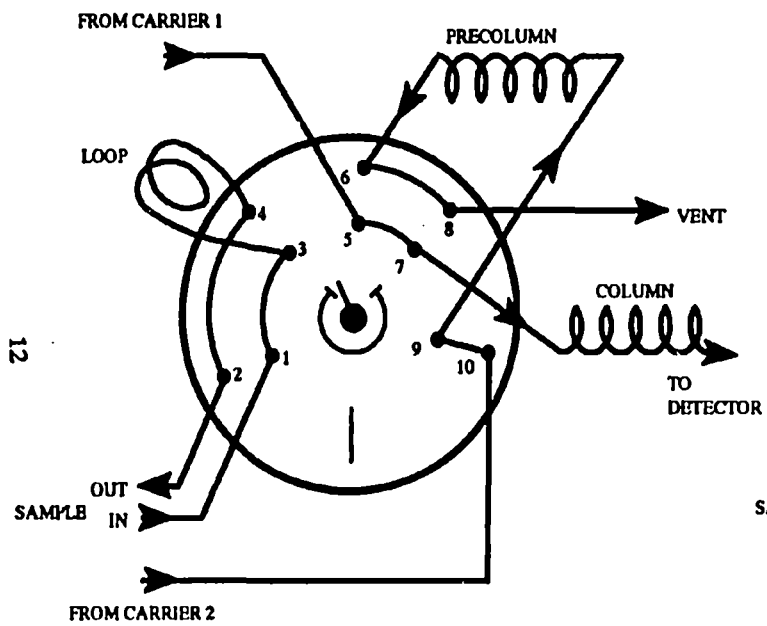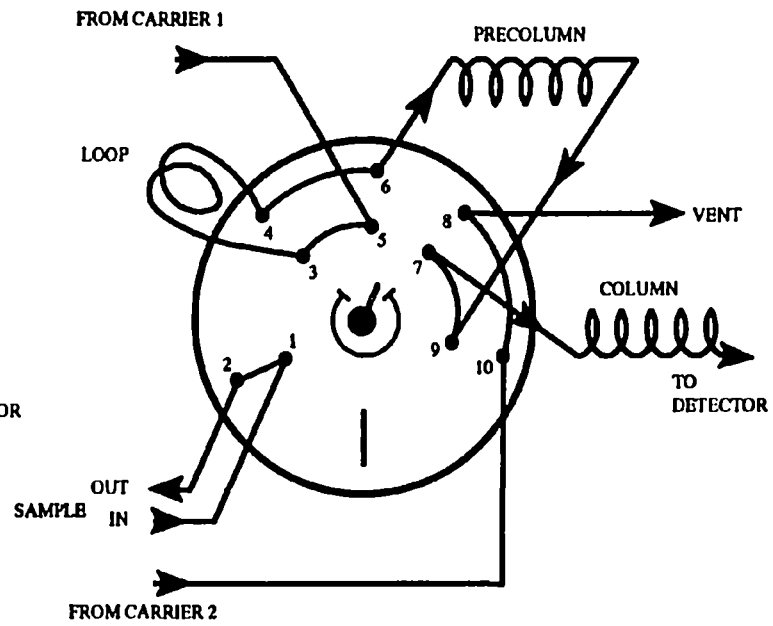
2-1b. On position.

Figure 2-1. Schematic diagram of 10-port valve system.

To eliminate the need for manual valve switching, an air actuator, controlled by the GC system, was used to change valve position. The automation of the valving system was accomplished by interfacing the GC and integrator to a timed event control module that converted digital commands from the integrator to time-controlled electrical switches. The integrator could be programmed to turn the solenoid valves on or off at specific times. The solenoid valves, when energized, allowed compressed air to pressurize the air actuator. When pressurized, the air actuator rotates the 10-port valve to the desired position.

The backflush system precolumn operating parameters were determined by characterizing the retention times of N_2O for the HayeSep D precolumns at varied isothermal oven temperatures. Both a 3-ft (0.91-m) and 6-ft (1.83-m) precolumn were characterized. These retention times were used to determine when the 10-port valve should be switched and backflushing initiated. The precolumns were then evaluated individually when incorporated into the entire analytical system. A decision was made to retain use of the 12-ft Porapak Q column as the analytical column. The 3-ft HayeSep D column displayed acceptable chromatographic resolution when coupled with the analytical column; however, baseline upset, resulting from pressure changes within the system during valve switching, interfered with integration of the N_2O peak. The isothermal oven temperature was varied in an attempt to eliminate the condition, but unsuccessfully. The carrier gas head pressures, required to obtain the targeted flow rates (20-30 cc/min), varied greatly between the 3-ft and 12-ft columns (~15 psig vs. ~40 psig). This pressure disparity was the likely source of the baseline upset.

The 6-ft HayeSep D column was evaluated with much more success. Baseline upsets were much less severe and ultimately disappeared altogether. The disparity between column-head pressures was also much less (~30 psig vs. 40 psig). Acceptable chromatographic resolution of N_2O was observed. Because of the encouraging results obtained with the 6-ft HayeSep D precolumn, this column was selected as the backflush method precolumn. All future tests were performed with this precolumn.

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To confirm the backflush activation time, the automated program was modified in small-time increments, to decrease the elapsed time into the run when backflushing was initiated. The elapsed time was reduced in 0.1-min increments until the N_2O component no longer eluted from the Porapak Q analytical column. Adding 0.2 min (12 sec) to this elapsed time into the run was felt to be sufficient to backflush the SO_2 and H_2O interferants.

At this time, the analytical system was ready for more rigorous evaluation. The GC/ECD backflush system was incorporated into the Flue Gas Simulation System (FGSS), described in detail in Section 3, to evaluate the method under more realistic conditions. A simulated flue gas, containing realistic concentrations of SO_2 (~1,200 ppm), NO (~600 ppm), and moisture (~5 percent by volume) was routed to the system. An ice bath moisture condenser and a P_2O_5 desiccant cartridge was located upstream of the 10-port valve sample loop to remove moisture. No difficulties were encountered during continuous analysis of the simulated flue gas sample. The system was subjected to varied sample moisture concentrations by varying the moisture removal devices. Tests were performed where only the ice bath was used for moisture removal. No discernable difference in system performance was observed. Similarly, no moisture removal was attempted; the unconditioned, simulated flue gas was routed straight to the sample loop. A long-term baseline upset and loss of detector sensitivity was observed under this condition.

At this point, two options were evident. A different precolumn, suitable for high moisture content use, could be identified and evaluated or, the system would require the moisture conditioning of the sample stream before sample loop delivery. The latter option was not compromising to analytical requirements, primarily because the analytical system would be used as an on-line monitoring device and moisture removal by refrigeration condensation was commonly used by continuous emission monitoring (CEM) sample conditioning systems. To verify this approach, the GC/ECD analytical system was incorporated into FGSS CEM system for long-term evaluation.

To further aid in analytical system automation, a solenoid valve was installed upstream of the 10-port valve sample loop. The purpose of this valve was to allow continuous purging of the sample loop until the actual time of analysis. By interfacing the solenoid valve to the timed event control system, the valve could be automatically controlled to open and close in coordination with analytical sequence. The valve was controlled so that the sample loop was continuously purged with the sample stream up to the time of analysis, at which time 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. This was essentially the last modification to the backflushing method.

At this point, the backflushing method analytical parameters were clearly defined. These parameters are as follows:

- Precolumn — 6-ft (1.8-m) by 0.125-in (0.32-cm) OD stainless steel, packed with HayeSep D - 100/120 mesh support; carrier flow of 30 cc/min (head pressure at ~30 psig)

- Analytical Column — 12-ft (3.7-m) by 0.125-in (0.32-cm) OD stainless steel, packed with Porapak Super Q - 80/100 mesh support; carrier flow of 30 cc/min (head pressure at ~40 psig)

- Carrier Gas — 5 or 10 percent methane in argon (P5, P10)

- Detector — ^{63}Ni constant current cell ECD maintained at 300 °C

- GC Oven Temperature — Isothermal, 50 °C

The sequence of timed events were programmed as follows (times denote elapsed time into run):

- 0.0 min — Close solenoid valve (stop sample flow to sample loop)

- 0.1 min — Actuate 10-port valve, move to analyze position

- 3.6 min — Actuate 10-port valve, move to backflush position

- 3.7 min — Open solenoid valve (restore sample flow to sample loop)

- 8.0 min — Stop run, integrate peak areas

Figure 2-2 depicts a schematic diagram of the automated system. The system was also capable of unattended, continuous operation, by incorporating the programmed timed events into a separate BASIC program capable of loop functions. At the end of the analytical run, the system was capable of automatically re-initiating the sequence of timed events.

2.5 ANALYTICAL METHOD PERFORMANCE

2.5.1 Method Quantitative Capabilities

The quantitation of N_2O is accomplished by relating integrated peak area to the linear relationship between calibration variables (N_2O concentration and peak area). A least squares linear regression of the calibration variables is a commonly used calibration approach. The linear relationship can be expressed by the equation:

$$y = mx + b$$

where: y = integrated peak area

m = the slope of the calibration curve

b = the intercept of the calibration curve

x = concentration

To determine unknown concentration, the following equation is used:

$$x = \frac{y - b}{m}$$

However, this quantitative approach has limitations. The non-linear response of the detector to N_2O concentrations nominally less than 20 ppm had been demonstrated early in the N_2O measurement program. As described in the original ROP 45 (Appendix C), this situation was compensated for by narrowing the quantitative concentration ranges. To improve quantitative accuracy as well as to expand the linear range of quantitation, the linear properties of the ECD were evaluated further. With

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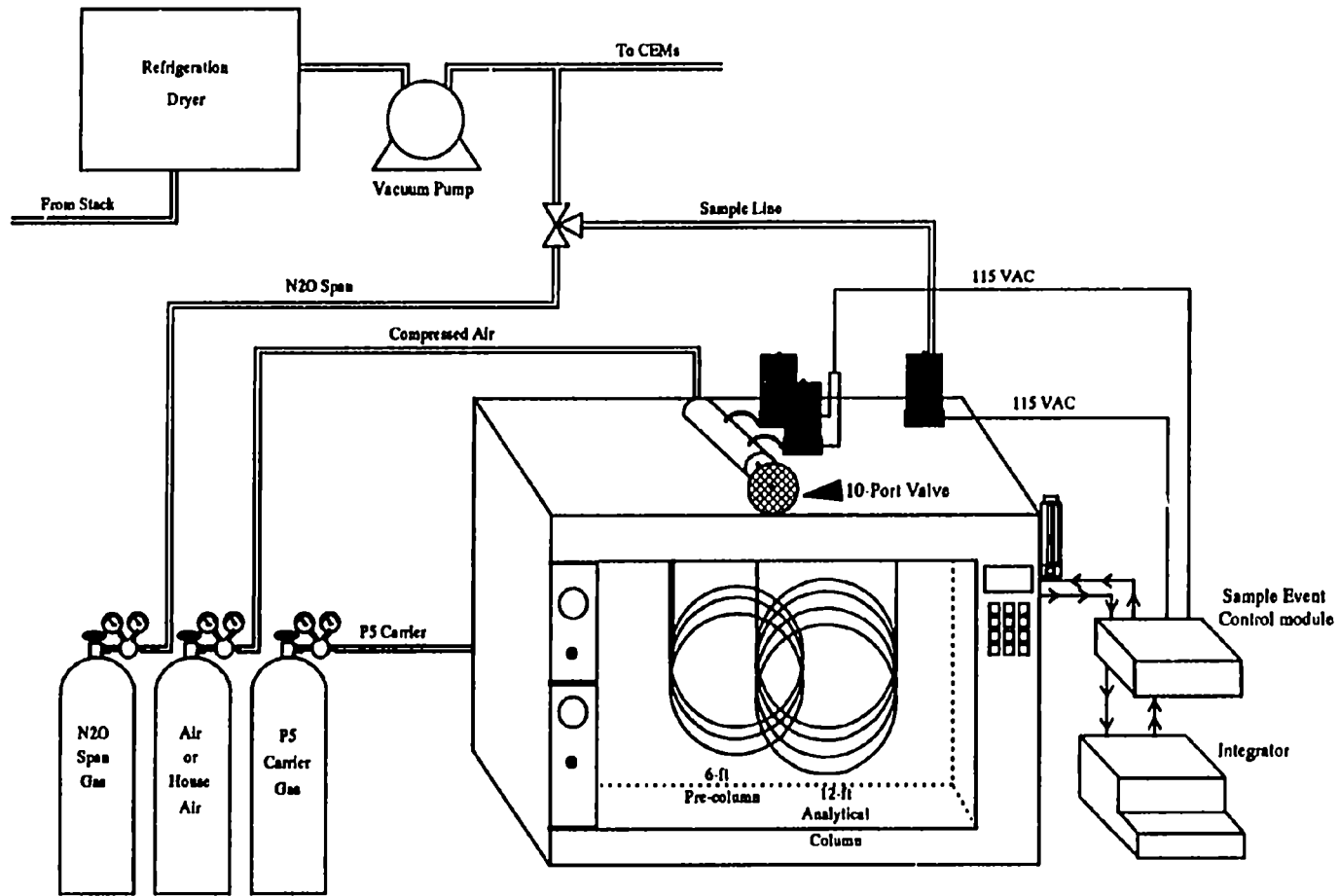
Figure 2-2. Automated, on-line GC/ECD N$_2$O monitoring system.

the assistance of the Research Triangle Institute (RTI), alternative mathematical approaches were considered.

The linear regression approach enables the determination of quantitative bias on an absolute basis. With this approach, error can be reported as less than a certain concentration, often reported as percentage of full scale or as deviation from the true or known value. A problem arises in that the estimated bias for low concentrations will be very large relative to the measured or true concentration.[14] By performing a linear regression of natural log (ln) transformed calibration variables, error is capable of being reported on a relative basis. The equation for the curve is of the form:

$$\ln(y) = m[\ln(x)] + \ln(b)$$

where: $\ln(y)$ = the natural log of integrated peak area

m = the slope of the calibration curve

$\ln(b)$ = the natural log of the intercept of the calibration curve

$\ln(x)$ = the natural log of the concentration

The unknown concentration is determined using the formula:

$$\ln(x) = \frac{\ln(y) - \ln(b)}{m}$$

A comparison of these two quantitative approaches are presented Figures 2-3 and 2-4 and Table 2-1. Figures 2-3 and 2-4 compare ECD response to the mathematical linearizing approach while Table 2-1 demonstrates the relative bias of calculated concentrations (relative to the true concentration)

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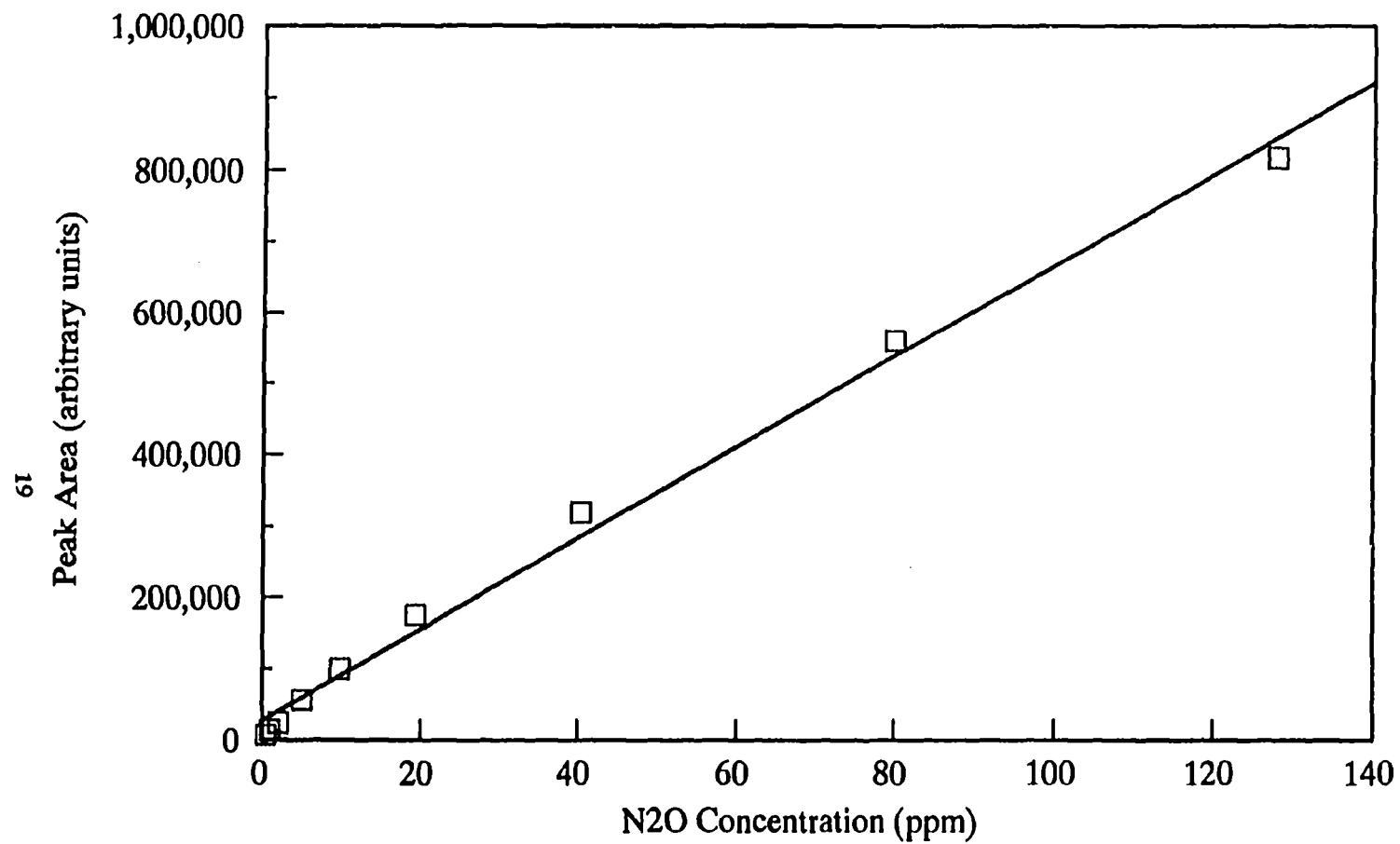
Figure 2-3. ECD response to N_2O calibration gases (linear regression).

R-square = 0.9935379

ln (Peak Area)

ln (N2O Concentration)
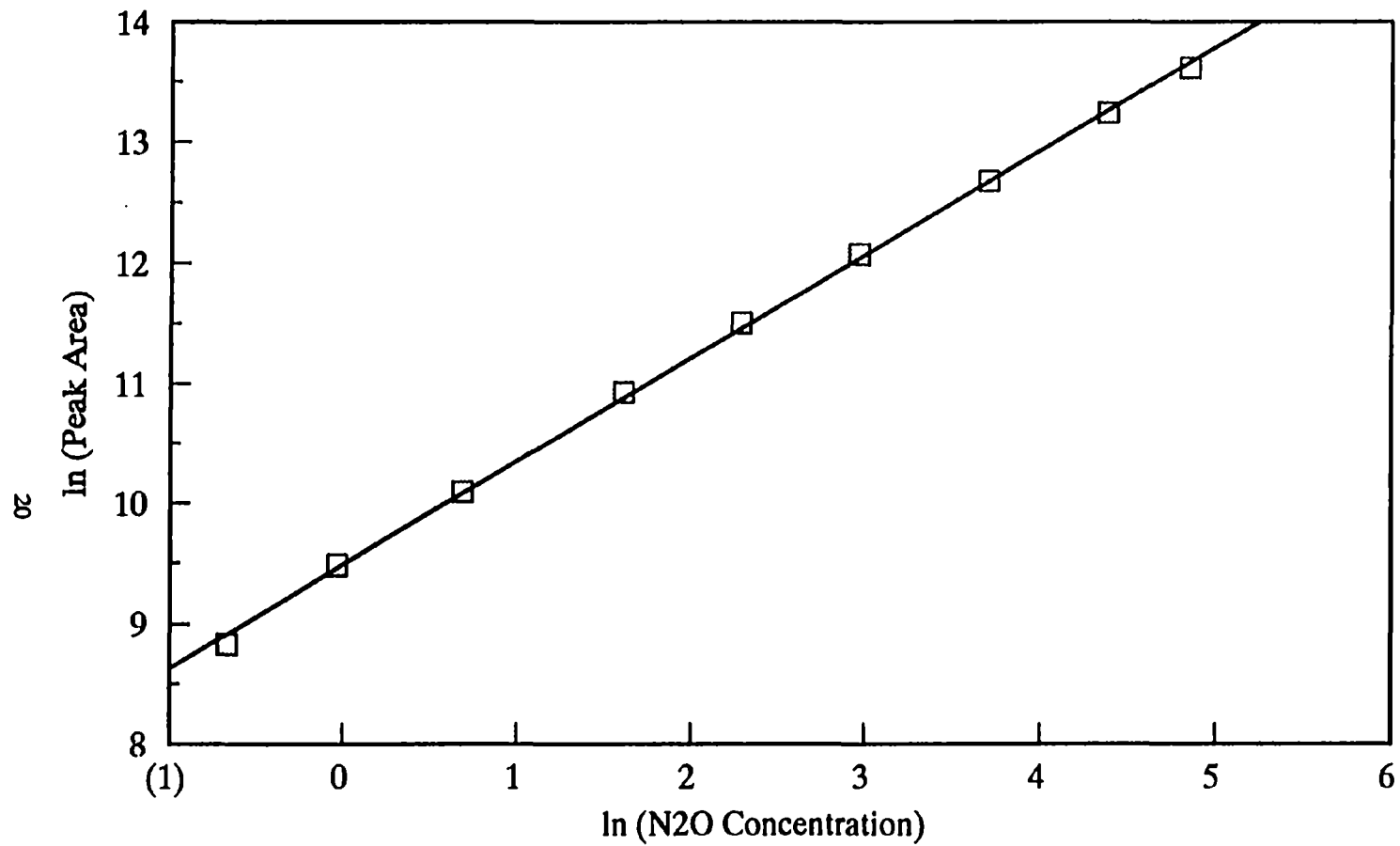
R-square = 0.9992821

Figure 2-4. ECD response to N_2O calibration gases (linear regression of log transformed variables).

using both quantitative approaches. The linear regression of the transformed calibration variables was

TABLE 2-1. COMPARISON OF RELATIVE BIAS USING DIFFERING MATHEMATICAL APPROACHES

N_2O Known ppm	Linear Regression (untransformed variables)		Linear Regression (transformed variables)	
	N_2O Calc. ppm	% Bias	N_2O Calc. ppm	% Bias
0.51	-3.11	-705.1	0.47	-8.6
0.97	-2.13	-319.6	0.99	2.1
1.99	-0.40	-120.1	2.02	1.5
5.03	4.58	-8.9	5.36	6.6
9.85	11.35	15.2	10.41	5.7
19.4	23.18	19.5	20.11	3.7
40.4	45.74	13.2	40.45	0.1
80.1	83.36	4.1	77.74	-2.9
128	123.68	-3.4	120.79	-5.6

effective in minimizing the relative error of calculated concentrations. Less than 10 percent bias was

observed over the entire quantitative range as opposed to as much as 700 percent relative bias for the

non-transformed quantitative approach.

2.5.2 On-line Monitoring Performance

The automated, on-line GC/ECD system was evaluated extensively on a number of diverse

EPA/AEERL fossil fuel combustion test facilities. Initially, the analytical system was used exclusively

during the development of the N_2O grab sampling method. On-line and grab sample measurements

were performed on gases generated by the Flue Gas Simulation System (FGSS). The on-line

concentrations measured were compared to grab sample measured concentrations to assess artifact

generation. These tests are described in detail in Section 3. Once the reliability of the analytical

system had been demonstrated, the on-line monitoring device was evaluated on actual combustion test

equipment.

For AEERL's Gas Cleaning Technology Branch (GCTB), the N_2O monitoring system was used to measure N_2O emissions resulting from the combustion of various coals during parametric SO_2 removal testing. These tests, performed on EPA's Innovative Furnace Reactor (IFR), are described in further detail in Section 3. The N_2O concentrations measured ranged from 0.5 to 10 ppm.

During these tests, quality control (QC) span checks were performed nearly every hour over the course of the 8-h test period. The QC checks were used to assess method analytical bias and precision over the course of the entire test period. The reliability of the analytical system was without question. All span checks performed were within method QC objective limits. The results of these QC checks in the form of a control chart, are graphically presented in Figure 2-5. The average bias observed (2.9 percent) was well within the targeted level of less than 15 percent. Similarly, the precision observed (2.7 percent), expressed as percent relative standard deviation (RSD) was well within the targeted level of less than 10 percent.

The on-line GC/ECD system was loaned to GCTB for a series of selective non-catalytic NO_x reduction (SNCR) tests. During these tests, additives such as ammonia and urea were injected into the IFR to reduce NO_x emissions. The on-line measurements were used to compare N_2O emissions with and without NO_x control. The N_2O concentrations measured ranged from 0.5 to 35 ppm. No difficulties were encountered during analysis. All QC checks were within method requirements. The analyzer was loaned to GCTB because their primary method of N_2O measurement, a tunable diode laser, was experiencing operating difficulties. During the development of the TDLIR system, the on-line GC/ECD system was relied on to establish the actual flue gas N_2O concentrations for performance evaluation purposes.

The automated, on-line GC/ECD system was also used by GCTB to characterize the N_2O emissions from a selective catalytic NO_x reduction (SCR) pilot-scale test facility. N_2O concentrations were measured both before and after the catalyst was evaluated. Measured concentrations ranged from 0.5 to 3 ppm. Again, the GC/ECD system performed reliably.

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Precision = 2.7 % RSD

Span = 5.03 ppm N2O in N2
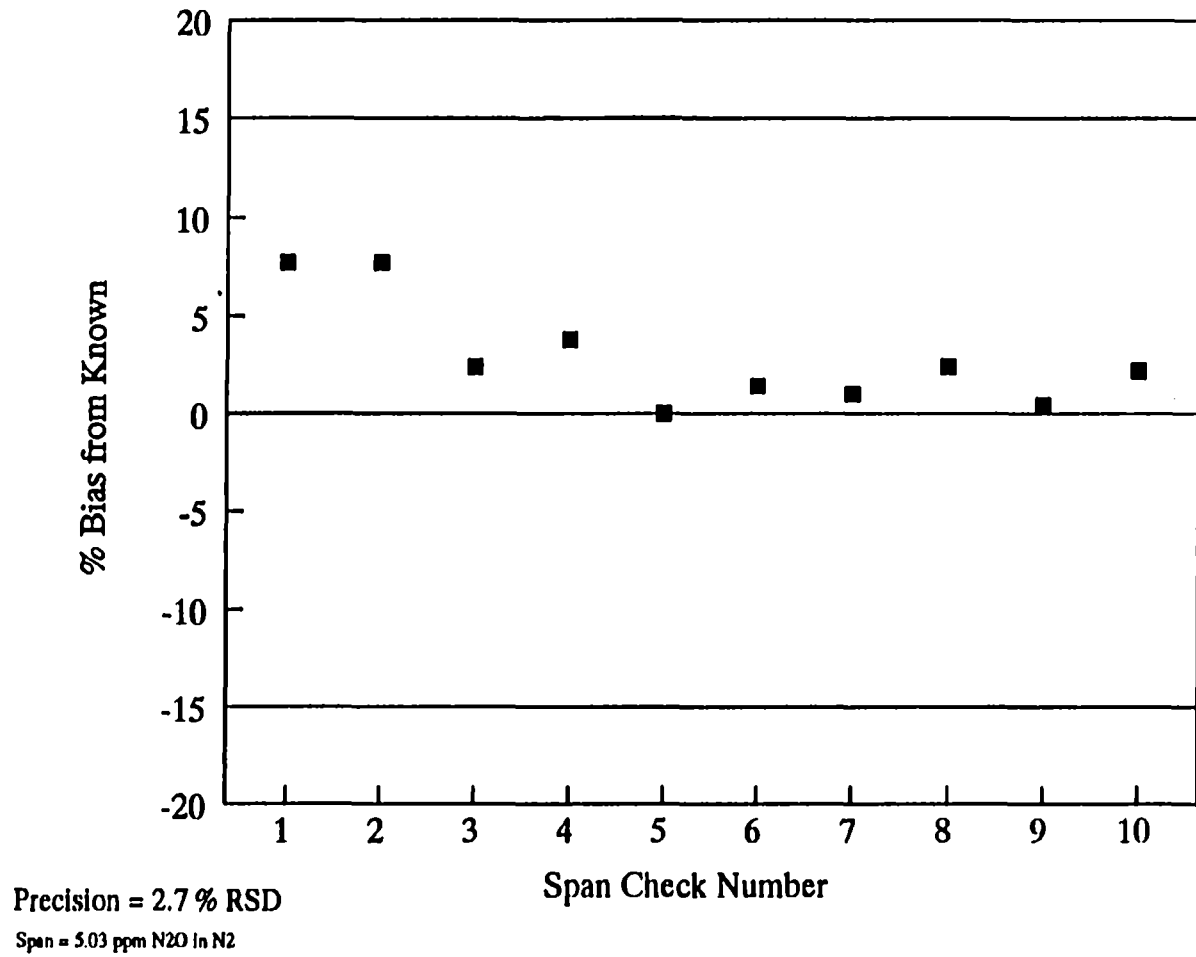
Figure 2-5. Automated N_2O analysis results of span checks over course of a test day.

The GC/ECD system was also evaluated under ambient conditions. For the Radon Mitigation Branch (RMB), the system was used to assess the N_2O mass emissions resulting from the open-hearth combustion of 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_2O to the environment from this combustion source. The N_2O 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.

These ambient measurements were performed over the course of several weeks. At the beginning and end of each test period, QC span checks were performed. The results of these QC checks are graphically presented in Figure 2-6 in the form of a control chart. The results demonstrate that the analytical system is capable of long-term, reliable performance. The average bias over the 2-week period was only 3.4 percent, whereas the average precision was 2.9 percent.

2.6 ANALYTICAL METHOD SUMMARY

The GC/ECD backflush method developed was found to be suitable for the measurement of N_2O 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 purposes. Analytical interferences, present in combustion process effluents, were negated through the use of a backflushing technique. Method accuracy, expressed as percent bias, and precision, expressed as percent relative standard deviation, were determined to be $\leq \pm 15$ percent and ≤ 10 percent, respectively. The method was found to be suitable for the quantitation of N_2O concentrations ranging from 0.100 to 200 ppm.

Using this method for on-line monitoring purposes allows a semicontinuous measurement approximately every 8 min. The system can be easily incorporated into most continuous emission monitoring sample delivery/conditioning systems. The only requirement is the removal of particulate and moisture from the sample stream by a refrigeration condenser. The sample stream should be diverted to the analytical system before further moisture conditioning by a desiccant.

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15

◇ PreTest Span Checks

△ Post Test Span Checks

10

% Bias from Known

5

0

-5

-10

-15

-20

10/30/91   11/06/91   11/08/91   11/12/91   11/13/91   11/14/91

Pretest Precision = 4.11 % RSD

Post Test Precision = 1.77 % RSD

Test Date

Span = 0.97 ppm N2O in N2
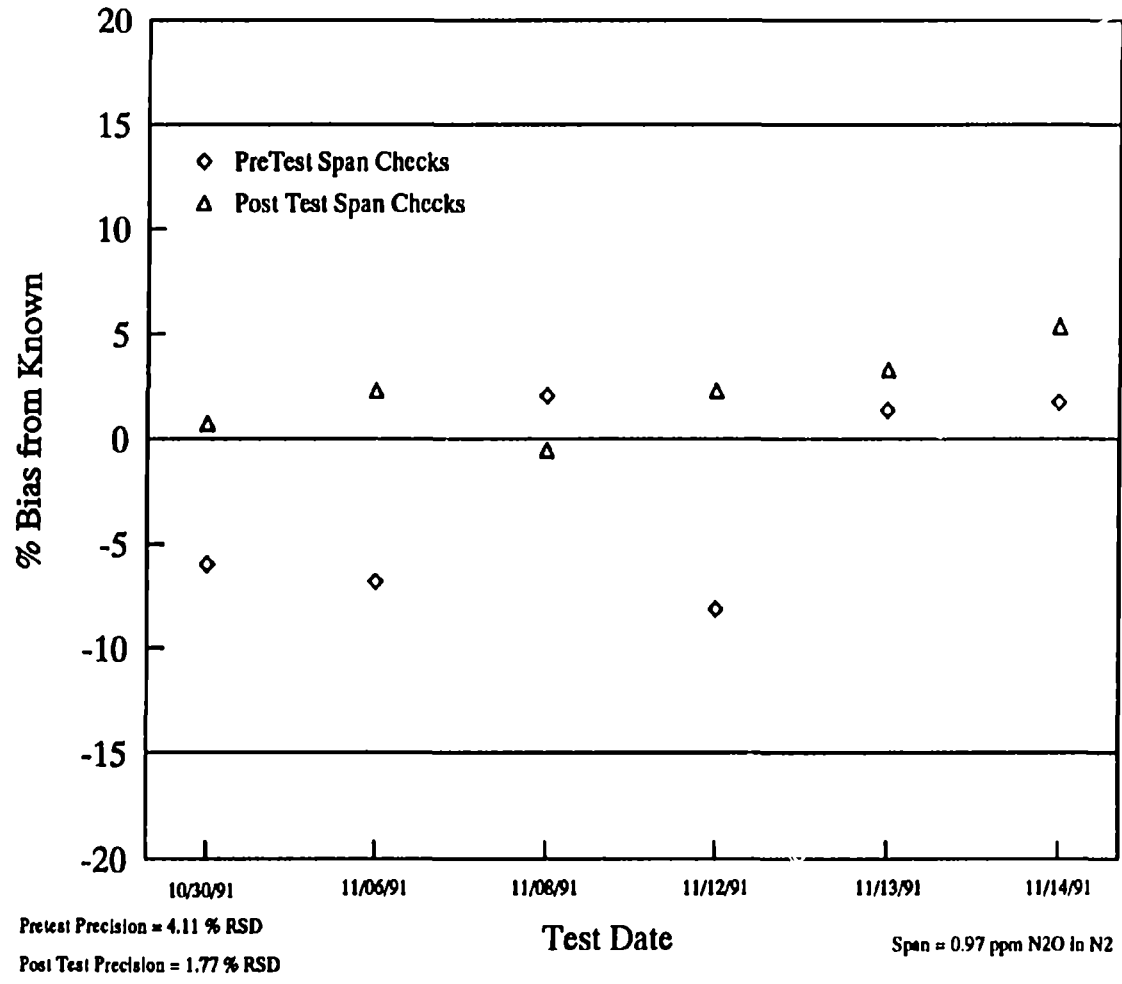
Figure 2-6. Automated N_2O analysis results of span checks over the course of a 2-week period.

Through use of the backflushing technique, known interferences such as SO_2 and moisture are isolated by a precolumn and purged from the system by backflushing the precolumn. Other common flue gas components such as O_2, CO, CO_2, NO_x, unburned hydrocarbons (THC), and ammonia (NH_3) were found not to interfere with the analytical procedure.

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.

SECTION 3

GRAB SAMPLE METHOD DEVELOPMENT

3.1 BACKGROUND

The discovery of the N_2O sampling artifact attenuated the need for a standardized, reliable sample method to accurately assess the N_2O emissions from fossil fuel combustion sources. As previously mentioned, much of the reported N_2O combustion emissions data was collected under conditions conducive to the N_2O sampling artifact.[10,12,21] Grab samples were collected in a variety of sampling containers including glass flasks, stainless steel canisters and Tedlar bags.

Muzio and Kramlich were among the first researchers to identify the sampling artifact reactants as well as potential formation mechanisms.[11,12] The group identified the key artifact reactants as SO_2, NO_x, and water, components present in most fossil fuel combustion process emissions. The sampling artifact was also independently confirmed by a number of other researchers.[12,22,23]

Solution-phase reactions between NO_x and SO_2 with N_2O as a product have been documented. Martin et al., identified N_2O as a product in the reactions of NO_x with SO_2 in the aqueous phase of atmospheric aerosols.[24] Chang et al., studying the chemistry of flue gas desulfurization, identified a mechanism in which hyponitric acid decomposed into N_2O.[25] Lyon and Cole have performed kinetic modeling on the proposed reactions occurring within aged grab sample containers.[26] DeSoete also conducted a detailed examination on the kinetics of solution-phase reactions leading to the formation of N_2O in grab sample containers.[27]

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The selective removal of any or all of these reactants was targeted as an approach to eliminating the sampling artifact. Tests performed by Muzio et al., evaluated the effect of drying the gas stream sampled as well as neutralizing SO_2 with NaOH scrubbing solutions.[12] Results of the performed tests indicated that N_2O generation within aged grab sample containers could be drastically reduced, possibly even eliminated.

AEERL/CRB also performed work that investigated the use of methods to minimize the sampling artifact.[13] Efforts focused on methods for removing moisture from the sample gas stream only. The use of a desiccant, phosphorus pentoxide (P_2O_5), was effective to drastically reduce the artifact generation but unable to eliminate it completely.

Realizing that it would be extremely difficult, if not impossible, to consistently eliminate the sampling artifact entirely, the AEERL/CRB believed that if N_2O generation within aged sample containers could be minimized to consistent levels, this would be suitable to screen for high N_2O-emitting combustion sources. Specifically, it was felt by AEERL researchers that if N_2O generation within grab sample containers could be consistently minimized to less than 10 ppm over a 1-2 week period, this would be more than acceptable to screen for high N_2O-emitting fossil fuel combustion sources. The screening technique could then be used to direct on-line monitoring efforts.

The screening of intended fossil fuel combustion sources would require the voluntary cooperation of commercial and research combustion facilities. Therefore, the grab sampling equipment and technique must be easy to use and pose minimal imposition to those participating in screening surveys. Specifically, the grab sampling method should not require a great degree of sampling expertise. In addition, the grab sample should be capable of being obtained in a manner compatible with commonly employed CEM sample delivery systems.

Because the screening of numerous fossil fuel combustion sources was intended, great consideration into the preparing, shipping, and receiving of the grab sampling equipment was essential.

The sampling equipment must be durable and compact. Similarly, the restrictions of shipping chemical reagents must be considered.

With these factors in mind, development of a N_2O grab sampling method was initiated. Specifically, the objective of this study was to determine, if possible, the conditions under which a grab sample could be collected that minimized the N_2O generation artifact while still allowing reliable, representative N_2O measurements so that major N_2O emitters could be isolated. Primary objectives of the study were as follows:

- Identify and evaluate materials that effectively remove the key flue gas constituents of SO_2 and moisture

- Incorporate and optimize these materials into an apparatus that can be easily adapted for use on existing on-line, continuous emission monitor systems

- Minimize the N_2O generation sampling artifact to less than 10 ppm

- Identify the NO_x, SO_2, and H_2O concentration ranges where the method is applicable

- Validate the sorbent system on an actual combustion systems

- Determine the methods suitability through field evaluations

The following information demonstrates the approach taken and the tests conducted to meet these objectives. The majority of the work was performed between January 1990 and August 1991. Ultimately, the sampling procedures developed were documented in the form of an EPA/AEERL ROP.[18]

3.2 GRAB SAMPLING EQUIPMENT CONSIDERATIONS

Ultimately, the grab sampling method, once developed, would be used to conduct a rigorous, comprehensive field survey of the emissions from various fossil fuel combustion sources including industrial boilers and power plants, fluidized bed combustors, and various pilot- and full-scale test facilities. Voluntary cooperation of solicited participants would be critical to the success of the

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screening campaign. Therefore, it was important that the collection of grab samples for screening purposes be as unobtrusive as possible.

The logistics of transporting the sample equipment would also be extremely important. The complexities of shipping the equipment both to and from prospective screening candidates must be considered. For example, the sealing and secondary containment of liquid samples would create an added burden to screening participants. In addition, if liquid chemical reagents were used, precautions could be necessary to ensure their safe shipment by screening participants. Similarly, chemical shipping restrictions could have an adverse impact on the screening efforts if liquid chemical reagents were used.

How the sampling system would be used was the most important factor when considering the ideal characteristics of the field grab sampling method. It was felt that to increase survey participation, the sampling method and equipment would need to be very simple to use. Potential N_2O screening survey participants may possess little, if any, stack or source sampling experience. In addition, it was believed that if the grab sampling equipment could be adapted or incorporated into existing gaseous sample delivery systems, then participation in the screening survey could be increased. It was expected that the vast majority, if not all, candidate combustion sources would possess some type of continuous emission monitoring system. If the N_2O grab sampling equipment could be incorporated into this system, the need for a stand-alone sampling system could be eliminated.

With these considerations, the actual components of the grab sampling equipment and method were further identified. The use of dry sorbents for the neutralization of SO_2 was chosen as a starting point. Dry, calcium-based sorbents are commonly used for flue gas desulfurization processes and could easily be used in a stack sampling configuration. The use of dry sorbents could eliminate the need for impingers and other glassware associated with the use of liquid scrubbers and, therefore, minimize glassware breakage problems. By using dry sorbents and thereby eliminating the use of

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liquid-filled impingers, the concern over N_2O solubility in water could be avoided. DeSoete has shown however, that N_2O solubility does not appear to be a problem.[22] The use of dry sorbents could also minimize sampling equipment shipping concerns, and thus, eliminating the risk of chemical spills or leakage.

The elimination of potential scrubbing solutions such as sodium hydroxide, which also removes CO_2, could possibly relieve potential quantitative concerns. If CO_2 were to be removed from the sample gas, the N_2O concentrations measured could be biased as a result. The contribution of CO_2 to the entire sample volume is significant (~8-15 percent), and the loss in volume would require a correction to measured N_2O concentrations. In addition, the remaining CO_2 concentration would have to be measured to complete the volume correction, requiring a separate analytical method for CO_2.

3.4 EXPERIMENTAL APPARATUS

Specially designed test equipment was used during the development of the grab sampling methodology. This equipment allowed independent evaluation and control of parameters effecting the integrity of aged grab samples. A test facility was designed and built that simulated typical combustion process effluents, both in composition and concentration. A separate emission monitoring system was used to determine generated gas concentrations. The individual components of these systems are described in following sections.

3.4.1 Flue Gas Simulation System (FGSS)

The objective when designing the Flue Gas Simulation System (FGSS) was to simulate a flue gas in the laboratory with the capability to vary the concentration of NO, SO_2, and moisture, independently (NO, 0-1,000 ppm; SO_2, 0-2,500 ppm; and moisture, 0-20 percent by volume). This system could then be used to conduct studies of the absorption of H_2O and SO_2 from a flue gas stream by solid sorbents. The system was engineered and assembled with the capacity to accomplish the following:

- Vary the concentrations of NO, SO_2, and moisture, independently

- Incorporate other gases into the system

- Continuously monitor for NO and SO_2 at varied locations

- Measure N_2O on-line

- Maintain stable readings

The FGSS is a combination of two independent systems: the flue gas generation system and the sampling system. This design allows for flexibility in sampling positions while continuously monitoring NO and SO_2.

3.4.2 Flue Gas Generation System

The FGSS requires three supply gases: nominally 2,000 ppm NO in nitrogen; 5,000 ppm SO_2 in air; and pure N_2. N_2O is introduced into the system from the NO cylinder which inherently contains between 1-5 ppm N_2O.

The three supply gases flow directly to four calibrated rotameters (Figure 3-1). The supply gases are then fed into the mixing system in two gas streams. Gas stream No. 1 contains NO and N_2. Gas stream No. 2 contains SO_2 and N_2. Both streams are balanced to the same flow rate, 9 L/min. The N_2 is a makeup gas in both gas streams (e.g., if the NO flow is decreased, the N_2 flow is increased to maintain the 9 L/min, flow rate). Both gas streams are equipped with pressure gauges to make rotameter flow corrections. These calculations and corrections are used to roughly set the rotameters. The actual SO_2 and NO_x concentrations are measured at the exit of the gas stream. Gas stream No. 1 is directed upstream of the moisture generator because of the relative insolubility of NO and N_2O in water. Gas stream No. 2 is introduced downstream of the moisture generator because of the greater solubility of SO_2 in water.

3.4.2.1 Moisture Generator

Moisture is generated from a 2-L, insulated, and temperature-controlled glass impinger and is filled with 1 L of deionized water. The flow rate of gas stream No. 1 into the impinger is held
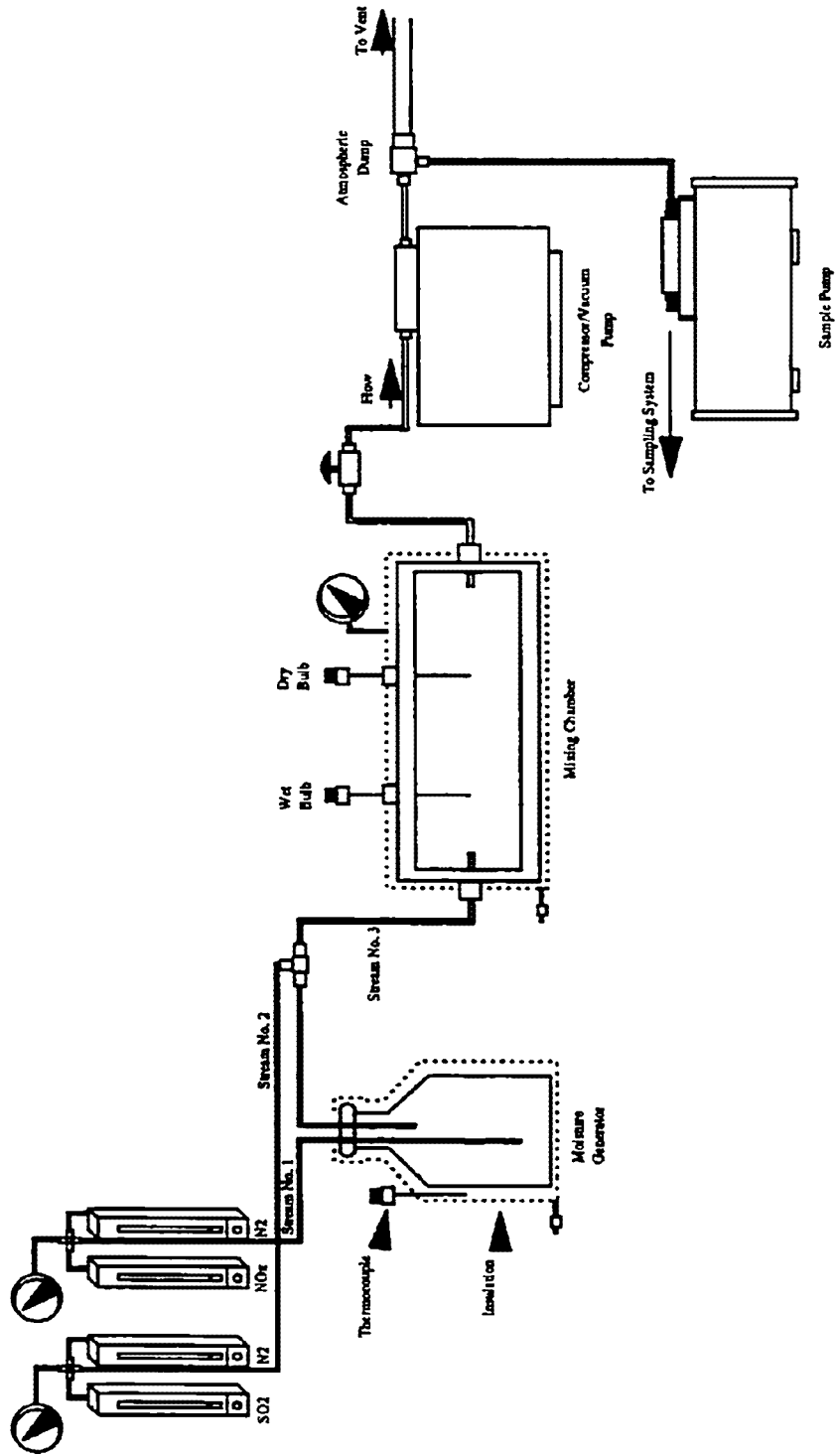
Figure 3-1. Flue gas generation system.

constant at 9 L/min while the temperature can be varied to change the percent moisture. A multipoint calibration ranging from 60-100 °C (5-15 percent moisture) was performed on the moisture generator.

3.4.2.2 Mixing Chamber

After the impinger, the two gas streams combine to make gas stream No. 3, which has a combined total flow rate of 18 L/min. At close to atmospheric pressure, stream No. 3 flows directly into a mixing chamber and then into a vacuum pump. The mixing chamber is an insulated and temperature controlled 6-in ID by 12-in stainless steel pipe (volume: 0.2 ft^3 or 5.6 L). The chamber temperature is held at 105 °C. The humidity of the gas stream during sampling is roughly monitored by wet and dry bulb temperatures. The wet and dry bulb temperatures are monitored separately. A regulating valve is located between the mixing chamber and the vacuum pump to balance the sample pressure in the system and to ensure a constant flow rate of 18 L/min. The chamber is also equipped with a pressure/vacuum gauge to monitor the chamber pressure.

For sampling purposes, an atmospheric dump is located on the outlet side of the chamber pump. The atmospheric dump allows a sample to be withdrawn without affecting the total flow of the flue gas generation system. This is achieved by enlarging the 1/4-in tubing to a 1/2-in tee. The majority of the simulated flue gas vents through the 1/2-in tee. The 1/2 in-tee also connects the flue gas generation system with the sampling system.

3.4.3 Sampling System

Through the addition of a smaller sample pump, the flue gas generation system and the sampling system can operate independently. The smaller sample pump pulls a fraction of the simulated flue gas into the sampling system from the 1/2-in tee (Figure 3-2). A 1/4-in tee is located at the outlet of the sample pump. Part of the gas is directed under positive pressure at a regulated flow through a 1/4-in heated Teflon sample line to a SO$_2$ "high" analyzer, 0-5,000 ppm (Teledyne UV). The remainder of the sample is directed to the common port of a three-way valve. The valve allows the sample to flow through either a "bypass" loop or a sorbent/sample loop.

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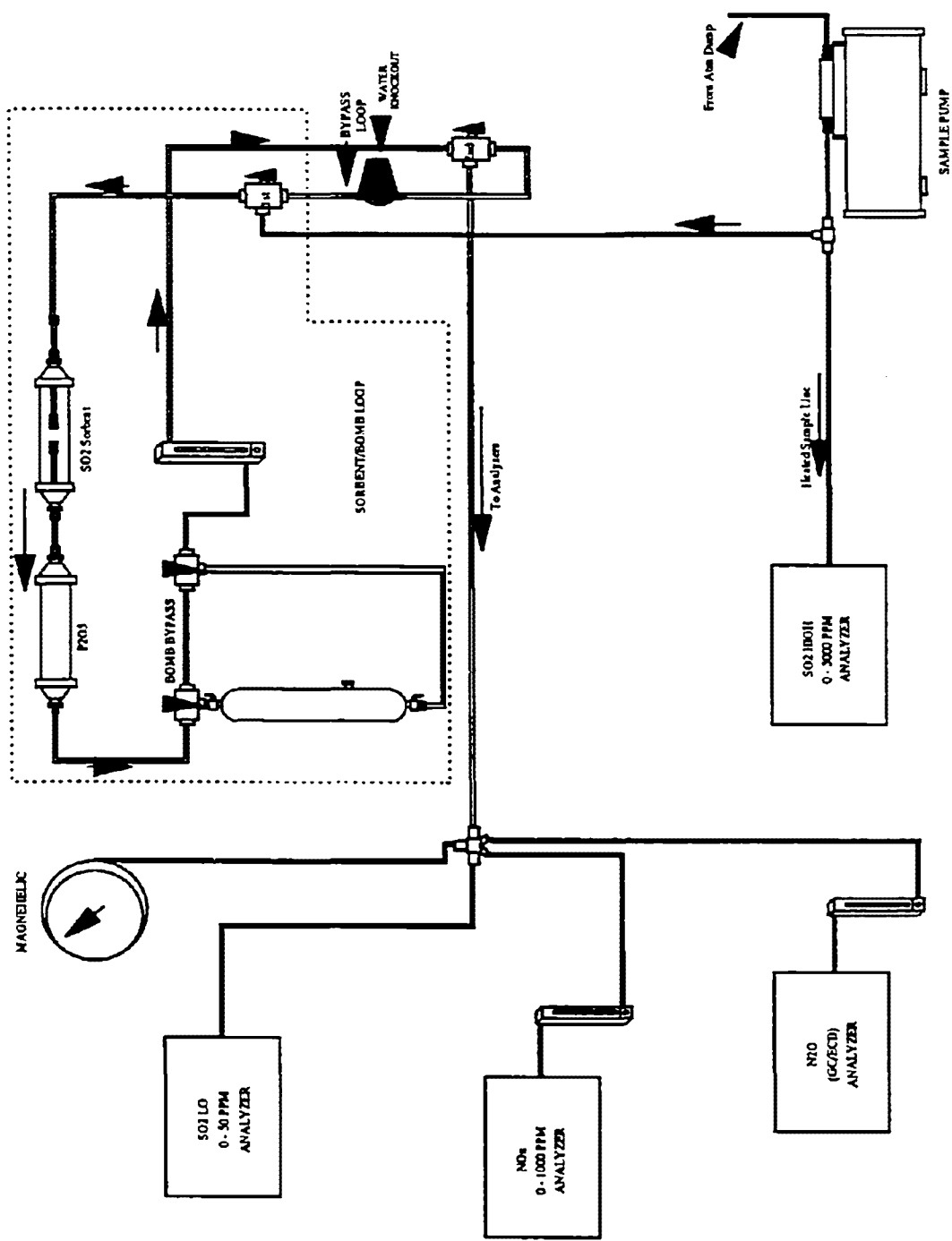
Figure 3-2. Flue gas sampling system.

3.4.3.1 Bypass Loop

The bypass loop (no sorbents) allows measurement of the initial flue gas concentrations (SO_2 high, NO, N_2O) untouched by sorbents. This allows the monitoring of any effects the sorbents may have on the initial flue gas concentrations once the sorbents are placed in-line. The sample flows into the first three-way valve through a water knockout device and then to a second three-way valve that directs the simulated flue gas to the analyzers.

3.4.3.2 Sorbent/Sample Bomb Loop

The sorbent/sample bomb loop allows measurement of the flue gas concentrations (SO_2 low, NO, and N_2O) after the gas flows through the sorbent system. The sorbent/sample bomb loop is equipped with a rotameter to measure the sample flow rate through the sample bombs. Another bypass loop between the sorbents and the bombs allows continuous flow through the sorbents when samples are not being collected. The exit of the sorbent/sample loop is connected to the second three-way valve.

3.4.3.3 Analyzers

The sample stream leaves the second three-way valve and is diverted four ways:

1. Through a rotameter to an NO analyzer, 0-1,000 ppm (Thermo Electron, Model 10, chemiluminescent $NO-NO_2-NO_x$ analyzer).

2. To a SO_2 low analyzer, 0-50 ppm (Thermo Electron, Series 40, pulsed fluorescent analyzer with the Perma Pure Dryer removed). The SO_2 analyzer is used only when sorbents are placed in the sorbent/sample bomb loop. The analyzer requires a dry sample.

3. Through a rotameter to a GC/ECD with a 1-mL sample loop for N_2O measurements.

4. To a differential pressure gauge (0-10" H_2O) with a needle valve to regulate pressure on the system and then to vent.

3.4.4 Flue Gas Measurements

3.4.4.1 Continuous Emission Monitors

The SO_2 and NO analyzers were calibrated to verify linearity before initial testing. The analyzers were then calibrated every 2 weeks or when the bias exceeded predetermined limits. These limits are shown in Table 3-1.

The calibration consisted of at least three points (zero, span, and mid-point). All span gases were delivered at a constant pressure and flow rates identical to those used during sampling.

The analog output from each CEM instrument was interfaced with a computer data acquisition system. Since the instrument was based on linear measurement properties, the slope or range was used to calculate concentration in ppm or percent. Data were collected over a timed average and were automatically stored on disk. A hard copy was also produced for permanent record. The daily QC checks conducted before and after each test period were used to validate data and monitor system performance.

3.4.4.2 GC/ECD and N_2O Measurements

N_2O measurements were performed on a Hewlett Packard 5890 GC/ECD configured for automated, on-line N_2O measurements. The analytical system has been previously described in

TABLE 3-1. PREDETERMINED LIMITS

Analyzer	Accuracy (% bias)	Precision (% RSD)
NO	± 20	10
SO_2	± 20	10
SO_2 lo	± 3 ppm	10

Section 2 EPA/AEERL ROP No. 45 was used as the procedural guidelines.[14] N_2O measurements were either taken on-line or through direct injection with a 10-mL glass syringe. A multipoint calibration was performed using the on-line method. The method of direct injection was verified using three different span gases. There was no bias between the two methods. The sample loop required at

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least seven volume exchanges to ensure a representative sample. This required two 10-mL syringe flushes before every N_2O measurement when using the direct injection method.

3.4.5 Sampling Procedure

A standardized test plan for the evaluation of sorbents was followed. The plan called for holding the FGSS conditions constant while varying the sand/sorbent mixtures, flow rates, and sampling positions.

Throughout the first part of the study the FGSS conditions were held constant (10 percent moisture, 1,200 ppm SO_2, 600 ppm NO, and about 0.5 ppm N_2O). These were referred to as the nominal inlet conditions.

The procedure for evaluating the sorbent cartridges (unless otherwise specified) was as follows:

1. Shoot standard on GC.

2. Span CEMs.

3. Fill impinger with 1 L of deionized H_2O.

4. Set temperatures: impinger, 60 °C; wet/dry bulb, 105 °C.

5. Insert sorbent cartridge system into FGSS.

6. Switch FGSS to bypass loop.

7. Turn on SO_2, NO, and N_2 supply gases.

8. Set rotameters at calculated values.

9. Let system equilibrate (~ 5 min).

10. Take on-line bypass N_2O measurement.

11. Switch to sorbent/sample loop.

12. Let flue gas run through sorbent cartridge (~5 min).

13. Take a 2-min bomb sample (~4 L/min).

14. Take on-line N_2O measurement from bomb exit.

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15. Let flue gas run through sorbent cartridge (~10 min).

16. Repeat steps 13-15 for two additional bombs.

17. Switch to bypass loop.

18. Take on-line bypass N_2O measurement.

19. Turn off supply gases.

20. Span CEMs.

21. Shoot GC standard.

22. Shut down system.

This procedure is for one sorbent cartridge system with the collection of three sample bombs. A test usually evaluated three sorbent cartridge systems at the same conditions with the collection of a total of nine bombs. Each of the two remaining cartridges were inserted after step 18 and steps 10-18 were repeated for each cartridge set. At least seven volume exchanges were passed through the 600 cc sample bombs to ensure a representative sample.

The bombs were nominally aged 5-7 days. The nine bombs from one test were aged the same amount of time. The aged bombs were then analyzed for N_2O by direct injection into a GC/ECD. Duplicate 10-mL samples were withdrawn through the septa on the sample bomb with a 10-mL glass syringe.

3.5 INITIAL SORBENT TESTS

3.5.1 Introduction

The initial series of tests necessitated a qualitative screening approach. Many of the tests were of the yes/no or go/no-go nature. These types of tests were required to identify candidate materials early in the study and then optimize their performance. The tests were conducted under the FGSS conditions of 10 percent moisture, 1,200 ppm SO_2, 600 ppm NO, and about 0.5 ppm N_2O and will be referred to as the nominal inlet conditions. These concentrations are representative of actual emissions

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from typical coal combustion facilities. Initial N_2O concentrations were inherent to the NO supply gas and varied with each individual cylinder.

The initial tests were concerned with SO_2 removal efficiencies of various dry sorbents and the best cartridge design. The SO_2 removal efficiency was defined, at this point in the study, as the measured SO_2 exit concentration of the flue gas after the gas had passed through the sorbent system. These SO_2 concentrations measured by the SO_2 low CEM in the sorbent/sample bomb loop, were referred to as the SO_2 breakthrough data. The initial efforts also included the use of SO_2 and acid color indicators. The various tests and their results are discussed in respective subsections.

3.5.2 Water Removal

As mentioned previously, P_2O_5 was the selected desiccant based on its greater moisture removing ability and its color indicating properties. The 120-cc refillable traps were filled with ~50 g of P_2O_5 and held in place by glass wool plugs. The water removal cartridge was placed, in series, after the SO_2 sorbent cartridge and before the sample bomb. The placement of the SO_2 cartridge was critical because SO_2 must dissociate in water to form an acid and then react with the sorbent, therefore, water was necessary to enhance the SO_2 neutralization process in the sorbent cartridge.

3.5.3 FGSS Shakedown Tests

The first set of tests took place during the design and construction of the FGSS. These first screening tests were performed to ascertain if a two-cartridge solid-sorbent design was feasible.

The first screening test was performed to evaluate SO_2 removal by a 40:1 (by weight) sand/$Ca(OH)_2$ mix and to evaluate the effect of the $Ca(OH)_2$ on the initial N_2O concentration. $Ca(OH)_2$ was initially chosen because of its proven ability to scrub SO_2. This test mix was added to an empty, gas-tight air purifier tube and then evaluated on the FGSS. A gas stream containing ~1,500 ppm SO_2, 600 ppm NO, and 8 percent moisture was passed through the sorbent cartridge. The SO_2 concentration exiting the cartridge was measured to be less than 10 ppm. The N_2O concentrations were measured by on-line GC/ECD upstream and downstream of the $Ca(OH)_2$ cartridge. A 0.8

percent difference existed between the upstream (initial) N_2O concentration and the downstream N_2O concentration. This difference was considered negligible.

The second screening test evaluated the use of an acid color indicator, methyl red, in the sorbent mix. The methyl red was added to the sorbent mix in an attempt to possibly indicate the expenditure of $Ca(OH)_2$ during sampling. A 40:1 sand/$Ca(OH)_2$ (80 g, 2 g, respectively) mix was made and 82 mg of methyl red was then added. This mix was evaluated under the same conditions as the previous test. The sand mixture changed color as the test progressed, but the color change did not occur evenly throughout the cartridge. The SO_2 exit concentrations and N_2O results were similar to those of the previous screening test.

These first screening tests indicated that a two-cartridge solid-sorbent system may indeed be feasible. The initial results also indicated that $Ca(OH)_2$ had no effect on the initial N_2O concentration. Initial N_2O concentration would become a critical measurement later on in the study. These initial tests also indicated a need for a bypass loop within the FGSS to allow measurement of the flue gas concentrations untouched by sorbents. A continuous data acquisition system was also necessary to monitor and archive the initial and exit concentrations of the flue gas.

3.5.4 Sorbent Cartridge Design

After completing the many FGSS modifications, the next study objective was to find commercially available gas-tight, swage-compatible cartridges to contain the SO_2 sorbent and the desiccant. The most desirable option was to purchase gas purifier tubes available through a variety of vendors. Vendors were contacted and asked whether the clear traps, empty of any purifying agent, could be obtained. One vendor was able to provide empty, 120-cc, refillable, and gas-tight cartridges. The cartridge end caps were compatible with stainless steel O-ring sealed straight thread to compression fitting connectors. These were added to the cartridge to ensure a leak-tight fitting and a 1/4-in compression fitting compatibility. These traps were used to contain both the SO_2 sorbent and the desiccant.

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A test was performed to evaluate the SO_2 removal efficiency of a 20:1 sand to $Ca(OH)_2$ mix using a slurry method of mixing then drying. The test mix was added to the 120-cc traps and was held in place by glass wool plugs. The SO_2 sorbent and the desiccant cartridges were placed in the sorbent/sample bomb loop and evaluated under nominal inlet conditions. Figure 3-3 is a plot of the nominal inlet conditions. A comparison of the initial SO_2 concentration and the SO_2 exit concentrations showed that the test mix was still removing 98 percent of the SO_2 after 20 min. This test verified the suitable operation of the FGSS and the sorbent cartridge sampling system. The cartridges were selected to be used in further testing.

3.5.5 Dispersion Tubes

The first few scoping tests gave insight into the sorbent system operation and enhancement. During these tests, there was concern that the contact between the flue gas and the reactant was less than optimal. To alleviate this concern, dispersion tubes were added to the inlet and outlet of the SO_2 sorbent cartridge. The dispersion tubes are designed to "spray" the flue gas through the solid sorbent thus maximizing the contact between gas and sorbent.

Dispersion tubes are made from 1/4-in Teflon tubing, 6 in long, with a compression fitting stainless steel nut, ferrules and cap on the end (Figure 3-4). About 70 0.6-mm holes are drilled in a 2-in section behind the nut and cap. The collective area of the 70 holes is greater than the inner annular area of the Teflon tubing. These tubes are used at both the inlet and outlet of the SO_2 sorbent cartridge.

A test was performed to evaluate the effect of the dispersion tubes on the SO_2 removal efficiency of the sorbent cartridge. The SO_2 breakthrough data were compared to a previous test where the tubes were not used (Figure 3-5). After 20 min, the dispersion tube cartridge had minimal SO_2 breakthrough (2 ppm) compared to the cartridge without tubes (25 ppm). Both tests used a 20:1 sand:$Ca(OH)_2$ slurry mix. Because of SO_2 removal efficiency enhancement, the dispersion tubes became a permanent part of the SO_2 sorbent cartridge design.

42
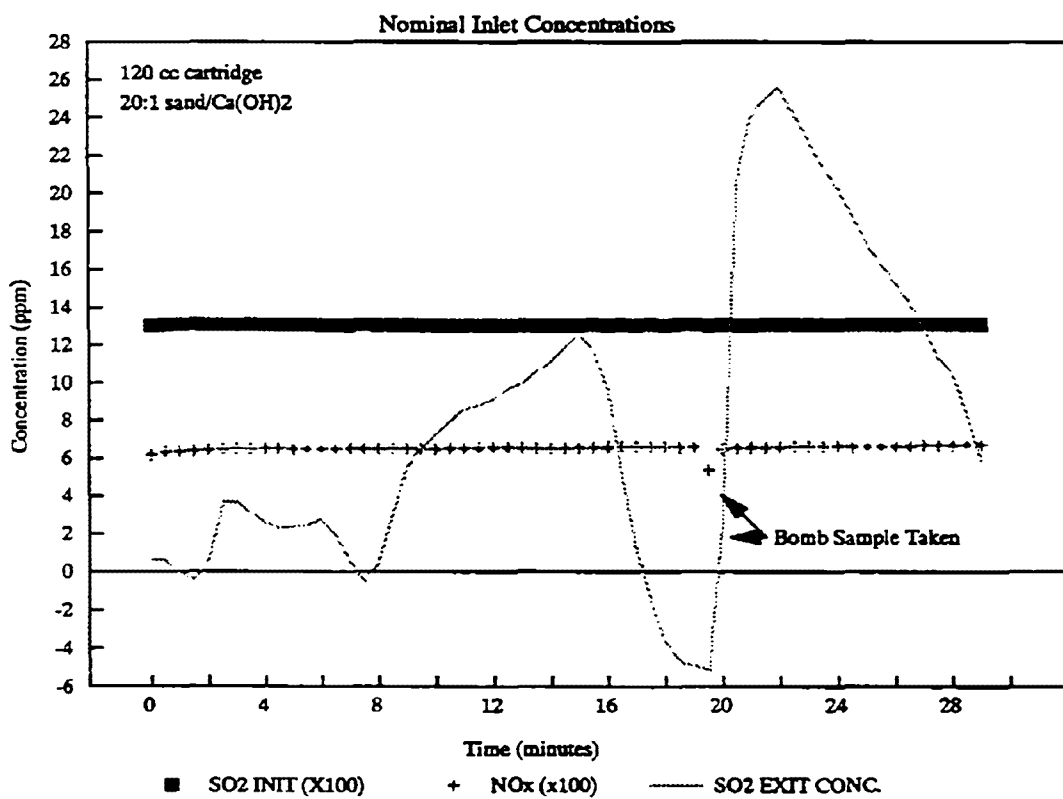
Figure 3-3. SO_2 removal with 20:1 sand/$Ca(OH)_2$ sorbent.

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1/4-in. ceramic-filled Teflon ferrule

120 cc refillable trap

1/4-in. nut

1/4-in. compression fitting

7/16-20-in.
straight
thread

SO₂ sorbent cartridge components.

stainless steel
O-ring seal connector

end cap

dispersion tube (w/0.0225-in. holes)

1/4-in. stainless steel ferrules

1/4-in. cap

1/4-in. ceramic-filled
Teflon ferrule

O-ring seal

end cap (O-ring inside end cap)

1/4-in. nut

Dispersion tube hardware.
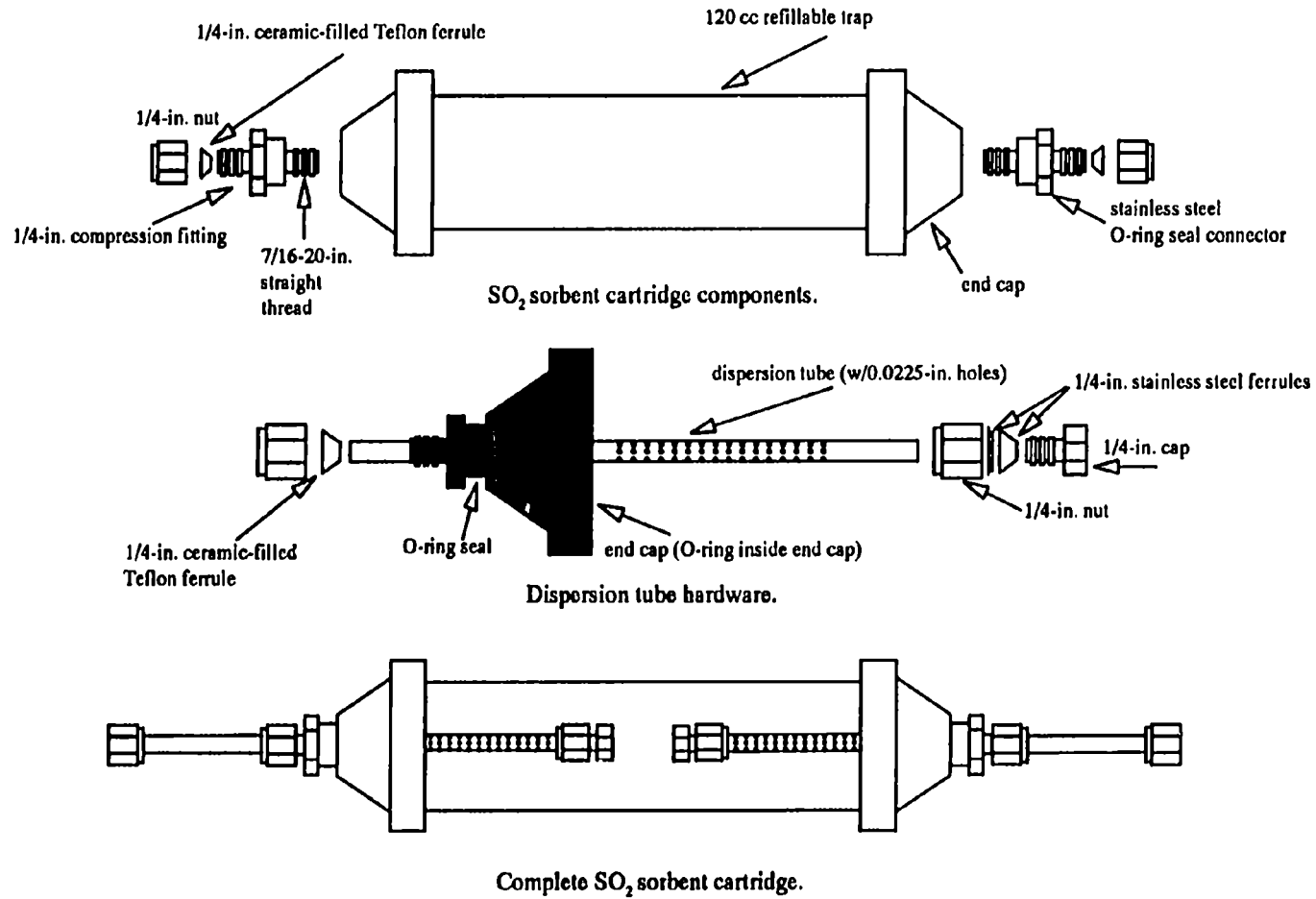
Complete SO₂ sorbent cartridge.

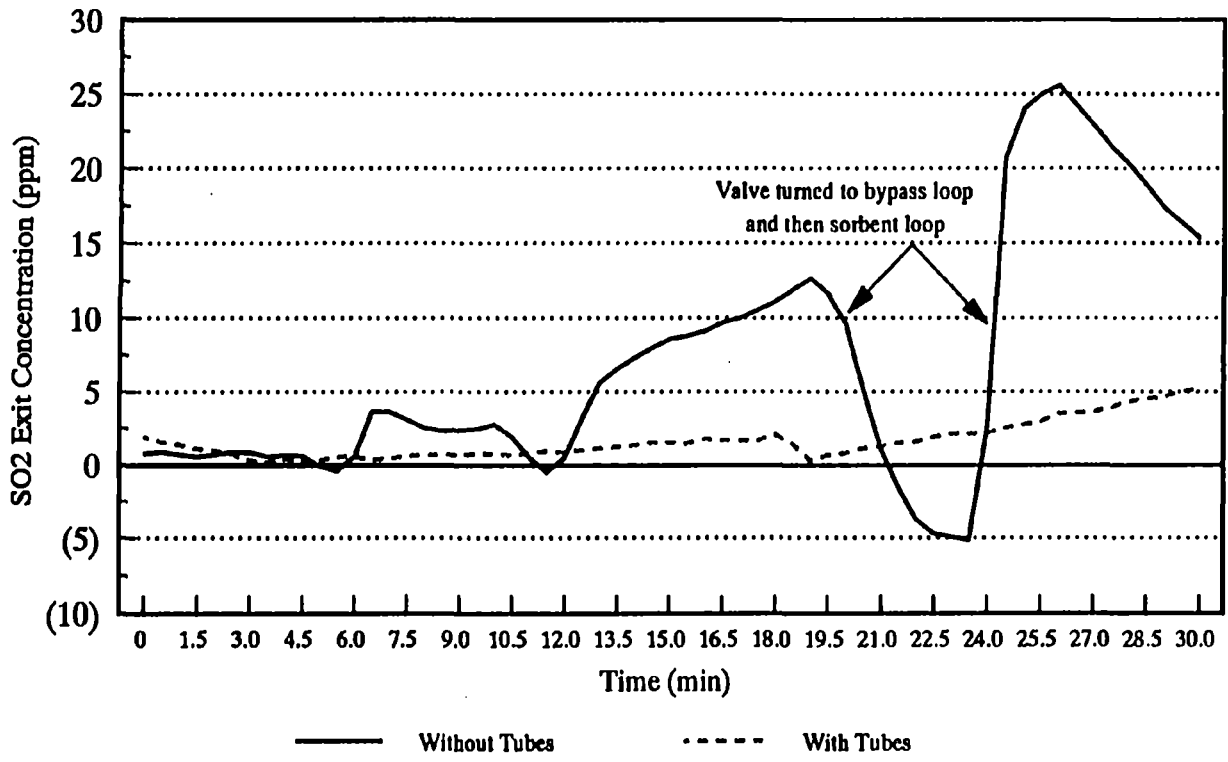Figure 3-4. SO₂ sorbent cartridge assembly.

44

Figure 3-5. Effect of dispersion tubes on SO_2 removal efficiency.

3.5.6 SO₂ Color Indicator

To investigate alternative SO_2 sorbents, considerable effort was made contacting vendors of commercial SO_2 air sampling tubes to inquire about the chemicals used in the indicating exposure tubes. The contents of these sampling tubes were appealing both from a standpoint of reactive specificity as well as quantitative indicating properties. The possibility of purchasing indicating sorbents in bulk form was explored. Unfortunately, the identity of the indicating reagents was proprietary. In addition, none of the materials were available in bulk form, some due to their toxicity.

Commercially available SO_2 color indicating and sampling tubes were investigated with the possibility that they would indicate the expenditure of the $Ca(OH)_2$ and/or divulge any major SO_2 breakthrough during field sampling. These tubes indicate the concentration of SO_2 in air through a linear color change along the length of cartridge proportional to volume and concentration. The tubes were tested along with a 10:1 sand/$Ca(OH)_2$ slurry mix. The air sampling tube was placed after the P_2O_5 cartridge to ensure dry gas was entering the air sampling tube. The results of the screening test indicated a large pressure drop, approximately 8 psig, across the sorbent system due to the relative small size (~6 mm diameter) of the air sampling tubes.

Also during testing, the color indicator along the tube did not change in a linear manner. The color change started in the middle of the cartridge with the beginning of the cartridge never changing color during the test. No further work was conducted on the SO_2 color indicators.

3.5.7 Chemical Sorbent Screening

As previously mentioned, $Ca(OH)_2$ was initially used in the study because of its proven ability to remove SO_2. To validate the use of $Ca(OH)_2$, scoping tests were performed to compare the length of time that three selected dry sorbent materials, $Ca(OH)_2$, NaOH, and Na_2CO_3, were effective in removing SO_2. NaOH and Na_2CO_3 were selected because of their similar basic natures. Each chemical was mixed with sand at a 20:1 sand-to-reactant ratio using a 20-30 mesh (0.85-.60 mm) Ottawa sand. The chemicals and sand were mixed using a slurry method with deionized water.

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The appropriate amounts of sand and sorbent were weighed and added to a large pan along with 50 mL of deionized water. The reagents were then mixed by hand with a putty knife for about 15 min. The pan and sorbent mix was then placed in an oven at 105 °C to dry overnight. A slurry method was chosen on the assumption that the reactants would coat the sand particles thus creating a larger reactive surface area and greater scrubbing efficiency.

The Na_2CO_3 mix exhibited difficulties during sorbent mix preparation. The Na_2CO_3 dried in clumps and did not disperse through the sand. The Na_2CO_3 was not evaluated owing to these problems in the sorbent preparation. The NaOH mixture dried to form a brick, which subsequently had to be broken up before addition to the cartridges. There were no problems encountered during the sand/$Ca(OH)_2$ preparation.

The NaOH and $Ca(OH)_2$ mixtures were added to the sorbent cartridges (with dispersion tubes) and placed in the sorbent position of the FGSS. They were then evaluated at nominal inlet conditions. The SO_2 exit concentrations were measured vs. time using a 10 ppm SO_2 breakthrough as the threshold.

Figure 3-6 shows that the sand/$Ca(OH)_2$ mix lasted much longer (~45 min) than the Na(OH) mix (~13 min). Also, the reaction of NaOH with moisture/SO_2 during testing was found to be very exothermic thus causing a safety concern. The sand/$Ca(OH)_2$ mix was chosen for use in additional studies because of its longer SO_2 removing capabilities and its ease in preparation.

3.6 SO_2 SORBENT OPTIMIZATION

3.6.1 Introduction

Once the SO_2 sorbent cartridge design and chemical sorbent had been selected, the next priority of the study was to enhance the SO_2 removal capabilities of the sand/$Ca(OH)_2$ mix. Tests were designed to determine an optimum sand/$Ca(OH)_2$ mix that would consistently minimize the N_2O generation to less than 10 ppm. This determination was accomplished by varying the sand particle
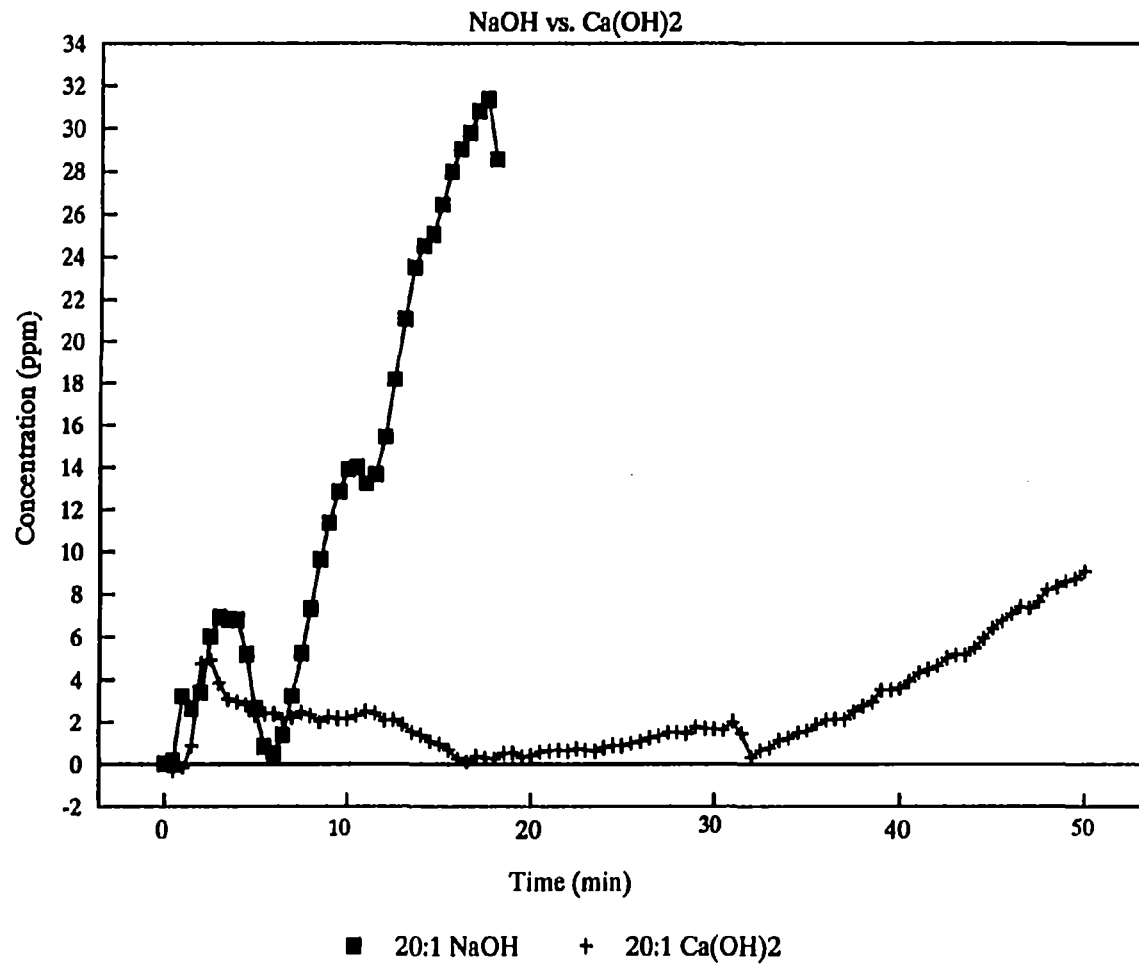
Figure 3-6. Comparison of candidate sorbents and SO_2 removal capability.

size, the sand-to-reactant ratio, sorbent volume, and the sorbent mix preparation. All tests were conducted under the nominal inlet conditions.

The previous screening tests defined the SO_2 removal efficiency of a sorbent by the length of time it was efficient in removing SO_2. This was achieved by measuring the SO_2 exit concentrations of the sorbent cartridges and plotting these concentrations vs time. The next tests were designed to further evaluate the SO_2 removal efficiency by measuring the effect of the sorbents on the minimization of the N_2O generation artifact in sample containers.

The N_2O generation measurement was defined as the difference between the initial N_2O concentration obtained from the bypass loop during testing and the actual N_2O concentration found in the aged sample containers. The SO_2 breakthrough data were used to quickly determine the SO_2 sorbent and the cartridge design. The study now focused on N_2O generation in sample containers. The SO_2 breakthrough data were still used as a variable in the decision making process. Each test and its results are discussed in the subsequent subsections.

3.6.2 Sand Particle Size

As previously mentioned, the $Ca(OH)_2$ was dispersed through sand to increase the reactant's usable surface area. It was then theorized that with the same cartridge volume, a decrease in the sand particle size would allow an increase in reactive surface area. Along with the increase of reactive surface area, there was also the possibility that the flow rate and pressure drop through the sorbent system could be compromised. The objective was to find a sand particle size that would increase the chemical's usable reactive surface area but not effect the flow rate and pressure drop through the sorbent system. Tests evaluated and compared the effect of three different sand particle sizes on the flow rate and pressure drop through the sorbent cartridges and also on the mix uniformity. Each particle size was mixed at a 20:1 ratio with $Ca(OH)_2$, using the slurry method. Each mix was then added to a sorbent cartridge and tested on the FGSS.

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The first sand evaluated was a commercially available "play" sand. The play sand was sifted to more than 18 mesh particle size (particle diameter > 1 mm). To collect the > 1 mm particle size sand, an 18-mesh sieve was placed on a shaker. The play sand was added and sifted. The sand that did not go through the sieve was collected for testing.

A slurried 20:1 mix was prepared with the > 1 mm sand. The sand and $Ca(OH)_2$ did not "mix" well. The larger sand particles caused the $Ca(OH)_2$ to form in clumps or pockets when the mixture was added to the cartridge. The > 1 mm sand/$Ca(OH)_2$ allowed a flow rate of > 7 L/min and a minimal pressure drop across the sorbent cartridges. Although this sand did not compromise the flow rate and pressure drop, the larger sand particles did compromise the mix homogeneity.

The second sand evaluated was a commercially available Ottawa sand (20-30 mesh). The sand mixed well with the $Ca(OH)_2$. The fine particle sand allowed a flow rate of 4 L/min, and caused a large pressure drop (7 psi) across the cartridges. Sand particles were also found in the dispersion tube holes.

The third sand evaluated was the commercially available "play" sand sifted to 18-20 mesh (particle diameter = 0.85-1.00 mm). To collect the 0.85-1.00 mm sand, an 18- and 20-mesh sieve were placed on a shaker with the 18-mesh sieve on top. The play sand was added and sifted. The sand that went through the 18-mesh sieve but not through the 20-mesh sieve was collected for testing.

There were no difficulties encountered with the preparation of a 20:1 mix using the 0.85-1.00 mm particle-size sand. This mix compared to the 20:1 Ottawa sand mix, gave a greater flow rate and a reduced pressure drop (6 L/min, 4 psi, respectively). Because of the enhanced flow rate, the 18-20 mesh sand was the choice for further studies.

3.6.3 Sand-to-Reactant Ratio

With a goal to further optimize the $Ca(OH)_2$ cartridge, the $Ca(OH)_2$ concentration in the sorbent cartridge was doubled from a 20:1 sand:$Ca(OH)_2$ mix to a 10:1 sand:$Ca(OH)_2$ mix. Tests

were performed evaluating the effect of each mix on the SO_2 breakthrough of each cartridge and the effect on N_2O generation in bomb samples.

The 20:1 mix and the 10:1 mix were prepared using the slurry method. Each mix was added to the sorbent cartridges and evaluated under nominal inlet conditions. Each test evaluated a single sorbent cartridge with the collection of one bomb at 7, 19, and 31 min after the sorbent was placed in the sample loop. A total of three bombs were collected for each cartridge tested. Each test mix was performed in triplicate with a total of nine bomb samples collected per mix. During two of the 10:1 mix tests, a fourth bomb sample was collected at the 45-min interval.

The initial N_2O concentration was established from the bypass loop before the placement of the sorbent system in the sorbent/bomb loop. N_2O measurements were also taken at the exit of the sorbent/sample bomb loop during the collection of each bomb sample. This measurement was taken to ascertain the effect of the cartridge system on initial N_2O concentration. Each bomb was then sealed and stored at room temperature.

The bombs collected with the 20:1 mix were aged 3 days and then analyzed for N_2O. The bombs collected with the 10:1 mix were aged 4 days and then analyzed for N_2O. Table 3-2 lists the conditions and results of the individual test cartridges and its replicate bomb samples. The SO_2 exit concentrations were not available because of an analyzer failure. Figure 3-7 graphically presents the N_2O generation of the bomb samples at each sample interval. N_2O generation is defined as the measured bomb concentration minus the initial (on-line) N_2O concentration. A comparison of these results revealed that the 10:1 sand:Ca(OH)$_2$ mix was consistent in minimizing the N_2O generation to < 5 ppm even after 45 min, whereas the 20:1 mix showed significant N_2O generation in the bomb samples after 31 min. The 10:1 sand-to-reactant ratio was chosen for use in further studies owing to its consistency in minimizing the generation artifact.

TABLE 3-2. N_2O GENERATION IN GRAB SAMPLES WHILE OPTIMIZING SO_2 SORBENTS

Sorbent Conditions and Tests Results

	Sorbent Conditions	No. Days Aged	Initial N2O Concentration	Bomb 1 Generation	Bomb 2 Generation	Bomb 3 Generation	Bomb 4 Generation	Avg Cart Generation
1A	20:1	3	1.4	2.0	5.1	22.4	--	9.8
1B	20:1	3	1.4	1.8	3.1	9.9	—	4.9
1C	20:1	3	1.4	5.5	0.1	2.4	--	2.7
2A	10:1 Slurry	4	0.4	1.5	2.8	1.9	1.3	1.9
2B	10:1 Slurry	4	0.5	2.3	3.2	2.3	1.5	2.3
2C	10:1 Slurry	4	0.5	4.1	3.8	3.4	—	3.8
3A	10:1 Dry	5	0.4	0.4	1.2	6.5	14.2	5.6
3B	10:1 Dry	5	0.4	2.2	9.0	0.9	1.7	3.5
3C	10:1 Dry	5	0.4	0.7	0.8	1.0	1.2	0.9
4A	10:1 (200 CC)	5	0.5	2.1	8.1	—	—	5.1
4B	10:1 (200 CC)	5	0.5	2.7	2.0	—	—	2.4

Concentrations in ppm

TEST NO. 1; 20:1 SAND:Ca(OH)2
N2O Generation per Bomb Sample

Cartridge A   Cartridge B   Cartridge C

Nominal Inlet Conditions

TEST NO. 2; 10:1 SAND:Ca(OH)2
N2O Generation per Bomb Sample

Cartridge A   Cartridge B   Cartridge C

Nominal Inlet Conditions

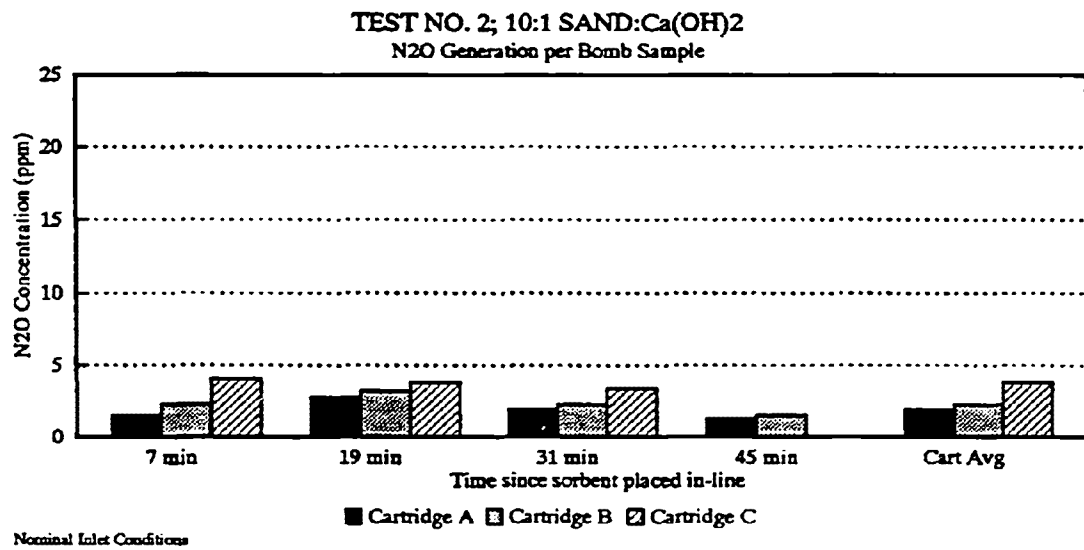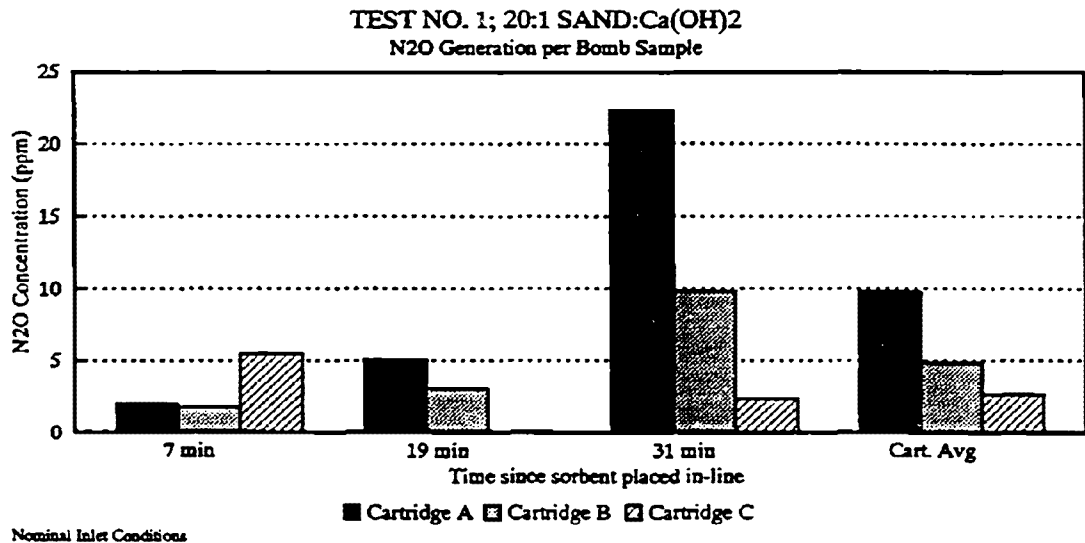Figure 3-7. Comparison sand-to-reactant ratios on N_2O generation.

3.6.4 Sand/Sorbent Preparation

The slurry method of mixing the sand and $Ca(OH)_2$ was chosen on the assumption that the water would cause a more uniform dispersion of the $Ca(OH)_2$ through the sand. This method was found to be time consuming because of the overnight drying process. A dry mix of 10:1 sand:$Ca(OH)_2$ was prepared and evaluated to ascertain whether the slurry process was necessary when dispersing the $Ca(OH)_2$ through sand. The mix was prepared by weighing out the appropriate amounts of sand and $Ca(OH)_2$ and adding them to a pan. The two solids were then mixed by hand using a putty knife for approximately 15 min. The mix was then added to the sorbent cartridges.

Test 3 evaluated one sorbent cartridge with the collection of one bomb at 7, 19, 31, and 45 min after the sorbent system had been placed in the sorbent loop for a total of four bombs collected per cartridge. The test is performed in triplicate. During testing, the SO_2 exit concentrations and initial N_2O concentrations were monitored. These results were compared to Test 2 where a 10:1 mix using the slurry method was evaluated.

Table 3-2 lists the results and conditions for each test. Figure 3-8 graphically compares the N_2O generation of the bomb samples in the replicate tests. From these results, the slurry process demonstrated a slight performance advantage over the dry mix. The resulting N_2O generation was still much less than 10 ppm. Although the dry mix exhibited a higher generation in the bombs, the dry method of preparation was chosen because of the short preparatory time. The excessive preparatory time for the slurried sorbent material was also hindering the progress of scoping tests.

3.6.5 Sorbent Volume

The sorbent volume was the last variable examined during the optimization of the SO_2 sorbent cartridge. The 120-cc cartridges contained about 160 g of sand and sorbent. To approximately double the sorbent volume, 200-cc refillable traps were filled with the 10:1 sand/$Ca(OH)_2$ dry mix and evaluated (Test 4). Table 3-2 shows that the SO_2 exit concentrations were similar to those observed using shorter cartridges (< 15 ppm after 40 min). Figure 3-9 shows that the N_2O generation results

TEST NO. 2; 10:1 SAND:Ca(OH)2 SLURRY
N2O Generation per Bomb Sample
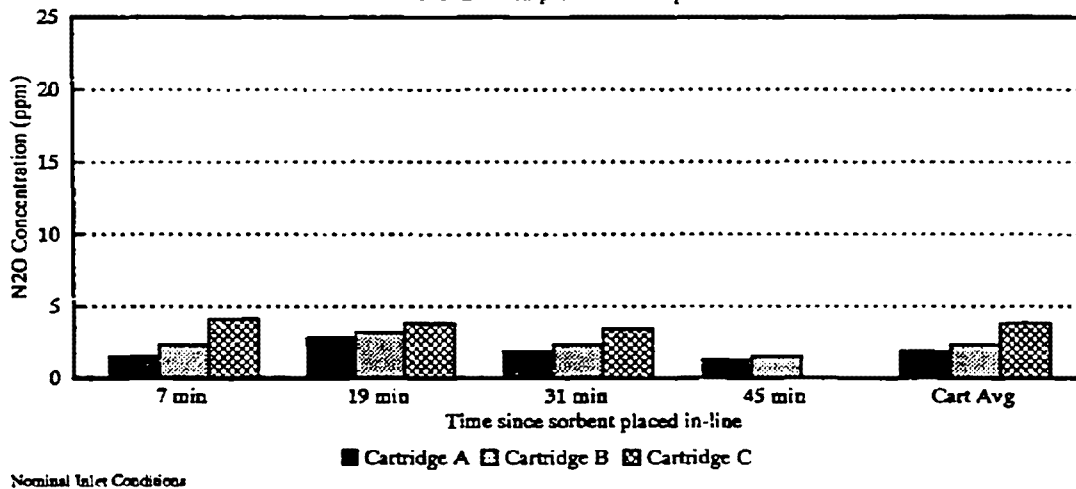
TEST NO. 3; 10:1 SAND:Ca(OH)2 DRY
N2O Generation per Bomb Sample
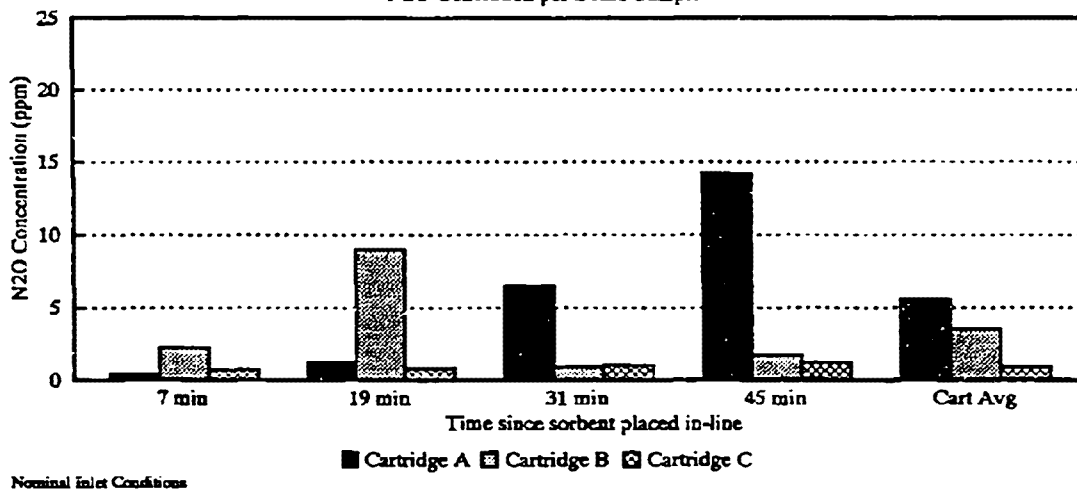
Figure 3-8. Effect of sorbent preparation process on N_2O generation.

TEST NO. 3; 10:1 SAND:Ca(OH)2 (120 CC)

N2O Generation per Bomb Sample

Nominal Inlet Conditions

TEST NO. 4; 10:1 SAND:Ca(OH)2 (200 CC)

N2O Generation per Bomb Sample
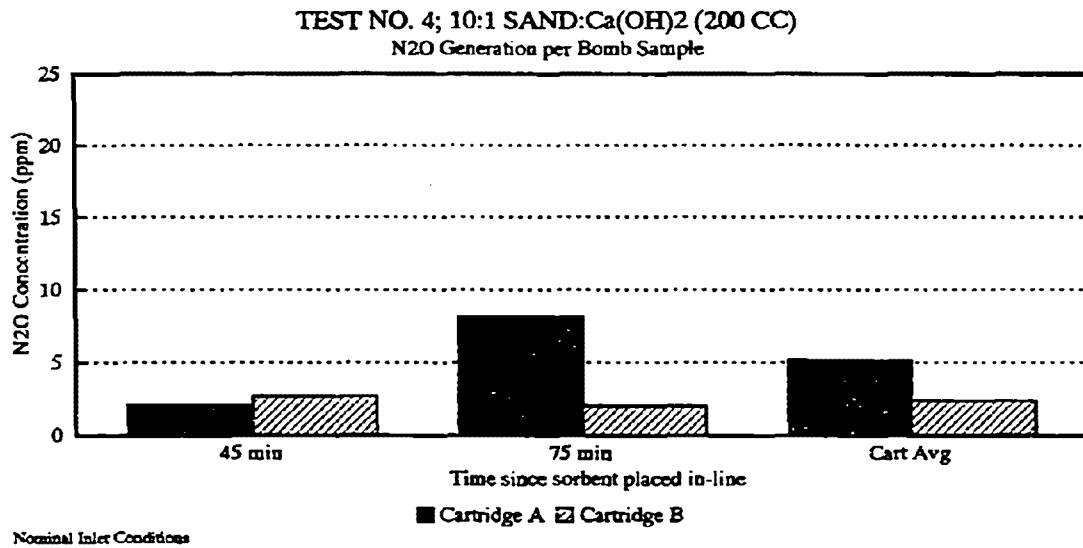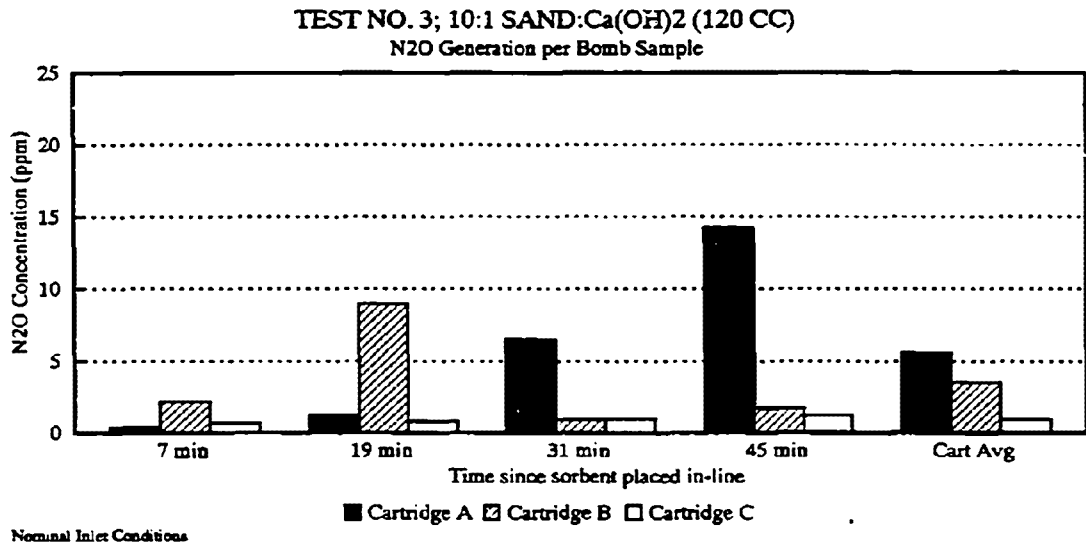

Nominal Inlet Conditions

Figure 3-9. Effect of sorbent volume on N_2O generation.

were also similar (5 days, < 5 ppm). The smaller volume was chosen because of the ease of handling and concerns over waste generation.

3.7 SAMPLE CONTAINER OPTIMIZATION

3.7.1 Introduction

Concern over N_2O generation inconsistencies between bomb samples led to improving methods to clean and condition the sample bombs. At this point, there was not a clear understanding of the reaction mechanisms between SO_2, NO_x, and H_2O that generated N_2O. Most of the proposed mechanisms hypothesized a liquid-phase wall reaction involving these three reactants. If this was indeed true the inconsistencies between replicate bomb samples could in part be caused by the inside walls of the sample bombs which were not consistent from container to container. The inconsistencies could also be caused by residual SO_2 and moisture in the bomb itself. Efforts then concentrated on creating greater uniformity between sample containers.

3.7.2 Sample Bomb Preparation

Initially, the 600 cc stainless steel sample containers went through a SO_2 neutralization process. The bombs were then washed, dried, and stored under vacuum. A method developed ensured a clean, dry, and pressurized bomb. The conditioning consisted of a hot, soapy water soak, a deionized water rinse, and a methanol rinse. The rinsed bombs were oven dried at 105 °C for 12 h. The hot bombs were sealed and cooled. Dry nitrogen was used to purge and pressurize the cooled bombs.

3.7.3 Teflon Coated Sample Bombs

To create greater uniformity between sample containers, the inner surfaces of several sample bombs were Teflon coated. A test using the Teflon-coated bombs with the sorbent/bomb system revealed little effect on the N_2O generation artifact (Figure 3-10). Both the stainless steel bombs and the Teflon-coated bombs had less than 5 ppm N_2O generation.

TEFLON COATED BOMBS

N2O Generation per Bomb Sample

Nominal Inlet Conditions
10:1 sand:Ca(OH)2 dry

RUN NO. 7A TEFLON BOMBS
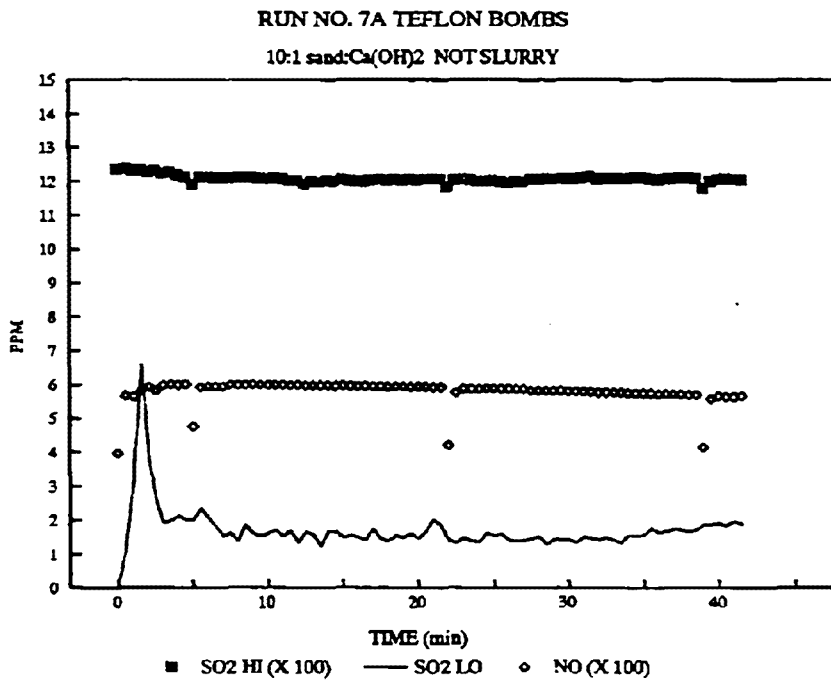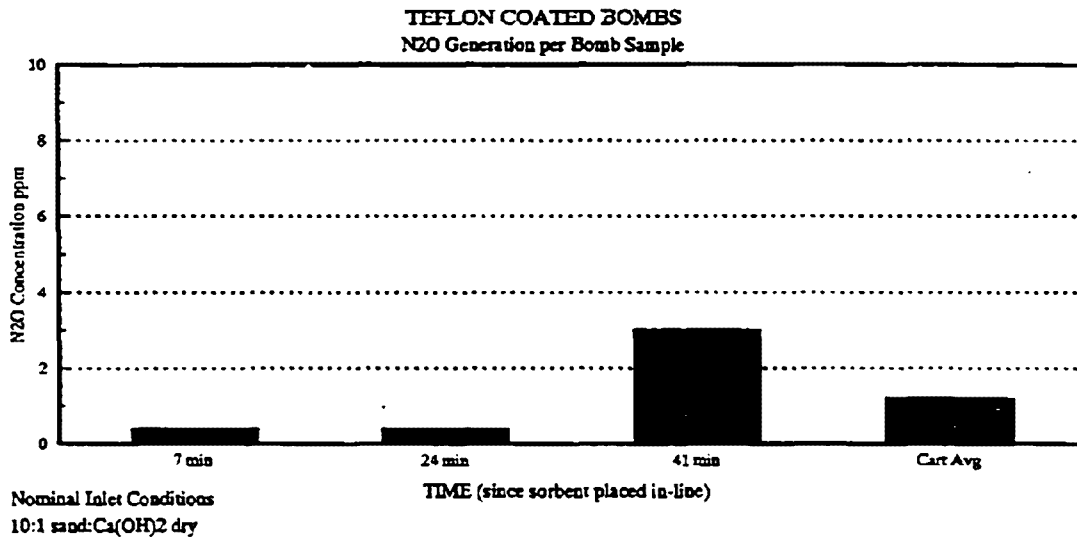
10:1 sand:Ca(OH)2 NOT SLURRY

Figure 3-10. Effect of Teflon coating on N_2O generation.

Although this test showed no visible performance enhancement from Teflon coating, a decision was made to Teflon coat the inner surfaces of all sample bombs. It was believed the Teflon coating would prolong the life of the stainless steel container, lessen the chance of SO_2 residue build-up along the container walls, and create a more inert sample contact surface.

3.8 COMBUSTION SOURCE GRAB SAMPLE METHOD EVALUATIONS

3.8.1 Introduction

At this point in the study, the sorbent/bomb system consisted of a two-cartridge, solid-sorbent system (~160 g 10:1 sand:Ca(OH)$_2$, dry; ~50 g P2O5) and a clean, dry, and pressurized 600-cc stainless steel sample container equipped with toggle valves and a side port for syringe injections (see Figure 3-11). The combination of reagents and equipment had demonstrated acceptable performance while incorporated into the FGSS. The focus now shifted to evaluating the sampling method as it would be used on actual combustion sources. This required the consideration of appropriate sampling equipment and sampling configuration. Emphasis was placed on the ability to incorporate the sampling equipment into conventional CEM sample delivery/conditioning systems.

3.8.2 Moisture Removing Devices

Realizing that many sampling systems use moisture removing devices, particularly refrigeration condensers, a test was conducted to monitor the effect of such a device on the performance of the sampling method. A Hankason refrigeration dryer was placed in the FGSS sampling system between the FGSS atmospheric dump and the sample pump of the nominal grab sampling system. The test conducted under the nominal inlet concentrations, monitored the effects of the dryer on the SO_2 removal efficiency of the calcium hydroxide. Two bomb samples were also collected. After 20 min, the SO_2 exit concentrations approached inlet conditions (1,200 ppm). Analysis of the bomb samples after 7 days exhibited N_2O generation of 10 ppm (Figure 3-12). The high SO_2 exit concentrations verified the importance of moisture (in the sample gas) on the neutralization of SO_2 in the sorbent

1/4-in. stainless steel nut

8/32-in. washer

3/8-in. OD septum

1/4-in. compression
fitting

Stainless steel
toggle valve

600 cc sample container
with septum port

1/4-in. NPT   1/4-in. NPT   1/4-in. compression fitting
(female)   (male)

60
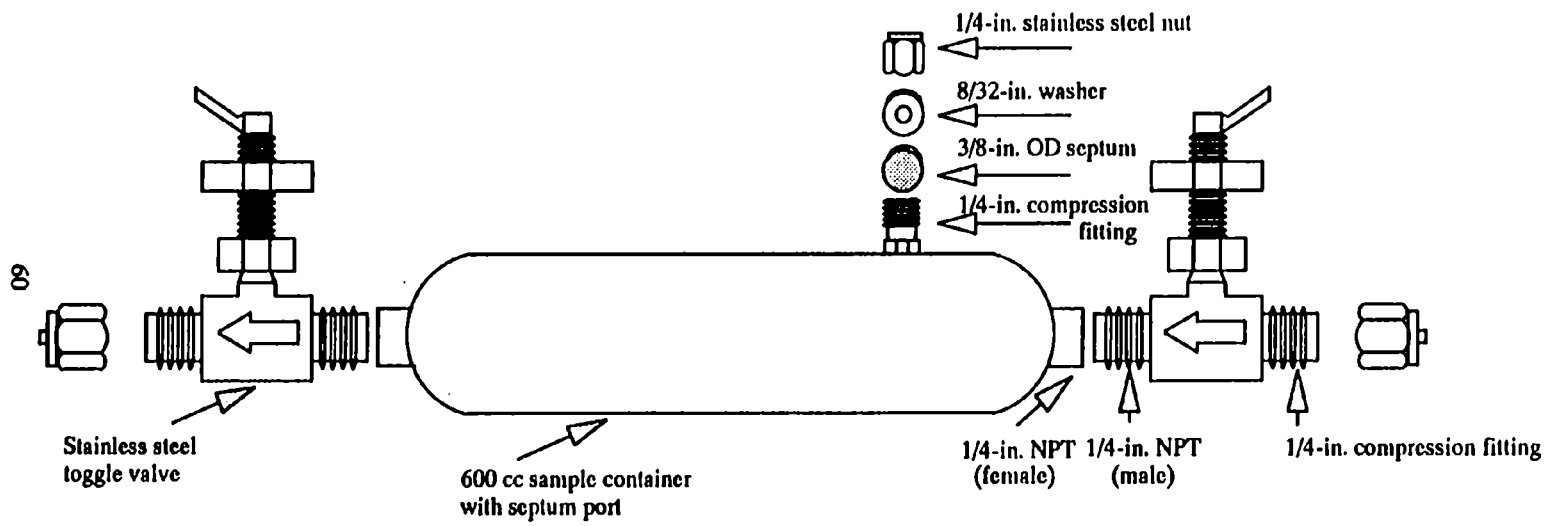
Figure 3-11. Sample container schematic.

REFRIGERATION CONDENSER
CEM data and N2O generation data

Nominal Inlet Conditions
10:1 sand:Ca(OH)2

SO2 HI   SO2 lo   NOx   N2O Generation (x10)
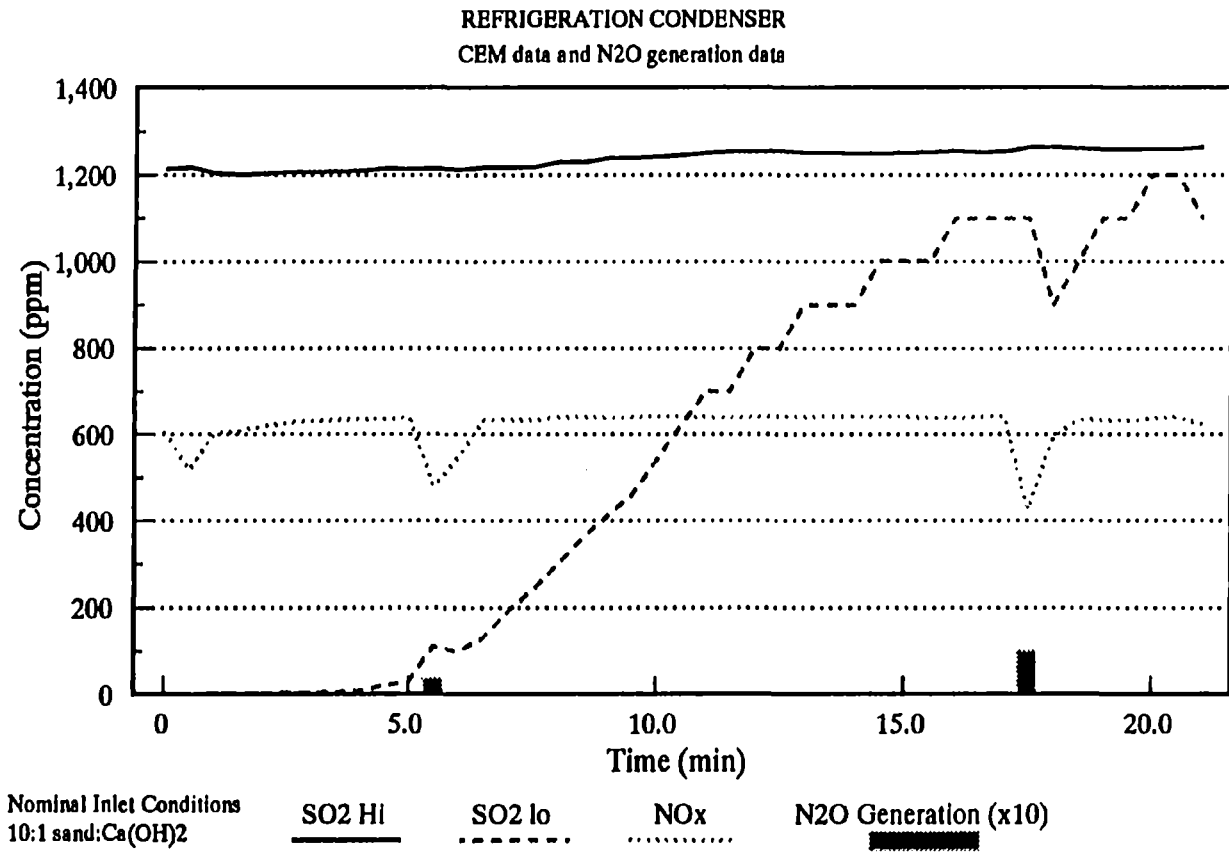
Figure 3-12. Effect of moisture removal on SO_2 sorbent performance.

cartridge. Because of the relatively high N_2O generation, sampling downstream of any moisture conditioning devices was no longer considered.

3.8.3 Evaluation of Source Sampling Configuration

The grab sampling configuration of the FGSS was designed such that a large number of method performance parameters could be monitored or measured concurrently. This tended to make the sampling system and equipment more complicated than necessary. To make the sampling system more compatible with conventional CEM sample delivery/conditioning systems, the system needed to be simplified. Essentially, all that was required was a means to extract a representative portion of a flue gas from the CEM sample system and push it through the grab sampling system. This could be accomplished with a small vacuum pump. The grab sample could be obtained in parallel to the CEM sample at a location between the stack and any CEM moisturing conditioning devices (see Figure 3-13).

To accomplish this, a sampling system separate from the normal FGSS sampling system was installed. A representative portion of the flue gas mix was pulled from the atmospheric dump section of the FGSS system and subsequently pushed through the SO_2 sorbent, the H_2O sorbent, and then directly into the sample container (see Figure 3-14). The gaseous sample was still obtained from the atmospheric dump (vent) of the FGSS. A toggle valve was located between the atmospheric dump and sample pump to isolate the sample delivery systems during sampling. The toggle valve was connected to the inlet of the sample pump by a 2-ft section of 1/4-in OD Teflon tubing. The sorbent cartridges and sample bomb were located at the outlet (positive pressure) side of the pump.

A rotameter was placed at the outlet of the sample container to measure the flow rate through the sorbent cartridge/sample bomb system. The gas stream exiting the rotameter was occasionally used to measure initial N_2O concentrations. Inlet NO, SO_2, and N_2O concentrations were monitored from nominal locations in the FGSS (bypass loop position). Outlet (exit) SO_2 concentrations were no longer measured.
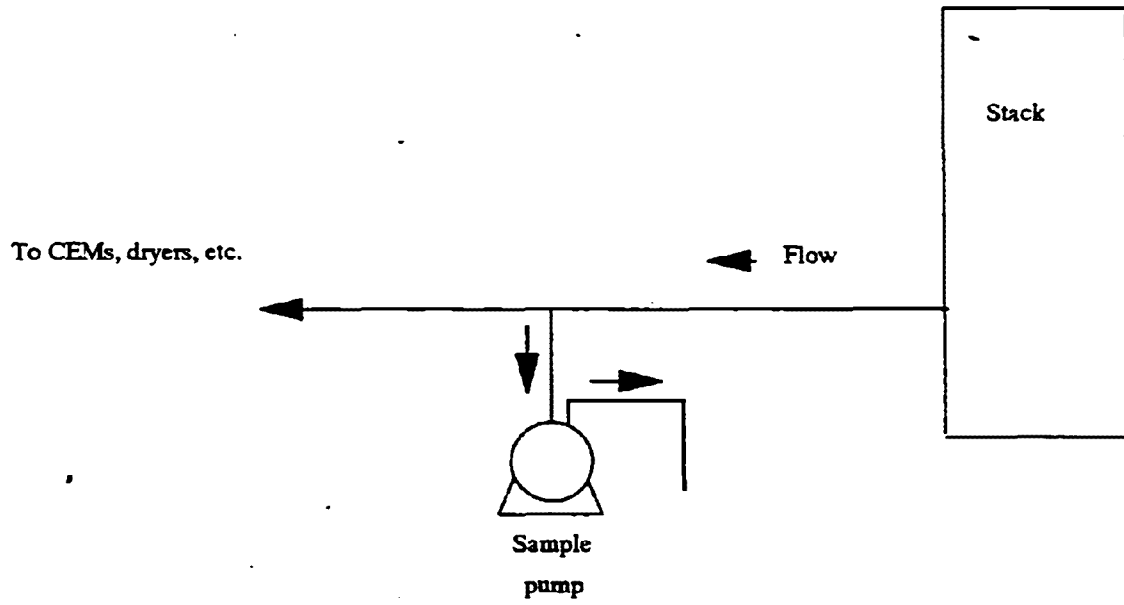
Figure 3-13. Location of sampling system.

From stack

Inlet

Outlet

SO2 sorbent

H2O sorbent
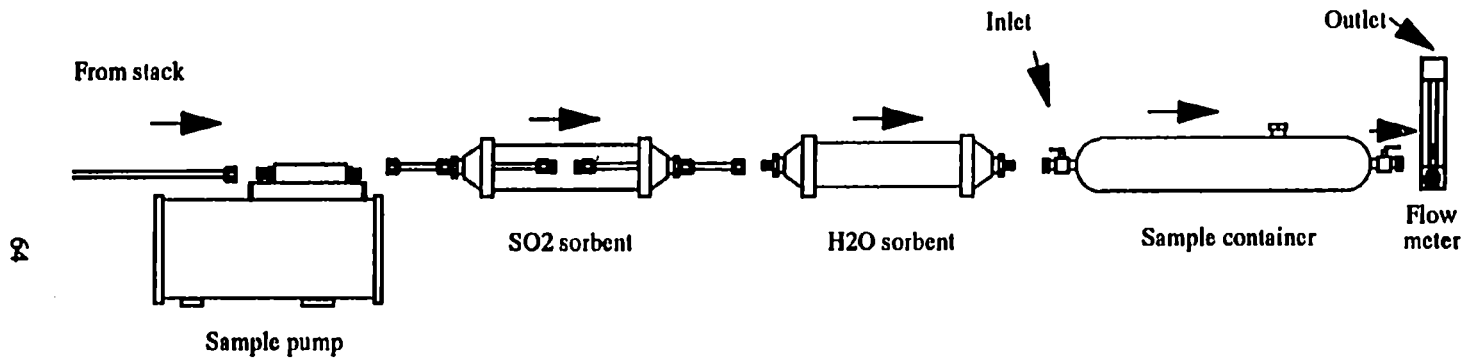
Sample container

Flow meter

Sample pump

64

Figure 3-14. Sorbent/sample container schematic.

Following design and installation of the sampling system, a test was designed to evaluate its performance relative to tests conducted to date. The nominal test condition simulated flue gas concentrations were used for this test. Several "wet" grab samples were collected without the use of any of the gas conditioning sorbents to demonstrate the full extent of N_2O generation.
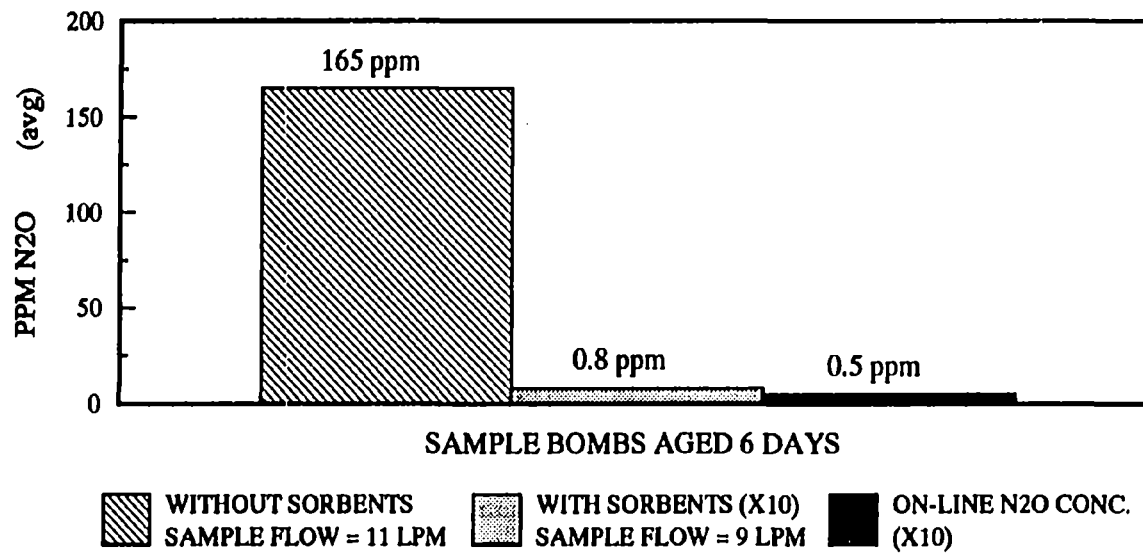
Once an on-line N_2O measurement was taken in the bypass loop of the sampling system, the toggle valve between the atmospheric dump and the grab sample pump was opened. The flue gas was allowed to run through the sorbents cartridges. Three separate bomb samples were collected. For each sample collected, the conditioned gas stream flowed through the sample bomb for at least 2 min. At the flow rate measured through the bomb, 9 L/min, a 2-min purge time ensured that a representative sample was collected. At least seven volume exchanges of the sample container took place. Also during the 2-min sample period, an on-line N_2O measurement was taken at the bomb exit to again verify that the sorbents had no effect on initial N_2O concentration. Three samples were also collected without the use of any sorbent cartridges at 11 L/min for 2 min each.

The samples collected using the sorbent cartridges demonstrated N_2O generation less than 1 ppm when analyzed after 6 days (Figure 3-15). The "wet" samples revealed N_2O generation of more than 150 ppm when analyzed after the same period. Because of the success of this test, the sampling configuration used was deemed acceptable for further testing.

3.8.4 EPA's Innovative Furnace Reactor

The next logical step in the sampling method evaluation process was the application of the sorbent cartridge sampling system to actual combustion situations containing similar flue gas constituents and concentrations. As a result, the sampling method was evaluated further on the EPA/AEERL-GCTB 15 kW (50,000 Btu/h) Innovative Furnace Reactor (IFR). The grab sample method was evaluated while the furnace fired on Illinois No. 2 coal. Samples were obtained by tapping into the existing CEM sampling system in parallel so that continuous CEM data could also be

FLUE GAS SIMULATION SYSTEM

N2O ARTIFACT GENERATION OF SAMPLES COLLECTED

165 ppm

0.8 ppm

0.5 ppm

SAMPLE BOMBS AGED 6 DAYS

WITHOUT SORBENTS
SAMPLE FLOW = 11 LPM

WITH SORBENTS (X10)
SAMPLE FLOW = 9 LPM

ON-LINE N2O CONC.
(X10)

SORBENT (10:1 SAND, Ca(OH)2 AND P2O5)
1,200 ppm SO2, 600 ppm NO, 10% MOISTURE
N2O INITIAL = 0.5 ppm

Figure 3-15. Comparison of N_2O sample container generation
with and without use of sorbents.

collected (see Figure 3-13). On-line N_2O measurements were also obtained using the automated, on-line GC/ECD system.

Figure 3-16 represents data from tests designed to evaluate the sampling method configuration on an actual fossil fuel combustion source. The first test used four sets of sorbent cartridges with a collection of three sample bombs per cartridge for a total of 12 bombs collected. The sample flow through the cartridge system was 2 L/min. Three bombs without sorbent cartridges were also collected. The average flue gas concentrations were 416 ppm NO and 1,900 ppm SO_2. The moisture content was not measured but estimated to be roughly 8 percent by volume. The grab samples when analyzed after 7 days showed excellent agreement with the on-line N_2O measurements. The "wet" samples were an order-of-magnitude larger, illustrating the N_2O generation artifact.

An additional test was conducted to further evaluate the effect of moisture removal on the collection of samples. Six samples were collected using two sorbent systems upstream of the condenser. Three samples were collected using one sorbent system downstream of the condenser. Three "wet" samples were taken both upstream and downstream. The sorbent sampling flow rates were also varied during upstream sampling. Figure 3-17 shows that minimal N_2O generation from within the sample containers when analyzed after 5 days. The flow rates and refrigeration condensers appear to have had negligible effect on the N_2O generation. However, given the results of the moisture conditioning tests conducted on the FGSS, the decision was made to remain sampling upstream of all moisture conditioning devices.

3.9 WORST CASE SCENARIO TESTS

3.9.1 Introduction

The tests conducted up to this point in the study confirmed that the development of a grab sampling method that minimized the N_2O generation artifact to the extent that meaningful N_2O measurements could be obtained was indeed possible. Under the nominal simulated flue gas concentrations tested (~600 ppm NO; ~1,200 ppm SO_2; and ~10 percent moisture) an unslurried 10:1

ILLINOIS NO. 2 COAL--INNOVATIVE FURNACE REACTOR
N2O ARTIFACT GENERATION OF SAMPLES COLLECTED
WITH AND WITH OUT SORBENTS
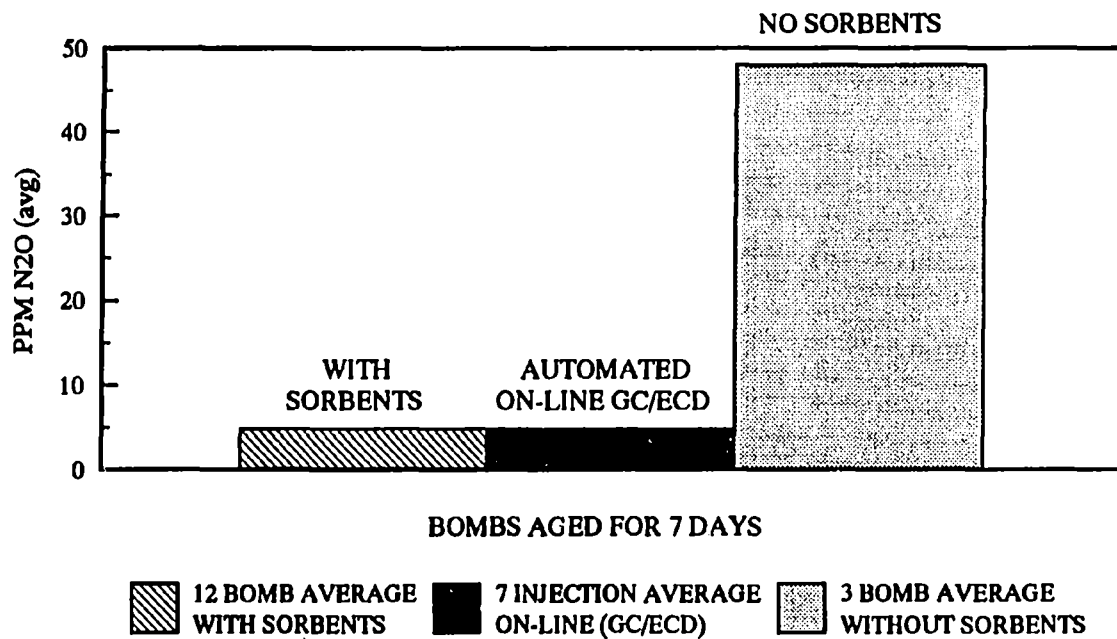
SORBENTS (10:1 SAND, Ca(OH)2 AND P2O5)
AVG NO = 416 ppm, CO = 166 ppm, CO2 = 14.3%
AVG O2 = 4.9%, SO2 = 1900 ppm, MOISTURE UNKNOWN
LOAD = 15 kW (50,000 Btu/h)

Figure 3-16. Performance of sampling method on actual combustion source.

ON-LINE N2O CONC. vs. AGED GRAB SAMPLE N2O CONC.

ILLINOIS NO. 2 COAL

INNOVATIVE FURNACE REACTOR   LOAD = 15 kW (50,000 Btu/h)
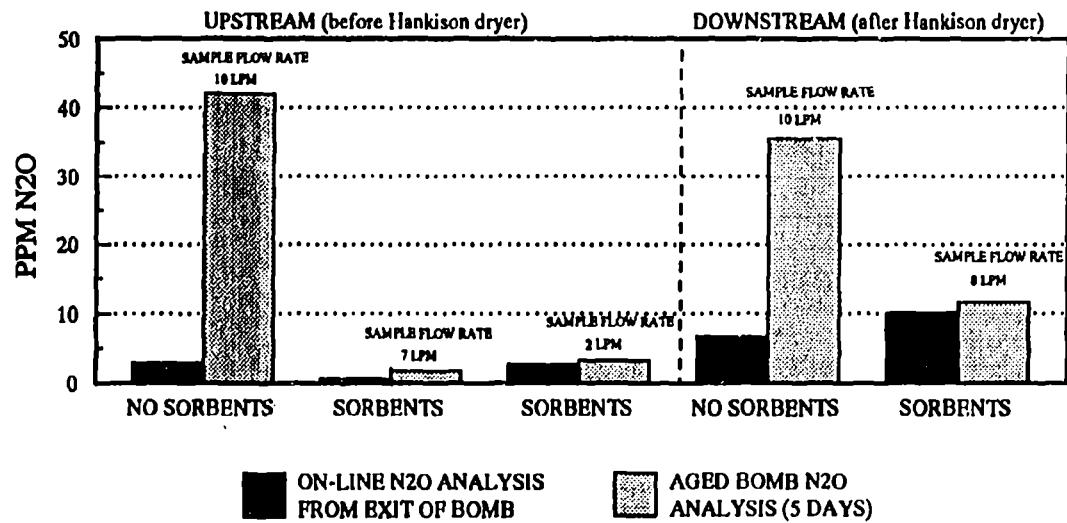
SORBENTS (10:1 SAND, Ca(OH)2 and P2O5)
AVG NO = 425 ppm, CO = 91 ppm, CO2 = 12.7%
AVG O2 = 7.8%, SO2 = 1,620 ppm, MOISTURE UNKNOWN

Figure 3-17. Comparison of effects of sample location on N_2O generation.

mix of sand/calcium hydroxide coupled with P_2O_5 was shown to be effective in minimizing the N_2O generation artifact in sample containers to less than 10 ppm when samples were analyzed within 1-2 weeks of collection. In addition, the sampling equipment and configuration developed was relatively simple to use and easily incorporated into conventional CEM sample delivery/conditioning systems.

Although the sorbent cartridge system had been evaluated under representative, controlled, and realistic conditions, the full extreme of potential flue gas concentrations that may be encountered had not been evaluated. The minimum moisture content critical to quantitative SO_2 neutralization had not been determined. Similarly, higher SO_2 and NO concentrations had yet to be investigated.

It was then determined that the next major step in the method development process was to determine the range of NO, SO_2, and H_2O concentrations under which the sorbent system can operate effectively. An emphasis was put on testing the worst case conditions to determine if high concentrations of SO_2 and NO or low moisture content would increase the potential for N_2O generation within the sample container. On the other extreme, low flue gas concentrations of SO_2 and NO were considered inconsequential and were therefore not considered for testing. Similarly, since the samples were intended to be collected upstream of any pollution control equipment, including wet scrubbers, high moisture concentrations were considered favorable and were also not considered for testing.

The worst case scenario was defined to be the maximum range of the key flue gas concentrations that would be found in the field. The worst case conditions were defined as 2,500 ppm SO_2, 900 ppm NO, and 5 percent H_2O.

3.9.2 Nominal Inlet Concentrations

Two tests were run at nominal inlet concentrations in order to repeat baseline conditions. Each test evaluated three sorbent cartridge sets with the collection of three bombs per cartridge set for a total of nine sample bombs. The initial N_2O concentration was measured from the bypass loop of the FGSS. The GC/ECD was programmed to automatically sample for N_2O every 8 min throughout the test. No N_2O measurements were made at the bomb exits.

The results revealed inordinately low N_2O generation when the bombs were analyzed after 5 days (Table 3-3). A comparison of Run 100 and Run 101 revealed the same low N_2O generation for both tests (Figure 3-18). Another review of the test data revealed a linear increase in the on-line initial N_2O concentrations (Figure 3-19). It was then suspected that N_2O was being generated within the FGSS. Since the initial N_2O concentration is dependent on the concentration of N_2O in the NO supply gas and the FGSS operates at "steady-state" conditions, an increase in initial N_2O concentration should not occur without changes in the measured concentrations of the other supply gases. Efforts were focused on finding the source of this generation since a correct initial N_2O concentration was crucial to the study. Knowing that the formation of N_2O occurs in the liquid phase, the investigation was centered on a source of "standing" water. The source was found to be a cyclone type water knock-out device that had been added to the system to remove water before the flue gas entered the CEMs and GC/ECD. The device's drain had plugged and the cyclone had filled with water.

This water removal device was replaced by a small refrigeration condenser. Tests were performed to confirm that the condenser removed water without effecting the initial flue gas N_2O concentrations. Figure 3-20 compares the on-line N_2O concentrations vs. time before and after the addition of the condenser.

3.9.3 Worst Case Conditions

With the N_2O problem solved and the verification that the FGSS was in acceptable operating order, two tests were performed to evaluate the sorbent cartridge system at worst case conditions

TABLE 3-3. REPEAT OF NOMINAL CONDITIONS

Sorbent Conditions and Tests Results

	Sorbent Conditions	No. Days Aged	Initial N2O Concentration	Bomb 1 Generation	Bomb 2 Generation	Bomb 3 Generation	Avg Cart Generation
100A	10:1 Dry	5	0.540	0.235	0.968	0.196	0.466
100B	10:1 Dry	5	0.610	3.302	1.710	2.874	2.630
100C	10:1 Dry	5	0.750	0.651	0.566	0.157	0.458
101A	10:1 Dry	5	0.822	0.147	0.276	0.137	0.190
101B	10:1 Dry	5	0.966	0.734	0.000	0.845	0.526
101C	10:1 Dry	5	1.046	0.214	0.014	0.067	0.098

Concentrations in ppm unless otherwise noted

NEW SAMPLING POSITION
Run No. 100; Nominal Inlet Conditions

Bomb Samples per Cartridge

■ Cartridge A □ Cartridge B ▨ Cartridge C

10:1 sand-Ca(OH)2

NEW SAMPLING POSITION
Run No. 101; Nominal Inlet Conditions

Bomb Samples per Cartridge

■ Cartridge A □ Cartridge B ▨ Cartridge C

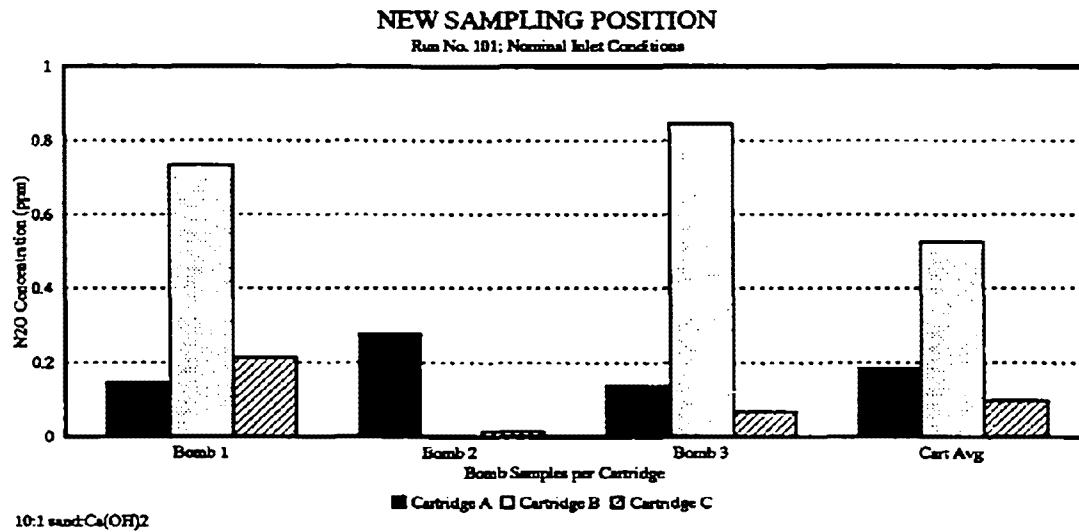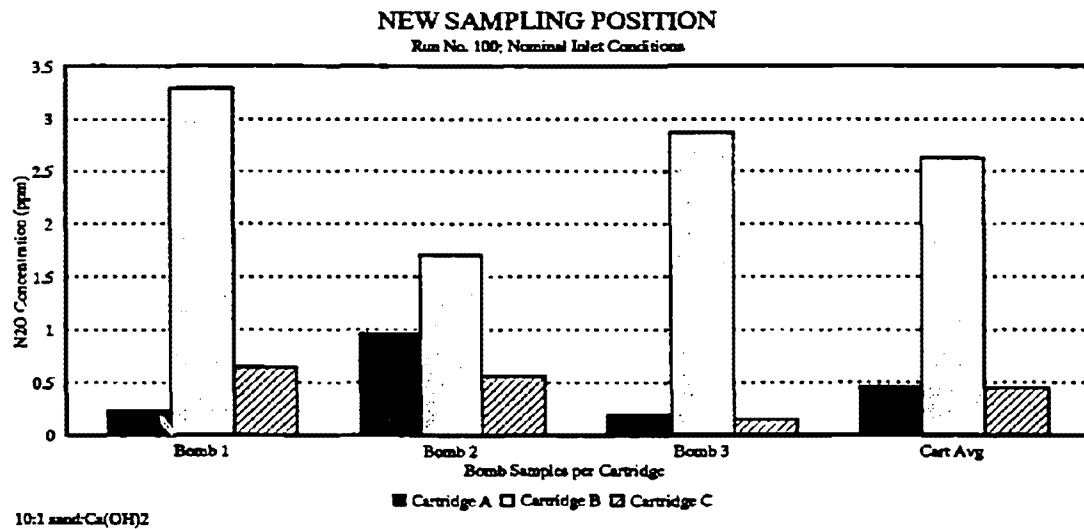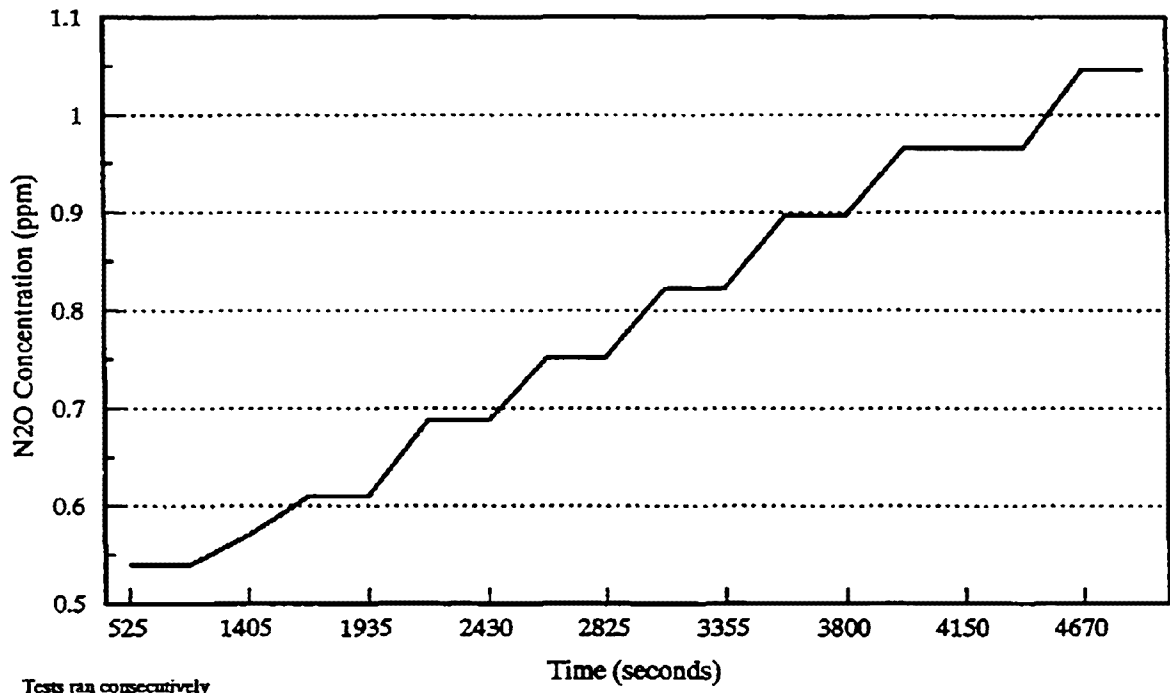10:1 sand-Ca(OH)2

Figure 3-18. N$_2$O generation in sample containers; repeat tests of nominal conditions.

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ON-LINE INITIAL N2O CONCENTRATIONS

Runs 100 & 101

Tests ran consecutively
Nominal Inlet Conditions

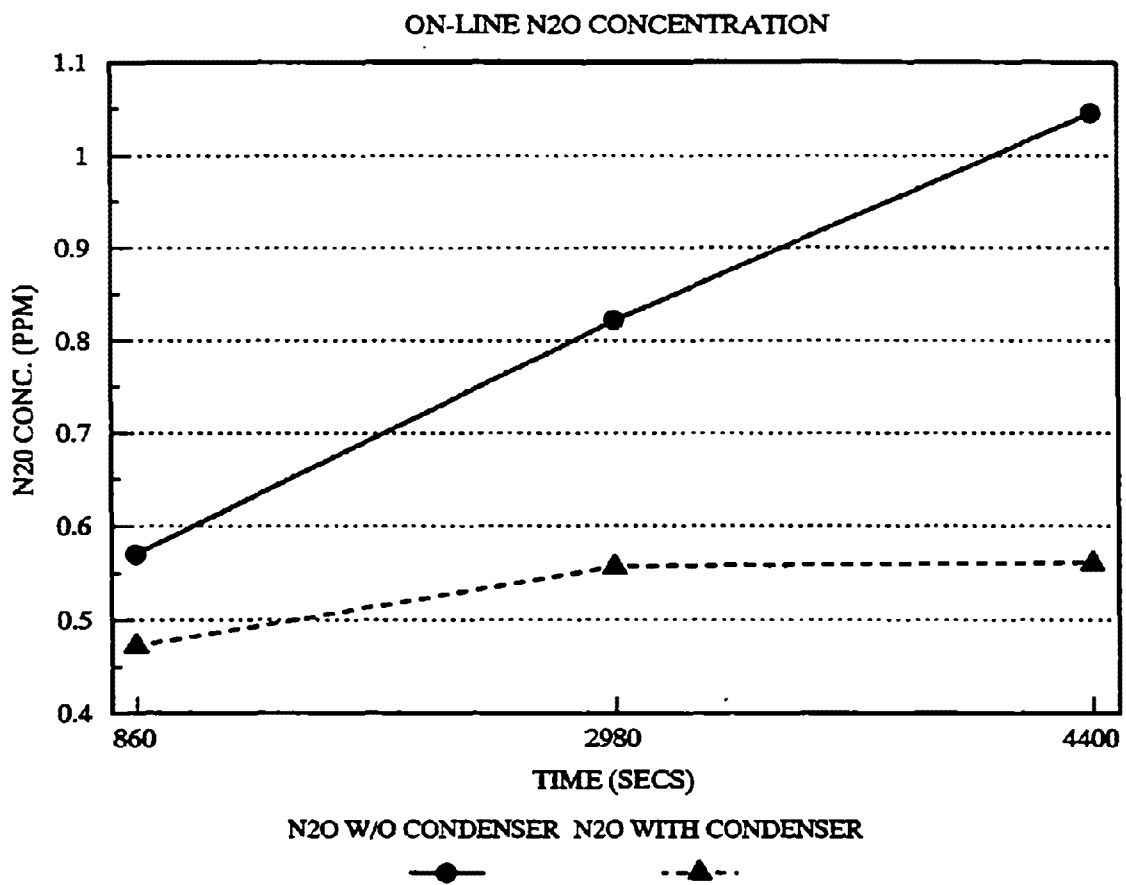Figure 3-19. N_2O generation in the refrigeration condenser.

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Figure 3-20. Effect of addition of refrigeration condenser on N_2O generation within the sample delivery system.

(2,500 ppm SO_2, 900 ppm NO, and 5 percent H_2O). The first test, Run 103, evaluated three sorbent-cartridge systems using the original design of earlier tests. This design placed a dispersion tube at the inlet and outlet of the SO_2 sorbent cartridge. The second test, Run 104, evaluated three modified sorbent-cartridge systems. The modification was performed on the SO_2 sorbent cartridge only. The dispersion tube was removed at the outlet of the SO_2 sorbent cartridge. This modification was performed to ascertain if the removal of the dispersion tube would generate a higher flow rate and less of a pressure drop without compromising the effectiveness of the $Ca(OH)_2$ to remove SO_2. Also, insertion of the second dispersion tube into the dry sorbent was extremely difficult. Elimination of the second dispersion tube would make SO_2 sorbent cartridge assembly much easier.

Three bombs were collected with each cartridge system with a total of nine bombs per run. The bombs were aged 7 days and then analyzed for N_2O. The average artifact N_2O generation for both runs appeared to be minimal (Table 3-4). The average artifact N_2O generation was observed to be greater with the modified cartridge and higher flow rate (Figure 3-21). The higher average N_2O generation for Run 104 may be due to the SO_2 sorbent packing. During testing, the sorbent appeared "loose;" thus, the actual contact between the flue gas and SO_2 sorbent may have been less than optimum. Run 103, with a lower N_2O generation and lower flow rate, appears to operate consistently from cartridge to cartridge. A decision was made to continue using two dispersion tubes in the SO_2 sorbent cartridge.

The results of the worst case scenario tests, performed under controlled conditions, indicate that the sampling configuration used is capable of controlling N_2O generation in the sample container to acceptable levels. The final performance evaluation would be to duplicate the worst case scenario tests under actual combustion process conditions.

3.9.4 EPA's Innovative Furnace Reactor: Worst Case Conditions

A final grab sampling method performance evaluation test was conducted on the EPA's IFR under similar worst case scenario conditions. The furnace was fired on natural gas. No SO_2 or NO_x

TABLE 3-4. N$_2$O GENERATION UNDER WORST CASE CONDITIONS

Sorbent Conditions and Tests Results

	Sorbent Conditions	No. Days Aged	Initial N2O Concentration	Bomb 1 Generation	Bomb 2 Generation	Bomb 3 Generation	Avg Cart Generation
103A	2 Disp Tubes	7	0.75	0.80	0.91	0.61	0.77
103B	2 Disp Tubes	7	0.96	0.63	0.94	0.96	0.84
103C	2 Disp Tubes	7	2.14	0.17	0.42	0.80	0.46
104A	1 Disp Tube	7	1.20	0.00	0.00	0.75	0.25
104B	1 Disp Tube	7	0.80	1.19	1.18	1.18	1.18
104C	1 Disp Tube	7	0.84	0.90	0.99	2.54	1.47

Concentrations in ppm unless noted   SO2 = 2,500 ppm, NO = 900 ppm, H2O = 5% v/v
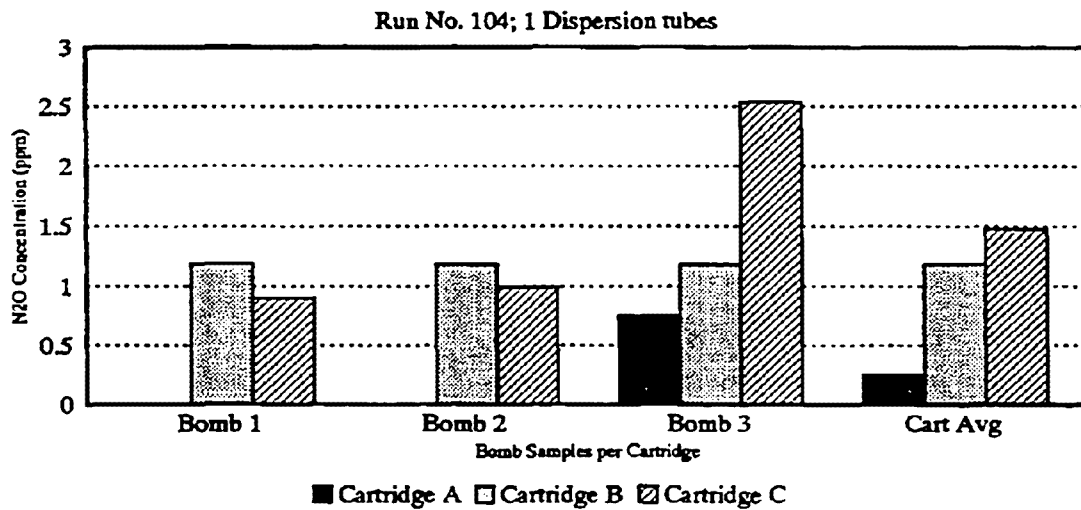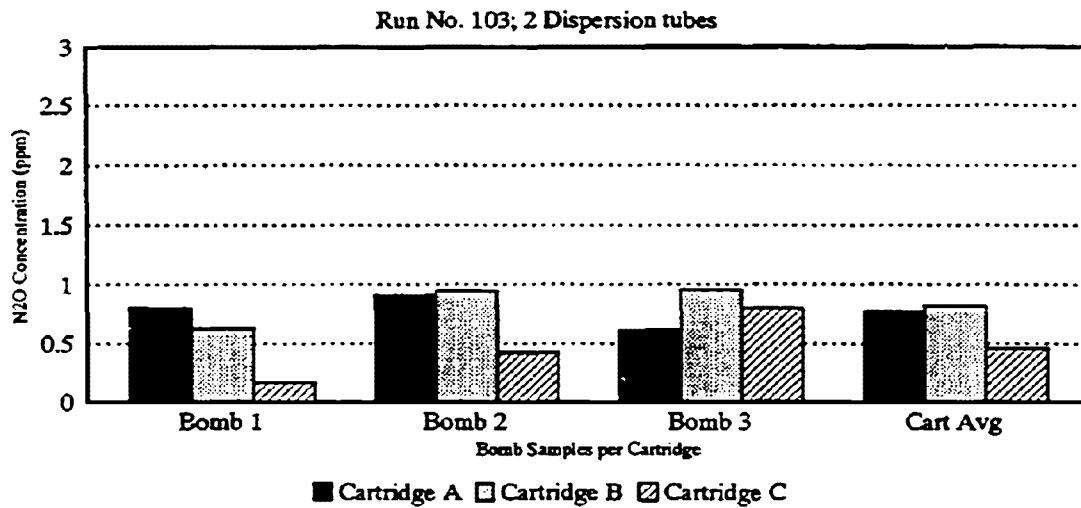
Figure 3-21. N_2O generation under worst case conditions.

pollution control devices or techniques were used during these tests. The concentrations of the key flue gas constituents measured during the worst case testing were approximately 3,200 ppm SO_2 and 1,500 ppm NO. Moisture was not measured but estimated to be approximately 10 percent by volume. The high levels of SO_2 and NO were obtained by doping the combustor with SO_2 and ammonia, respectively.

The grab samples were collected from the same location as the earlier performance evaluation tests. Specifically, the samples were obtained at a location in the CEM sample delivery system upstream of the moisture conditioning unit. Three sorbent cartridge systems were evaluated with a collection of three bombs per cartridge. The initial N_2O concentration was determined by the on-line GC/ECD which also sampled from the same location in the CEM system. N_2O measurements were made as closely to the time of grab sampling as possible.

The bomb samples were aged for 8 days and then analyzed for N_2O. Table 3-5 lists the conditions and results of the three tests. All three tests resulted in the generation of N_2O within the aged bomb sample. The average N_2O generation ranged from 3-7 ppm. One of the nine bomb samples did exhibit generation greater than 10 ppm (11.2 ppm).

Because the data were acceptable for this final performance evaluation test, the grab sampling method was deemed suitable for the screening of high N_2O-emitting fossil fuel combustion sources.

3.10 FURTHER METHOD EVALUATION: SNCR TESTS

Although this procedure was designed and tested for use with flue gases from conventional combustion sources without the application of any pollution control techniques or devices, an opportunity was presented to evaluate the grab sampling method on a NO_x control technique. The control technology employed, SNCR, uses additive reactants such as urea and cyanuric acid, injected in the post-combustion zone, to control NO_x emissions. This technology, however, has the potential to increase N_2O emissions. During this particular test, a proprietary reagent, hereafter referred to as NO_x-OUT, was evaluated.

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TABLE 3-5. EVALUATION OF SAMPLING METHOD ON ACTUAL COMBUSTION FACILITY UNDER WORST CASE CONDITIONS

Performed on the C-Wing IFR

Conditions and Results

Test	CRUN5	CRUN6	CRUN7
Date	06/24/91	06/24/91	06/24/91
Fuel	Nat. Gas	Nat. Gas	Nat. Gas
SO2 ppm	3175	3200	3220
NOx ppm	1562	1537	1537
CO ppm	25	20	18
CO2 %	10.02	9.94	9.78
O2 %	2.875	2.85	2.875
NOxOUT	no	no	no
Aged Days	8	8	8
Init N2O	.52	.53	1.04
N2O Gen Bomb A	2.46	1.81	2.66
N2O Gen Bomb B	2.94	7.04	4.92
N2O Gen Bomb C	3.41	11.23	5.36
Avg Cart Gen	2.94	6.69	4.31

Avg Bomb N2O = 3 bomb avg

Concentrations in ppm unless noted

Because the automated, on-line GC/ECD N_2O monitoring system was on loan to GCTB to measure N_2O emissions, it was an opportune time to evaluate the grab sampling method. Bomb samples were collected while the NO_x-OUT reagents were injected into the Down-fired Tunnel Furnace. Four tests were performed, each on separate days. Each test consisted of the collection of three bomb samples, which were then aged for more than 7 days and were then analyzed for N_2O. Table 3-6 gives the conditions and results for the four tests.

The results of these analyses demonstrated that no N_2O generation was observed. In fact, the N_2O concentration decreased from the initial, on-line N_2O concentration that was taken before the flue gas was sampled. The average reduction from initial N_2O to aged N_2O concentrations was 31 percent. In an attempt to explain the N_2O concentration decrease, the bombs were checked for leaks and found to be under pressure. The daily GC/ECD QC checks exhibited analytical bias of less than 3 percent, so an analytical error was also ruled out.

No explanation for the decrease in N_2O concentration in the aged bomb samples is apparent. A potential explanation may be linked to high stack concentrations of ammonia (NH_3), a byproduct of the NO_x-OUT additive. It may be possible that the ammonia participates in a reversible N_2O reaction within the bomb because of the basic nature of NH_3. The basic property alone is not enough to explain the reduction, as sodium hydroxide, a strong base, has been used in impinger solutions to scrub SO_2 from combustion flue gas samples for subsequent sampling for N_2O measurement. No negative bias on grab sample analyses have been isolated. However, an important conclusion can be drawn from this test; the grab sample method should be used on conventional combustion sources without the application of any pollution control equipment or technique only.

3.11 GRAB SAMPLING METHOD SUMMARY

The method developed was designed so that it could be used compatibly with continuous emission monitoring sample delivery/conditioning systems or as a stand alone procedure. Specifically, the method developed employs the use of reactant-specific dry sorbents to remove the gaseous

TABLE 3-6. N_2O GENERATION IN SAMPLES COLLECTED DURING NO_x CONTROL TESTS

Selective Non-catalytic Reduction

Performed on the C-Wing IFR

Conditions and Results

Test	CRUN1	CRUN2	CRUN3	CRUN4
Date	06/10/91	06/11/91	06/12/91	06/17/91
Fuel	Nat. Gas	Nat. Gas	Nat. Gas	Pitt No. 8 Coal
SO2 ppm	725	1625	1570	100
NOx ppm	80	90	388	280
CO ppm	30	80	33	10
CO2 %	7.6	7.46	7.6	8.6
O2 %	7.475	7.85	7.45	10.625
NOxOUT	yes	yes	yes	yes
Aged Days	9	8	7	9
Init. N2O	38.6	52.9	33.6	8.79
N2O Gen Bomb A	(5.06)	(19.73)	(9.5)	(2.00)
N2O Gen Bomb B	(6.98)	(8.05)	(6.58)	(2.95)
N2O Gen Bomb C	(9.32)	(24.38)	(12.65)	(2.90)
N2O Artifact	(7.12)	(17.39)	(9.58)	(2.62)

Avg bomb N2O = 3 bomb avg

Concentrations in ppm unless noted

( ) indicates negative values

components of SO_2 and H_2O to the degree that N_2O generation in stored (1-2 weeks) sample containers is consistently minimized to < 10 ppm. Sequentially, SO_2 is neutralized, and H_2O is removed from a fossil fuel combustion process flue gas sample stream before entering a Teflon-lined stainless steel container. The neutralization of SO_2 requires the presence of H_2O in the flue gas stream. Therefore, the flue gas sample must be collected upstream of any moisture conditioning devices such as condensers and/or desiccants that may be present in CEM sample delivery/conditioning systems.

The flue gas sample is extracted from the combustion source using a vacuum pump which pushes the gaseous sample through the two-cartridge, solid sorbent system and ultimately through the grab sample container or "sample bomb." The sample container is sealed and stored for up to two weeks at room temperature. The sample containers can be analyzed for N_2O at any point during the 2-week holding period.

This procedure was developed for use with flue gases from conventional fossil fuel combustion sources and processes. Samples were designed to be collected upstream of any pollution control equipment or on combustion facilities where pollution control equipment did not exist. This grab sampling method may not be suitable for use where sampling is performed downstream of pollution control devices or processes.

During the development of this sampling method, tests were conducted to determine the fossil fuel combustion process flue gas NO, SO_2, and H_2O concentration ranges where N_2O generation in aged (1-2 week) samples would be consistently minimized to less than 10 ppm. This method was found suitable for use on combustion systems with flue gas concentrations in the following ranges:

- SO_2 — 0-2,500 ppm

- NO — 0-1,000 ppm

- H_2O — 5-25 percent (by volume)

These flue gas concentration ranges were verified under actual combustion conditions as well. During these tests, the flue gas components of CO, CO_2, and unburned hydrocarbons, typically present in fossil fuel combustion process streams, were found not to interfere with sampling method performance. Other common flue gas components such as hydrogen chloride (HCl) and ammonia (NH_3) were not evaluated and may act as interferences.

SECTION 4

SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

The analytical and sampling methods developed during this project were found to be effective tools for the characterization of N_2O emissions from fossil fuel combustion processes and equipment. The automated, on-line monitoring system has proved to be a particularly effective means to acquire accurate, near real-time N_2O measurements from diverse combustion sources. The prototype instrument developed has since been duplicated and field tested at a commercial power utility. Application of the grab sampling methodology has not been as aggressive, primarily because of the need for absolute measurement of N_2O.

Because of the N_2O generation sampling artifact, the reliability of accurate measurements becomes even more critical. The procedures developed through this task are by no means the ultimate answers to N_2O sampling and analysis needs. The procedures developed were meant to rapidly enable the characterization of fossil fuel combustion source emissions. Although the automated, on-line GC/ECD monitoring system has proved to be accurate and reliable, it is not a real-time analyzer and is therefore not capable of continuous monitoring or measurement. Unfortunately, the commercial availability of dedicated, state-of-the-art combustion process N_2O monitoring equipment is extremely limited. Of those available, detection levels may be insufficient. In addition, these NDIR systems are susceptible to interferences from other combustion process gases that absorb IR radiation at wavelengths close to those that are absorbed by N_2O. These interferences are often minimized through the use of elaborate sample gas conditioning systems.

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Realizing that the continued development of continuous on-line monitoring instrumentation is likely, consideration should also be given to the sample delivery systems. The residence time in these systems may be long enough that generation of N_2O within the system may be possible. The volume and length of sample tubing along with sample flow rate should be considered. During tests performed by AEERL where a TDLIR continuous monitoring system was used, N_2O concentration spikes were observed following flow stoppage in sample delivery lines. These spikes were observed even when sample flow was stopped only for a period of several minutes. It is possible that sample delivery systems exist where the residence time between the source and analyzer can approach several minutes. Further examination of sample delivery systems are warranted.

The grab sampling method developed, although suitable for the screening of high N_2O-emitting fossil fuel combustion sources, is not suitable for the collection of grab samples for the determination of absolute N_2O measurements. The authors are unaware of a grab sampling method(s) that ensures the collection of uncompromised grab samples where generation does not take place, even after long periods of storage. In addition, although most researchers measuring N_2O emissions from combustion using grab sampling techniques take means to collect samples where the sampling artifact is drastically minimized, the variety of procedures to do so are quite diverse. It seems logical that some type of standardized grab sampling approach be developed.

In summary, the procedures developed during the course of this project were sufficient to meet AEERL's fossil fuel combustion source characterization needs. These procedures are documented in the form of EPA-AEERL ROPs. The ROPs contain detailed descriptions of the respective methodologies.

SECTION 5

QUALITY CONTROL EVALUATION REPORT

This study was conducted following quality assurance/quality control guidelines set by EPA/AEERL. This study was performed under an AEERL Category IV Quality Assurance Project Plan (QTRAK No. 89014) reviewed and approved by EPA. The goal of the project was to develop sampling and analytical methodologies suitable for the characterization of N_2O emissions from fossil fuel combustion sources.

The approach taken during this study was predominantly qualitative in nature. Many of the tests conducted were based on a go/no go or yes/no approach in order to effectively screen candidate sorbents for the development of the grab sampling method.

The measurements made by this project were of sufficient quality to more than adequately accomplish project goals. Essentially, the only measurements made were for NO, SO_2, and N_2O. The accuracy requirements, expressed as percent bias, were 20, 20, and 15 percent, respectively. Unless stated otherwise in the report, all data validating quality control checks performed before, during and/or after each test were within these limits.

SECTION 6

REFERENCES

1. D. Pierotti, R. A. Rasmussen, "Combustion as a source of nitrous oxide in the atmosphere," Geophysical Research Letters, 3(5): 265-267 (1976)

2   W. M. Hao, S. C. Wofsy, M. B. McElroy, "Sources of atmospheric nitrous oxide from combustion," Journal of Geophysical Research, 92(D3): 3098-3104 (1987)

3   R. F. Weiss, H. Craig, "Production of atmospheric nitrous oxide by combustion," Geophysical Research Letters, 3(12): 751-753 (1976)

4   M. A. Kahlil, R. A. Rasmussen, "Increase in seasonal cycles of nitrous oxide in the earth's atmosphere," Tellus, 35B: 161-169 (1983)

5   V. Ramanathan, R. J. Ciccrone, H. B. Singh, J. T. Kiehl,. "Trace gas trends and their potential role in climate change," Journal of Geophysical Research, 90(D3): 5547-5566 (1985)

6   G. I. Pearman, D. Etheridge, F. de Silva, P. J. Fraser, "Evidence of changing concentrations of atmospheric CO_2, N_2O, and CH_4 from air bubbles in Antarctic ice," Nature, 320: 248-250 (1986)

7   C. Castaldini, R. DeRosier, L. R. Waterland, H. B. Mason, "Environmental assessment of industrial process combustion equipment modified for low-NO_x operation," Proceedings of the 1982 Joint Symposium on Stationary Combustion NO_x Control, Vol. II, EPA-600-9-85-022b (NTIS PB85-235612), U.S. Environmental Protection Agency, Research Triangle Park, 1985

8   W. S. Lanier, S. B. Robinson, EPA Workshop on N_2O Emission from Combustion, EPA-600-8-86-035 (NTIS PB87-113742), U.S. Environmental Protection Agency, Research Triangle Park, 1986

9   J. C. Kramlich, R. K. Lyon, W. S. Lanier, EPA/NOAA/NASA/USDA N_2O Workshop, Vol. I: Measurement Studies and Combustion Sources, EPA-600-8-88-079 (NTIS PB88-214911), U.S. Environmental Protection Agency, Research Triangle Park, 1988

10 J. V. Ryan, R. K. Srivastava, EPA/IFP European Workshop on the Emission of Nitrous Oxide from Fossil Fuel Combustion, EPA-600-9-89-089 (NTIS PB90-126038), U.S. Environmental Protection Agency, Research Triangle Park, 1989

11   L. J. Muzio, J. C. Kramlich, "An artifact in the measurement of N$_2$O from combustion sources," Geophysical Research Letters, 15(12): 1369-1372 (1988)

12   L. J. Muzio, M. E. Teague, J. C. Kramlich, J. A. Cole, J. M. McCarthy, R. K. Lyon, "Errors in grab sample measurements of N$_2$O from combustion sources," JAPCA, 39: 287-293 (1989)

13   W. P. Linak, J. A. McSorley, R. E. Hall, J. V. Ryan, R. K. Srivastava, J. O. L. Wendt, J. B. Mereb, "Nitrous oxide emissions from fossil fuel combustion," Journal of Geophysical Research, 95(D6): 7533-7541 (1990)

14   J. S. Ford, Recommended Operating Procedure No. 45: Analysis of Nitrous Oxide from Combustion Sources, EPA-600-8-90-053 (NTIS PB90-238502), U.S. Environmental Protection Agency, Research Triangle Park, 1990

15   T. A. Montgomery, G. S. Samuelson, L. J. Muzio, "Continuous infrared analysis of N$_2$O in combustion products," JAPCA, 39: 721-726 (1989)

16   F. E. Briden, D. F. Natschke, R. B. Snoddy, "The practical application of tunable diode laser infrared spectroscopy to the monitoring of nitrous oxide and other combustion process stream gases," presented at 1991 Joint Symposium on Stationary Combustion NO$_x$ Control, Washington, DC (March 1991)

17   J. V. Ryan, S. A. Karns, "On-line monitoring of nitrous oxide from combustion sources using an automated gas chromatograph system," Presented at the Air and Waste Management Association Conference on Measurement of Toxic and Related Air Pollutants, Durham, NC, May 1992

18   J. V. Ryan, S. A. Karns, Recommended Operating Procedure No. 56: Collection of Gaseous Grab Samples from Combustion Sources for Nitrous Oxide Measurement, EPA-600-R-92-141 (NTIS PB92-216928), U.S. Environmental Protection Agency, Research Triangle Park, 1992

19   R. Clayton, A. S. Sykes, R. Machilek, K. Krebs, J. Ryan, N$_2$O Field Study, EPA-600-2-89-006 (NTIS PB89-166623), U.S. Environmental Protection Agency, Research Triangle Park, 1989

20   R. F. Weiss, "Determination of carbon dioxide and methane by dual catalyst flame ionization chromatography and nitrous oxide by electron capture chromatography," Journal of Chromatographic Science, 19: 611-616 (1981)

21   R. K. Lyon, J. C. Kramlich, J. A. Cole, "Nitrous oxide: Sources, sampling, and science policy," Environmental Science and Technology, 23(4): 392-393 (1989)

22   G. G. deSoete, Parametric Study of N$_2$O Formation from Sulfur Oxides and Nitric Oxide During Storage of Flue Gas Samples, Report 36 732, Institute Francais du Petrol, Rueil-Malmaison, France (1988)

23   S. A. Sloan, C. K. Laird, "Measurements of nitrous oxide emissions from P. F. fired power stations," Atmospheric Environment, 5: 1199-1206 (1990)

24   L. R. Martin, D. E. Damschen, H. S. Judeikis, "The reactions of nitrogen oxides with SO_2 in aqueous aerosols," Atmospheric Environment, 15: 191-195 (1981)

25   S. G. Chang, D. Littlejohn, N. H. Lin, In Flue Desulfurization; J. L. Hudson, G. T. Rochelle, Ed.; ACS Symposium Series 168; American Chemical Society: Washington, DC, 1982; 127-152

26   R. K. Lyon, J. A. Cole, "Kinetic modeling of artifacts in the measurement of N_2O from combustion sources," Combustion and Flame, 77: 139-143 (1989)

APPENDIX A

NON-CONTINUOUS SAMPLING AND ANALYSIS OF NITROUS OXIDE
FROM COMBUSTION SOURCES
ROP NO. 43

PREFACE

This appended method is included for historical perspective only. Aspects of this method were evaluated to develop the sampling and analytical methods described in this report. Specifically, the vacuum evacuation method for transferring the gaseous sample from the sample container to the analytical system was evaluated. The vacuum evacuation method was found to be susceptible to system leaks and was found not to be suitable for small volume samples. The sample introduction method ultimately selected used syringe injection.

NON-CONTINUOUS SAMPLING AND ANALYSIS OF NITROUS OXIDE
FROM COMBUSTION SOURCES
ROP NO. 43

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1.0   Introduction

The method described below uses the principle of gas chromatographic separation and electron capture detection for the measurement of nitrous oxide (N$_2$O) in combustion gas samples. Performance of this method should not be attempted by those who are unfamiliar with the operation of a gas chromatograph or with source sampling, because knowledge beyond the scope of this presentation is required.

2.0   Principle and Applicability

2.1 Principle: A gas sample is extracted from a combustion source and is used to fill an evacuated sample container. The sample is analyzed for nitrous oxide (N$_2$O) by gas chromatographic (GC) separation and electron capture detection (ECD).

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2.2 **Applicability.** The approach is used for measuring the N_2O content of combustion gases, both within the flame and in flue gases.

3.0 **Range and Sensitivity**

This method is designed for the 1 to 500 ppm range. As needed, the upper limit can be extended by proper calibration and by dilution of the sample. The lower limit can be extended by increasing the size of the sample loop beyond the 0.6 milliliters employed here.

4.0 **Interferences**

4.1 **Particulate Matter.** Particulate matter in gas samples may cause interference by clogging of the sampling system. This interference must be eliminated by use of a probe filter.

4.2 **Moisture.** Moisture condensation may cause interferences or unreproducible behavior within the analytical system due to the flow disturbances that accompany such vaporization. Water is removed by the trap described in the procedure.

4.3 **Halogenated Compounds.** Halogenated compounds, in particular fluorinated hydrocarbons, can contaminate the ECD and lead to long-term baseline offsets. This interference is avoided by use of the precolumn/ backflush system described in the method.

4.4 **Carbon Dioxide.** Carbon dioxide can cause a negative interference on the detector, particularly if it co-elutes with N_2O under the high concentrations present in combustion sources. The column used in the present method avoids this problem by eluting N_2O before CO_2. Also, the use of an Ar/CH_4 carrier gas, as described in the method, prevents the interference.

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4.5 Oxygen. The detector becomes desensitized by exposure to oxygen. Because of the oxygen present in the samples, a progressive desensitization of the detector cannot be avoided during repetitive analysis. As outlined in the procedure, a repetitive calibration is performed throughout the sample run and the data are corrected for the drift. Overnight conditioning returns the detector to the baseline sensitivity.

5.0 Apparatus

5.1 Sampling Probe. The probe should meed the standards required for EPA Method 7, with the following exceptions. The probe material may be stainless steel, quartz, or Teflon, although Teflon should not be used above 190°C. Probe cooling must be used when sampling from streams above 200°C. This is principally to prevent N₂O loss on the probe surface and to quench in-flame reactions. Water is an appropriate cooling media.

5.2 Sample Line. Teflon or stainless steel lines are used. The connection between the end of the probe and the sample container should be as short as reasonable.

5.3 Sample Filter. A glass wool plug is inserted into the sample line; alternatively, an out of stack filter may be placed at the end of the probe.

5.4 Sample Container. A glass or stainless steel sample flask is used which provides sample ports and valves at both ends. The containers should be no smaller than 125 milliliters, and should be capable of withstanding a full vacuum. If values other than Teflon stopcocks are used (e.g., stainless steel valves) then the open ends of the valves should be plugged by a pressure tight cap to prevent slow leakage

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through the valves. Sample containers with free septa should not be used.

5.5 <u>Sample Train</u>. The sample train consists of the probe, sample filter, and sample container. The outlet of the sample container is connected through a flow metering device to a sample pump. The pump and flow meter should be sized to allow a flow of 5 liters/min. A condensate knockout may be used between the sample container and the flow meter, if desired.

5.6 <u>Gas Chromatograph</u>. Any gas chromatograph system may be used which possesses the following attributes. The oven must be capable of operating at 250°C. Also, an ECD must be mounted on the oven wall and must be capable of operating at 350°C. Figure 1 details the apparatus needed for the GC analysis. The carrier gas must be a 95 percent argon/5 percent methane mixture that has been specifically prepared for ECD analyzers. An in-line silica gel purifier is used. The sample bulb is connected to a 1 x 1/4 inch tube containing the absorbent aquasorb (Mallinchroft, St. Louis, Missouri) which is impregnated with P_2O_5. This removes water vapor. Two sample/switching valves are required; these may either be 6-port valves or 10-port valves with jumpers. Three carrier gas controllers are required, (1) carrier gas, (2) backflush gas for the precolumn, and (3) detector makeup gas. A second oven operating at 70°C is used for the precolumn. Sample is drawn through the system by a vacuum pump which is isolated by a 4-foot isolation coil; the absolute pressure in the sample loop is determined by a mercury manometer. The column is a 3 foot x 1/8 inch stainless steel tube packed with Molecular Sieve 5A, 60/80 mesh (Supelco Inc., Bellefonte, PA). The precolumn is a 6 inch x 1/8 inch stainless steel tube packed with Porapak Q, 80/100 mesh (Alltech Associates, Inc., Deerfield, IL).
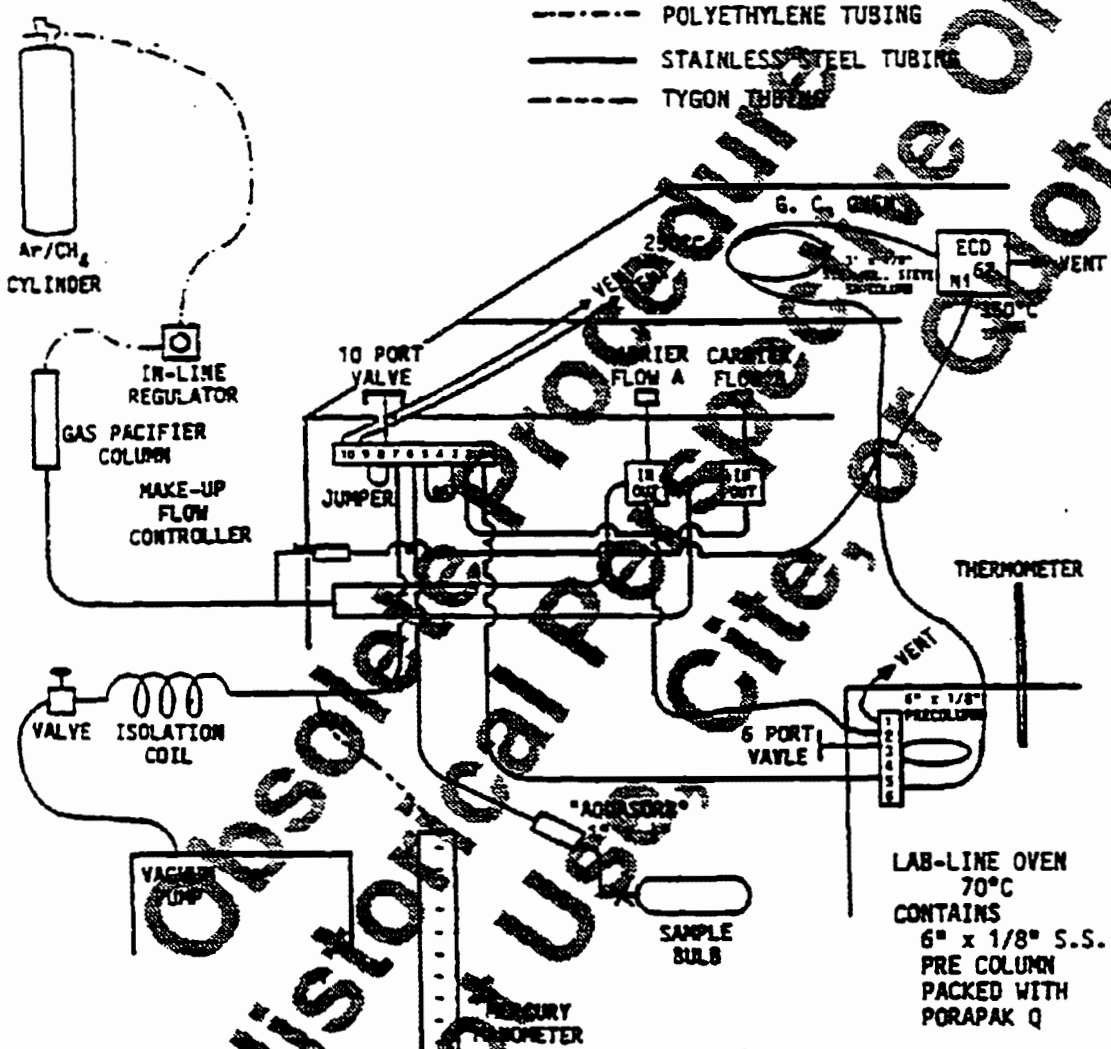
A-5

Figure 1. Detailed diagram of the N_2O analysis system.

6.0   Calibration

Two levels of calibration are used. The most detailed level is
performed after the initial setup, whenever the system has undergone an
upset, and whenever the system is repowered after a full shut-down and
cool off. The second level is performed to check for day to day
variations in system response, and to provide a correction for detector
drift during the analytical day.

6.1 Detailed Calibration. Nitrous oxide emission concentrations from
pulverized coal flames generally fall between 70 and 150 ppm. This is
the recommended initial calibration interval, with the proviso that the
interval be extended to include any values outside this range
encountered during analysis. Note that other sources can yield markedly
different N2O emissions; reference to the literature will provide the
best guidance on selecting an initial calibration interval.

The instrument response should be determined at five evenly separated
concentrations in order to detect any non-linearities in the detector
response. Each separate span gas should be measured at least in
triplicate.

6.1.1 Calibration standards. Any of the normal means used for
preparing known dilutions of gases may be employed, including the
purchase of precalibrated standards. The normal procedure is to prepare
the sample in glass flasks of known volumes which are fitted with
septia. The flask is evacuated to less than 1 mm Hg using a vacuum pump
and a known amount of N2O is injected through the septum port. The
pressure is measured by any means capable of resolving 1 mm Hg pressure.
The cylinder is then backfilled with nitrogen to atmospheric pressure.
The N2O mole fraction is calculated as follows:

$$[N_2O] = P_{N_2O}/P_{cyl} \qquad\qquad [1]$$

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where V_{N_2O} and V_{cyl} are the volume of the injected N_2O and the flask volume, respectively. Note that if the N_2O and the dilution nitrogen are all at ambient pressure and temperature, then no correction is required for these variables.

6.1.2 Procedure. Once the standards are prepared, the calibration procedure follow exactly the analysis step described below for the samples. As samples are withdrawn from the cylinder, its pressure decreases. Since a fixed volume. sample loop is used to measure the aliquot, it is necessary to correct the response for this pressure to develop a standard calibration curve. This procedure follows.

The initial calibration will result in a table that will contain three entries for each calibration point. These are: (1) the N_2O concentration in the standard, (2) the area of the N_2O peak, as obtained from the gas chromatograph, and (3) the sample pressure. The N_2O concentration corrected to 1.0 atm pressure is calculated as follows:

$$[N_2O]_{curve} = [N_2O] \times P_{standard}/760 \qquad [2]$$

where $P_{standard}$ is the pressure in the sample loop at the time of injection in mm Hg (this measurement is described in the analytical procedures section). A plot of peak area against $[N_2O]_{curve}$ yields the true calibration curve for a 1 atm sample loop pressure. Figure 2 shows a typical calibration curve generated over a 10 to 150 ppm range. The calibration is generally linear except for a slight non-linearity at low sensitivities. Such a non-linearity is consistant with ECD characteristics for theoretical reasons discussed by Weiss (1981). Figure 3 shows a similar plot that covers a more sensitive range: 0.5 to 15 ppm.

6.2 Second Level Calibration. The ECD sensitivity is subject to drift from day to day, and within a single day. For N_2O analysis from
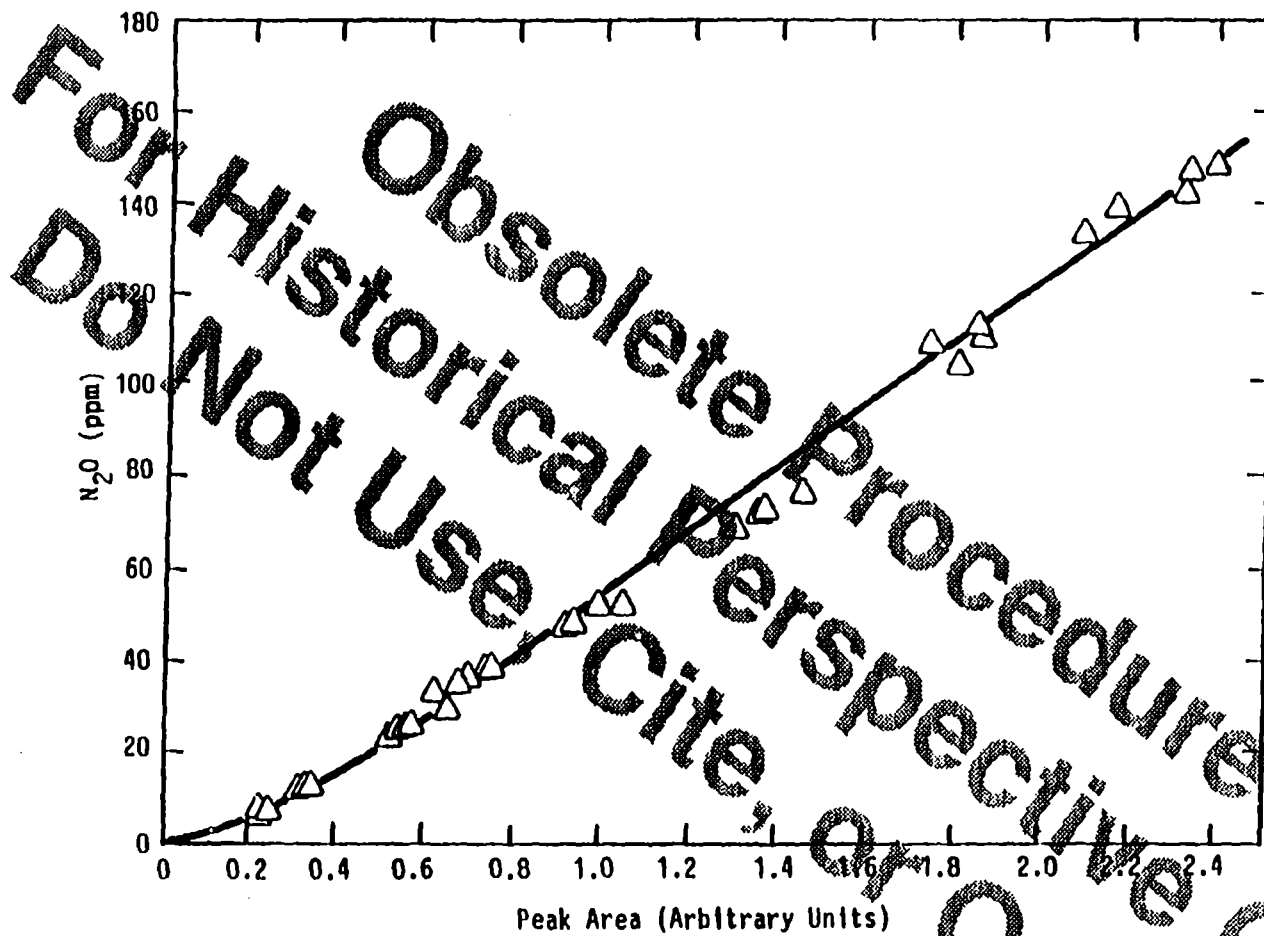
Figure 2. Example N_2O calibration curve.
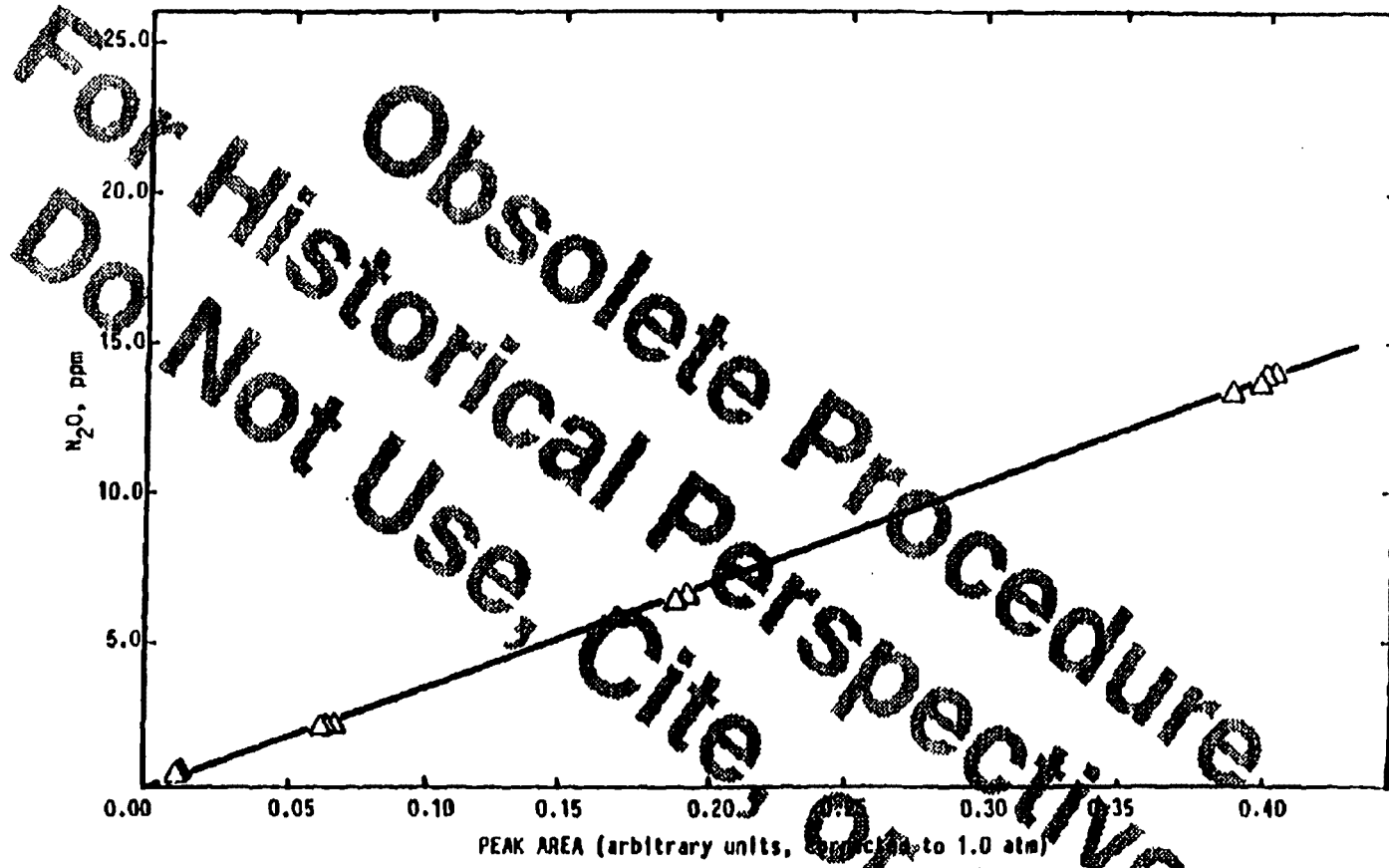
Figure 3.   Calibration curve for N$_2$O.

combustion gas, this drift is mainly due to the exposure of the detector to the oxygen in the sample. Since this is unavoidable, the data are corrected by repetitive single point calibrations during the analytical day. A calibration is performed at least once for each two samples (i.e., the sequence is duplicate determination of calibration gas, duplicate determination of sample A, duplicate determination of sample B, and return to calibration gas).

6.2.1 **Calibration Standards.** This should be a single standard whose concentration is selected to be near the midpoint of the expected concentration of the samples. For N₂0 measurement from coal combustion a good value is 100 ppm. A commercially prepared span gas in a high pressure cylinder is the most convenient approach. The high stability of N₂0 in such cylinders ensures consistant day to day performance.

6.2.2 **Procedure.** The calibration gas is passed through the cylinder pressure regulator, and into the sample valve via the sample bottle connector. When the sample loop has been fully flushed and allowed to relax to ambient pressure by stopping the flow, the analysis is performed as described in the analytical procedures section. The N₂0 concentration is corrected to 1.0 atm by the following:

$$[N_2O]_{standard} = [N_2O]_{bottle} \times P_{atm}/760 \qquad [3]$$

where P_{atm} is the ambient pressure in mm Hg. This value is used as a proportional adjustment on the calibration curve as described in the calculations section.

7.0 **Sampling Procedure.**

7.1 **General Considerations.** At least two levels of sampling complexity may be selected. The choice depends on the nature of the source and the degree of characterization desired. Systems in which the sample gases

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are well homogenized and time steady may be well characterized by a single measurement at a single location. Characterization of N₂O in highly stratified flows will necessarily require detailed traverses of the duct or stack. Procedures for both approaches are described.

7.2 **Single Point Characterization.** The sample train is assembled as described in Section 5.0. The sample container is wrapped in glass wool or a similar insulating material. The coolant flow is started (if used) and the probe is inserted into the flow. The sample pump is started and the flow is adjusted to a point in the 1.0 to 5.0 liter/min range. The sample container is continuously purged with sample until the container reaches thermal equilibrium with the probe temperature. In no case, however, should the container have less than ten times its volume purged through it (e.g., no less than 2.5 liters should be drawn through a 250 ml. container). At the conclusion, the downstream container valve is first closed, and a moment is allowed for the container pressure to equilibrate with the duct or stack pressure. The upstream valve is then closed, and the container is removed from the sampling system. If required, the open valve fittings are capped, and the containers are ready for analysis.

7.3 **Full Duct Characterization.** A full duct characterization will involve collecting N₂O samples on a sufficiently fine grid across a duct that the crude emission factor can be obtained by integrating N₂O concentration with flow velocity. Due to the specialized hardware required, this method is applicable only to streams below 200°C. The procedure follows that described in Section 7.2, with the following exceptions:

(1) The probe is modified to include the pitot probe, thermal sensor, and probe tip specified for EPA Method 5. The EPA Method 5 probe is a suitable probe for this application.

(2) The pitot manometer, pump, and flow measurement system specified for EPA Method 5 are used.

(3) Operation procedures specified in Section 7.2 are followed here, with the exception that the flow is set to provide an isokinetic sampling rate by use of the procedures specified in EPA Method 5.

(4) EPA Method 1 may be used as a guide to select the number of traverse points required, and their location. As this can require an overly large number of samples (e.g., over 25), the recommended approach is to reduce the number of sampling points by an even multiple of the Method 1 specification.

(5) The average N₂O concentration across the duct or stack is calculated in accordance with the procedures outlined in EPA Method 5.

8.0   Analysis Procedure

Refer to Figure 2 for a simplified schematic of the analytical system. Comparison of Figures 1 and 2 will facilitate the identification of the relationship between hardware and function.

The carrier gas flow is set to 20 milliliters/minute. This initially flows through the 10-port sample valve, the precolumn, the main column, and the detector. The sample flask is connected into the system, and a small flow is withdrawn through the carrier, the 10-port sample valve, (including the 0.6 milliliter sample loop), the isolation coil, and into the vacuum pump. The manometer is used to monitor the flow indirectly by measuring the rate at which the flask is evacuated. When the sample loop has been filled with sample, the vacuum pump valve is closed and the system is allowed to come to pressure equilibrium. The manometer reading is recorded to allow calculation of the total corrected volume of sample within the sample loop. The direct

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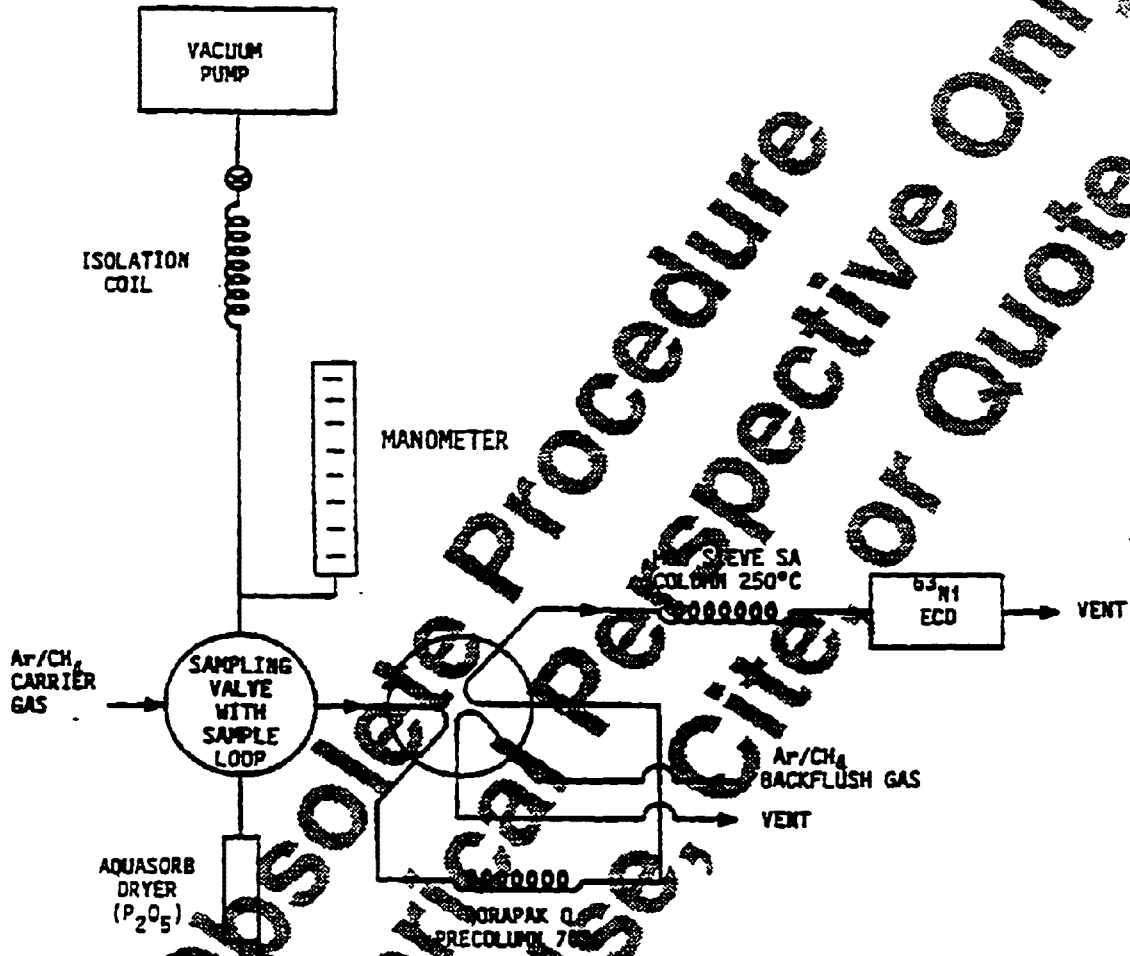
Figure 4. Simplified flow schematic of the analysis system.

analysis is started by switching the 10-port valve so the sample loop is placed into the carrier gas flow path. The carrier flow is directed through the precolumn for 2.5 minutes. This time is sufficient for the N2O to fully elute onto the main column, but for any fluorinated compounds to be retained on the precolumn. As the 6-port valve is switched, the precolumn is removed from the carrier gas stream. A 20-milliliter/minute carrier gas flow backflushes the precolumn during this time. As shown in the sample chromatogram in Figure 5, the N2O elutes approximately 2.4 minutes after injection. The sample run is not terminated until the 15 minutes have elapsed, however. This is to allow the large CO2 peak to fully elute. This step ensures that the subsequent sample will not experience CO2 interference from the preceding analysis. The response from the ECD amplifier is recorded by a chart recorder or a digital integrator.

9.0   Calculations

The following calculations are necessary to determine the N2O concentration. The reported peak area is used with the calibration curve to obtain an uncorrected N2O concentration. This is corrected for the sample loop pressure and the calibration drift as follows:

$$[N_2O]_{dry} = [N_2O]_{raw} ([N_2O]_{std} / [N_2O]_{curve}) (760/P_{loop}) \qquad [4]$$

where: $[N_2O]_{dry}$ = actual N2O concentration in the sample on a dry basis.

   $[N_2O]_{raw}$ = value obtained form the peak area and the calibration chart.

   $[N_2O]_{std}$ = corrected N2O concentration in the commercial second-level standards (from equation 3). This is the average of the calibration determinations made immediately before and after the sample analysis.
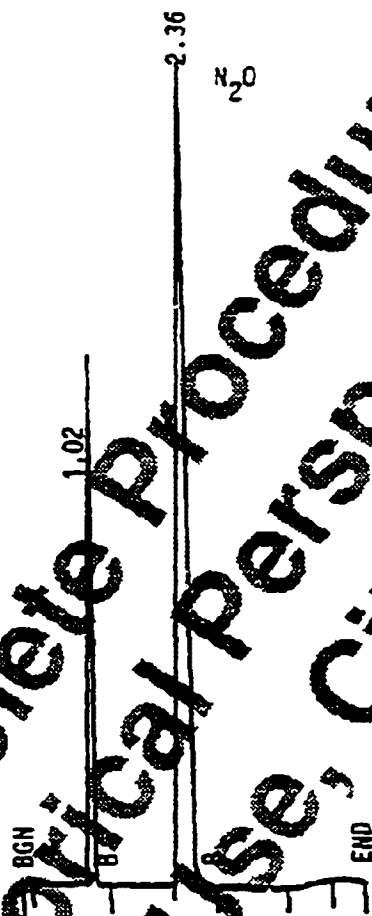
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Figure 3. Example chromatogram for N$_2$O analysis.

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$[N_2O]_{curve}$ = N$_2$O corcentration obtained from the calibration curve using the peak area generated by the second-level standard.

P_{loop} = absolute pressure in the sample loop prior to injection, mm Hg.

The dry N$_2$O value can be corrected to any other dry stoichiometry basis by use of the following:

$$[N_2O]_{dry,x\%0} = [N_2O]_{dry} (21-x)/(21-y)$$ [5]

where: x = dry percent O$_2$ to which the N$_2$O concentration is to be corrected.

y = measured dry percent O$_2$ in the sample gas.

Note that this equation only holds for air driven combustion with neither oxygen enrichment or nitrogen dilution. To correct to a moist basis:

$$[N_2O]_{wet} = [N_2O]_{dry} (Moles_{dry}/Moles_{wet})$$ [6]

where: Moles$_{wet}$ = moles of product produced by burning one mole of fuel.

Moles$_{dry}$ = moles of product, exclusive of water, produced by burning one mole of fuel.

An example calculation is described in Appendix A.

10.0   Quality Control

10.1   Primary Calibration. The primary calibration is performed at any time the system is repowered from a cold start, or anytime the second-level

calibration is outside the bounds described below. In theory the calibration should be linear with the exception of a curving at low concentrations, as shown in Figure 2. The recommendation approach is to manually fit a line through the curved portion of the curve, and use a linear least squares fit to derive a straight line through the linear portion of the curve. The two curves are constrained to meet both in term of absolute value and slope.

The goodness of fit is estimated by calculating the relative standard deviation for all the points:

$$s = \sqrt{\frac{[(y_i - f(x_i))/f(x_i)]^2}{n-1}}$$

where: y_i = N2O concentration for each point

$f(x_i)$ = N2O concentration calculated from the curve at the same peak area

n = number of points

Although the selection of an acceptance/rejection criteria is somewhat arbitrary, past experience has shown that if s is greater than 0.1 the calibration is unacceptable.

10.2 Second Level Calibration. If the second level calibration is consistantly greater than 25% from the primary calibration, the primary claibration should be redone.

10.3 Consistency Checks. As described above, the second level calibration is performed at least once between every two samples. All samples are performed in duplicate, and in all cases additional aliquots are analyzed if the relative difference between replicates is greater than 5%. A blank cylinder containing nitrogen is analyzed once each day. The response

of the second level calibration should be maintained as a quality control chart.

11.0   Bibliography

The following references discuss various approaches to the N$_2$O measurement problem. The approach described above is a modification of that reported by Weiss (1981). The modifications were required to transform an ambient measurement technique into one suitable for combustion flue gas. We wish to acknowledge the advice Dr. Weiss provided us.

1.   Bowman, C. T. and R. J. Roby: Combust. Flame 70, 129 (1987).

2.   Hao, W. M.: Industrial Sources of Atmospheric N$_2$O, CH$_3$Cl, and CH$_3$Br, Ph.D. dissertation, Division of Applied Sciences, Harvard University, Cambridge, MA (1986).

3.   Kramlich, J. C., R. K. Lyon, J. A. Cole, J. M. McCarthy, D. W. Pershing, and M. P. Heap: Combust. Flame 48, 101 (1982).

4.   Pierotti, D. and R. A. Rasmussen: Geophys. Res. Lett. 3, 265 (1976).

5.   Weiss, R. F.: J. Chrom. Sci. 19, 611 (1981).

6.   Weiss, R. F. and H. Craig: Geophys. Res. Lett. 3, 751 (1976).

EXAMPLE CALCULATION

The following example provides a guide to the data reduction procedures. The input conditions are as follows:

o   Methane/air combustion with 4% O$_2$ (dry) measured in the post-grate gas.

o   Peak area obtained from the sample is 1.0 at a sample loop pressure of 450 mm Hg. From Figure 2 this yields a value of [N$_2$O]$_{raw}$ = 54 ppm.

o   The secondary standard is 100 ppm, for which the measured peak area is 1.5 at an atmospheric pressure of 750 mm Hg.

Since the calibration curve is based on a 1.0 atm sample pressure, the first step is to correct the secondary standard to 1 atm by equation 3.

$$[N_2O]_{std,1atm} = (100 \text{ ppm}) (750)/(760) = 98.7 \text{ ppm.}$$

Because of the slightly reduced pressure in the sample loop, the loop would contain only 98.7 ppm N$_2$O if its pressure were adjusted to 760 mm Hg; by isothermal dilution. Next, the calibration curve is entered with the measured secondary standard peak area, 1.5, and the value recovered is: [N$_2$O]$_{curve}$ = 88 ppm. The dry N$_2$O value in the sample is calculated by equation 4.

$$[N_2O]_{dry} = (54 \text{ ppm}) (98.7 \text{ ppm}/88 \text{ ppm}) (760 \text{mmHg}/450 \text{mmHg}) = 102.3 \text{ ppm.}$$

In essence, this equation corrects the raw reading for the downward detector drift and the fact that the sample pressure was reduced.

To correct the N_2O value to 0% O_2, equation 5 is used:

$$[N_2O]_{dry,0\%O} \quad = \quad (102.3) \ (21)/(21-4) \quad = \quad 126.4 \ ppm.$$

To correct to a wet basis requires a calculation of the products of combustion for CH_4/air at 4% (dry) O_2. The total dry moles of product produced per mole of CH_4 is 10.52, while the number of wet moles is 12.52. Thus, the wet basis N_2O is calculated from equation 6 as:

$$[N_2O]_{wet} \quad = \quad (102.3ppm) \ (10.52/12.52) \quad = \quad 86.0 \ ppm.$$

This calculation basicly represents the fact that the N_2O is spread over a larger basis.

APPENDIX B

STANDARD OPERATING PROCEDURE FOR DETERMINING
NITROUS OXIDE CONCENTRATIONS IN COMBUSTION FLUE GAS

PREFACE

This appended method is included for historical perspective only. The chromatographic conditions contained in this method were selected for evaluation during development of sampling and analysis methodologies. The chromatographic conditions were found to be susceptible to baseline upsets and chromatographic difficulties resulting from interferences present is combustion samples.

Aug. 29, 1984

STANDARD OPERATING PROCEDURE FOR DETERMINING
NITROUS OXIDE CONCENTRATIONS IN COMBUSTION FLUE GAS

By

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Signature Approvals and Dates

Immediate Supervisor: _____ Date Signed: _____

Office Director: _____ Date Signed: _____

Effective Date: _____

Disclaimer: This Standard Operating Procedure
has been prepared for the sole use of the
Industrial Environmental Research Laboratory
of EPA at Research Triangle Park, North Carolina
and may not be specifically applicable to the
activities of other organizations.

1.   APPLICABILITY AND PRINCIPLE

    1.1 Scope: This method is applicable to quantitation of
nitrous oxide (N$_2$O) in combustion flue gas. The method is based
on the separation of nitrous oxide from flue gas components by
using a gas chromatographic column and selectively detecting N$_2$O
with an electron capture detector (ECD).

    1.2 Range of Applicability: The upper end of applicability
is limited by the electron capture detector saturation. The
useful upper limit concentration is 500 parts per million.

    The minimum detectable limit (MDL) is 1-2 parts per million.

    1.3 Precision and Accuracy: Duplicate results by the same
operator can be obtained with precision and accuracy of ± 15%
from the previous value injected.

    1.4 Interferences: The analytical system must be initially
demonstrated to be free from internal contaminants by running a
calibration standard, then a sample of the flue gas. The base-
line should be monitored for an extended time to determine if
additional peaks elute which could interfere with consecutive
injections of flue gas samples.

2.   ANALYSIS PROCEDURE

    2.1 Instrumental Parameters:
    Column: Porapak Super Q, 12 ft. x 1/8 in. stainless
                   steel, conditioned at 220°C
    Oven Temperature: 35 degrees C
    Injector: 80 degrees C
    Detector (Electron Capture): Ni 63 at 350 degrees C
    Carrier Gas: Nitrogen at 20 mL/min

Gas Sample Value: Valco 6-port with 1 mL loop, stain-
less steel

2.2 Calibration: Calibration is accomplished through the use of known concentrations of N_2O in nitrogen. Gas mixtures can be obtained from Scott Environmental (Plumsteadville, PA) at concentrations in the range of 4.0 ppm to 500 ppm.

The gas sample valve is placed in the load position and the standard gas mixture is purged through the loop to equilibrate the valve. The flow of standard is then shut off, and the pressure allowed to equilibrate to atmospheric (approximately 15 sec.). The sample valve is then moved to the inject position. Several *A minimum of 3* injections should be made until repeatable results are obtained. *< ± 15%* Each standard concentration must be injected to obtain a standard curve.

2.3 Daily Operating Procedures of GC/ECD:

1. Start-up GC instrument as suggested by the manu-facturer.

2. Allow detector, injector and oven temperatures to equilibrate *overnight*.

3. Condition column at 220°C with nitrogen flow of 20 mL/min until baseline is stable, *then reset to 35°C.*

4. Run standard gas mixtures *in triplicate* using 6-port gas sample valve.

5. Measure peak height (or area) of standards and plot vs. concentration.

6. Analyze samples using the same technique as employed with standards.

2.4 Data Reduction: A response factor can be calculated from the standards by dividing the concentration (ppm) of a standard by the peak height or the area counts. The

concentration of the unknown sample is computed by multiplying its peak height (or area) by the response factor.

3. QUALITY ASSURANCE/QUALITY CONTROL

Each sample should be injected a minimum of three (3) times to establish repeatability. *The calibration curve should be linear and must have a correlation coefficient greater than 0.9 using 3 concentrations of standards.*

After sample injection, sufficient time should be given to allow later eluting peaks to exit the column before another injection is made.

As with all electron capture detectors, periodic standing current and sensitivity checks must be performed according to the manufacturer's recommendations. Wipe tests of the detector are also required to check for radiation leaks.

General periodic maintenance of the gas chromatograph is needed with appropriate documentation. The carrier gas used should be at least 99.99% grade, with trace oxygen filters installed between the cylinder and the gas chromatograph.

All sample lines should be cleaned and periodically checked to verify the absence of contamination.

Also a calibration curve of three (3) points can be constructed by fitting a linear regression equation to the results of the analysis of the standard gas mixtures.

Standard Calibration Equation:

$$R_i = (M) C_i + (B)$$

R_i = ECD Response / injection M = Slope of line

APPENDIX C

RECOMMENDED OPERATING PROCEDURE FOR ANALYSIS OF NITROUS OXIDE IN COMBUSTION FLUE GASES AEERL/ROP NO. 45

PREFACE

This appended method is included for historical perspective only. This was the original AEERL/ROP No. 45 which has since been revised and published. This appended method was developed combining sample introduction aspects of Appendix A with chromatographic conditions contained in Appendix B. The vacuum evacuation method for transferring the gaseous sample from the sample container to the analytical system was evaluated. The vacuum evacuation method was found to be susceptible to system leaks and was found not to be suitable for small volume samples. The sample introduction method ultimately selected used syringe injection. The chromatographic conditions were found to be susceptible to baseline upsets and chromatographic difficulties resulting from interferences present is combustion samples. Detector response to N_2O concentration was not linear over the desired range of quantitation.

RECOMMENDED OPERATING PROCEDURE FOR ANALYSIS OF NITROUS OXIDE IN COMBUSTION FLUE GASES

AEERL/ROP No. 45

by

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RECOMMENDED OPERATING PROCEDURE FOR
ANALYSIS OF NITROUS OXIDE IN COMBUSTION FLUE GASES

1.0 PROCEDURAL ELEMENTS

1.1 Scope and Application

Based on the principles of gas chromatographic separation and electron capture detection, this method is applicable to the measurement of nitrous oxide (N_2O) in dry grab samples of combustion flue gases and is designed for a 5 to 200 ppm range. The upper limits can be extended by changing the sample loop pressure to reduce the volume of sample in the loop or by dilution of samples; the sensitivity limits shall be determined by the minimum detectable concentration of standards.

This method requires that the analyst have at least of a bachelors degree in chemistry with two (2) years of experience in gas chromatography.

1.2 Summary of Method

This method quantifies N_2O in a sample of gas extracted from a combustion source, and is intended for use with a gas chromatograph (GC) that is equipped with a packed column connected to an electron capture detector (ECD).

The sample is drawn through a drying column and into an evacuated fixed volume sample loop. After the sample loop is filled and pressure equilibrium is achieved, the sample is passed directly to the GC and the ECD for separation and quantification, respectively. The ECD response is translated by a digital integrator and recorded on a data acquisition system (DAS).

The relationship between ECD response and N_2O concentration is determined by a least squares linear regression equation generated from calibration data derived by analysis of standards covering the expected sample concentration range.

1.3 Definitions

- *DAS*: data acquisition system; a computerized peak measurement system tailored to gas chromatographic data.

- *Accuracy*: the degree of agreement of an average measurement ($\bar{X}$) with an accepted reference or true value, expressed as a percentage of the reference or true value.

- *Precision*: the degree of mutual agreement among individual measurements made under prescribed conditions.

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- **MDL**: minimum detection limit: the concentration corresponding to five (5x) times the background noise level of the measurement.

- **MQL**: minimum quantifiable limit: the concentration corresponding to ten (10x) times the background noise level of the measurement. or the lowest calibration standard.

1.4 Interferences

The analytical system shall be demonstrated to be free from contaminants on a daily basis by a two-point calibration check prior to sample analysis and by concurrent analysis of quality control (QC) samples with unknown samples.

Sample must be pulled through a non-reactive drying system (silica gel should not be used), however. the analytical system shall be protected from interference caused by the presence of moisture in the sample gas by placing a moisture trap in line prior to the sample container outlet valve. Interference caused by organics will be controlled by adding activated charcoal to the moisture trap.

1.5 Apparatus

1.5.1 Analysis

- **Gas Chromatograph**: Capable of operating at 35°C and 330°C connected to an electron capture detector with Ni constant current cell. and capable of operating at 330°C.

- **GC Column**: 3.7 m x 0.32 cm (12 ft x 0.125 in.) O.D. stainless steel. packed with 80/100 mesh support (e.g. Porapak Super Q, Alltech Associates. Inc.. Deerfield. IL).

- **Carrier Gas**: Argon-methane mixture specially prepared for ECD analysis. containing 95 percent Ar and 5 percent CH₄.

- **Moisture Trap**: 3.81 cm x 0.64 cm (1.5 in. x 0.25 in.) O.D. Teflon tube containing 50 percent Aquasorb (P₂O₅ indicating absorbent by Mallinckrodt. St. Louis. MO) and 50 percent activated charcoal.

- **Vacuum Pump**: Oil-immersion. rotary-vaned: capable of pulling 29 inches of mercury.

- **DAS**: Data acquisition system.

- **Compressed Gas Cylinders**: Six. containing various known concentrations of N₂O/in pure N₂.

- **Compressed Gas Cylinders**: Three. containing known concentrations of mixed components (N₂O, CO₂ and O₂).

- *Isolation Coil:* 1.5 m x 0.032 cm (5 ft x 0.125 in.) stainless steel.

- *Thermometer:* Certified accuracy of ± 0.5%.

- *Sample:* Dry grab sample extracted from a combustion source, contained in a glass or stainless steel sample cylinder (no smaller than 250 mL) with sample valves at both ends and capable of withstanding a full vacuum.

1.6 Analytical System

This method is intended for use with a gas chromatograph (GC) equipped with an electron capture detector (ECD) and capable of operating at 35°C and 220°C. The GC uses a 3.7 m 0.32 cm (12 ft x 0.125 in.) stainless steel column packed with a Porapak Super Q 80/100 mesh support. The ECD is a Ni^{63} constant current cell operated at 350°C. The carrier gas, a mixture specially prepared for ECD analysis, is 95 percent argon and 5 percent methane. The carrier gas initially flows through a 5A molecular sieve and an oxygen scrubber before reaching the main column and the detector. The sample is supplied to the system by a short length of 0.32 cm (0.125 in.) O.D. stainless steel tubing connected to a 1-cc sample loop. A 3.5 cm x 0.64 cm (1.5 x 0.25 in.) Teflon tube containing a P_2O_5 acidic absorbent and activated charcoal for the removal of moisture and organics, respectively, is placed in line between the sample container outlet and the first length of stainless steel tubing. The tube must be arranged so that the sample flows through the Aquasorb prior to flowing through the activated charcoal. A vacuum pump, isolated by a 1.5 m (5 ft) stainless steel isolation coil is used to supply the sample to the system. The absolute pressure in the sample loop is monitored with a mercury manometer. The sample flows from the sample loop directly to the GC column. The eluted constituents then pass to the ECD for eluted quantification. A schematic of the analytical system is shown in Figure 1.

1.7 Calibration

CAUTION

Do not connect pressurized gas cylinders directly to the gas chromatograph. Use a sample valve to avoid damaging the instrument.
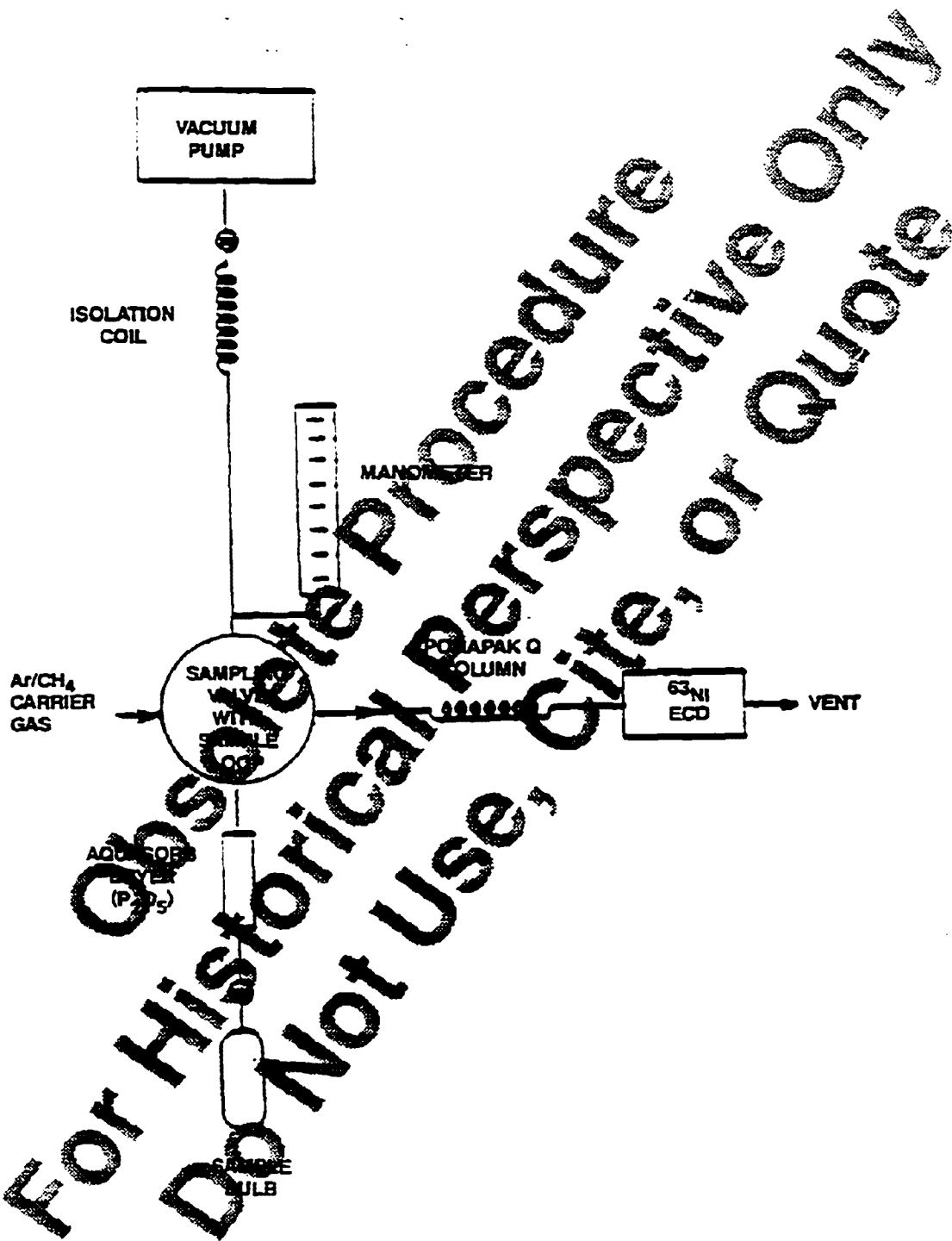
Figure 1. Schematic of configuration used in analysis of combustion flue gases.

1.7.1 Pre-Calibration

- Refer to the analytical system's operations manual for specific steps of the startup, analysis and shutdown.

- Open the main valve of the carrier gas cylinder and set the pressure to 4.92 kg/cm² (70 psi).

- Adjust the carrier gas flow to 20 cc/min.

- Disconnect the GC column from the ECD. cap off the inlet to the ECD and allow the GC column to vent into the oven.

- Turn power on.

- Condition the GC column overnight at 220°C.

- Obtain six compressed gas cylinders containing certified concentrations of N_2O in pure N_2 in the range of 5 to 200 ppm.

- Verify the accuracy and stability of the certified concentration of each gas cylinder.

- Use verified concentration of the gas cylinder to conduct a multipoint calibration.

1.7.2 Multipoint Calibration

The following multipoint calibration procedure will be conducted prior to analysis of samples. The integrity of the calibration will be monitored by daily mid-point calibration check prior to analysis of samples and by analysis of QC samples throughout the analysis period.

- Remove the end cap from the ECD inlet and connect the detector to the GC.

- Set detector temperature approximately twenty degrees below the maximum operating temperature (e.g. 330°C if maximum temperature is 350°C).

- Allow the GC column to cool to 35°C.

- Access the data acquisition system.

- Establish the stability of the column temperature.

- Connect the N_2O calibration standard containing the lowest concentration of N_2O so that the standard flows from the cylinder regulator into the connector for the sample container and finally to the GC inlet.

- Measure the ECD response (in terms of integrated peak area) to each calibration standard in triplicate.

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- Calculate the response in terms of average integrated peak area (PA) for each standard.

- Repeat the analysis for the remaining calibration gases.

Note: Figure 2 shows that the ECD output is a nonlinear function of concentration. Because the relationship between the two variables exhibits a curve at the lower end of the line, this method will use two calibration curves to verify concentrations of QC samples and to determine N_2O concentration in combustion gas samples. Figures 3 and 4 show calibration curves generated for the upper and lower ranges. The mid-range calibration gas represents the lowest point of the first curve and the highest point of the second curve.

- Correct verified N_2O concentration to standard pressure and temperature using the following equation:

$$[N_2O]_{corrected} = [N_2O]_{verified} \times P_{mmHg}/760) \times (273.16/T^\circ C - 273.16)$$

- Linearize the response of the analytical system by calculating the two linear regression equation (see Note) in the least squares form, $y = mX + b$. The regression parameters, slope (m) and intercept (b), shall be determined by plotting the corrected N_2O concentration against the average peak area, where:

$$X = [N_2O]_{corrected}$$

$$y = \overline{PA}$$

The correlation coefficient of each curve must be ≥ 0.998.

- Verify the acceptability of each calibration curve by back-calculating the concentration ($X = [N_2O]$) of each calibration standard. Apply the average peak area for each standard ($\overline{PA}$) to the appropriate least squares regression, where:

$$X = (y - b)/m$$

- Calculate the percent difference (D) between the verified N_2O concentration ($[N_2O]_{corrected}$) and the back-calculated N_2O concentration ($[N_2O]_{curve}$), where:

$$D = 100 \times ([N_2O]_{curve} - [N_2O]_{corr.})/[N_2O]_{corr.}$$

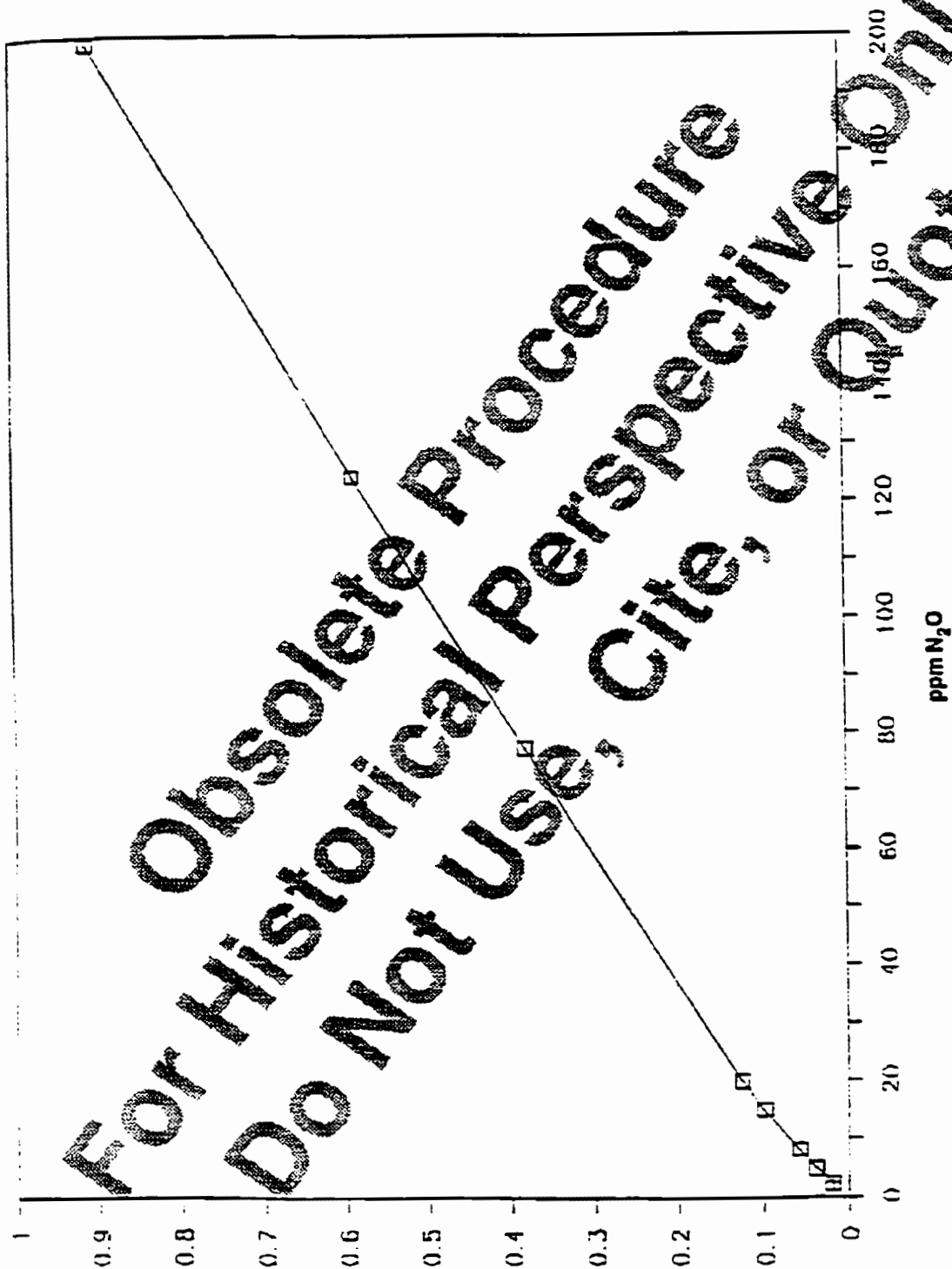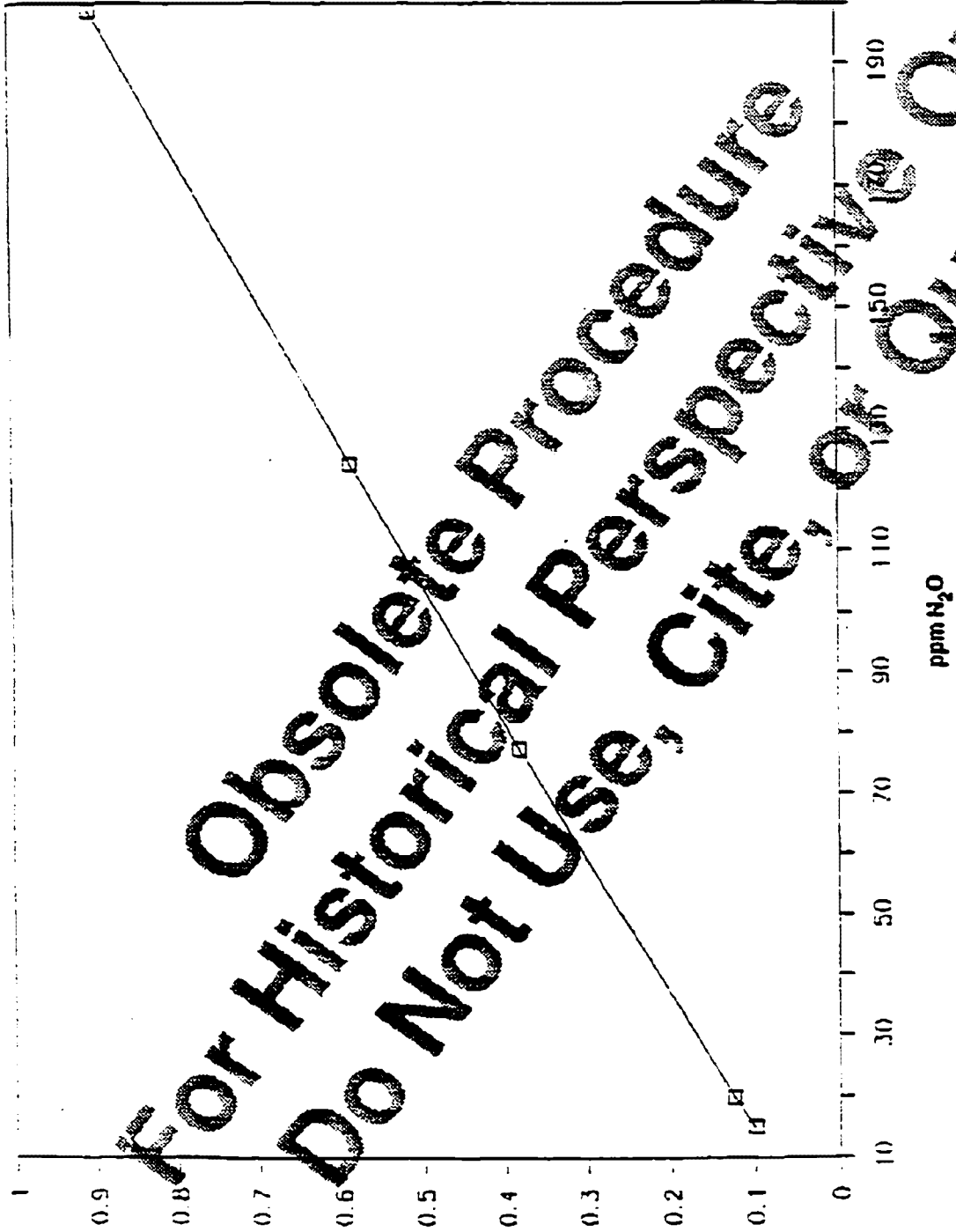- If $|D| < 2.5\%$ for each standard, the calibration is acceptable.

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Figure 2. Detector response to known concentrations of N_2O.

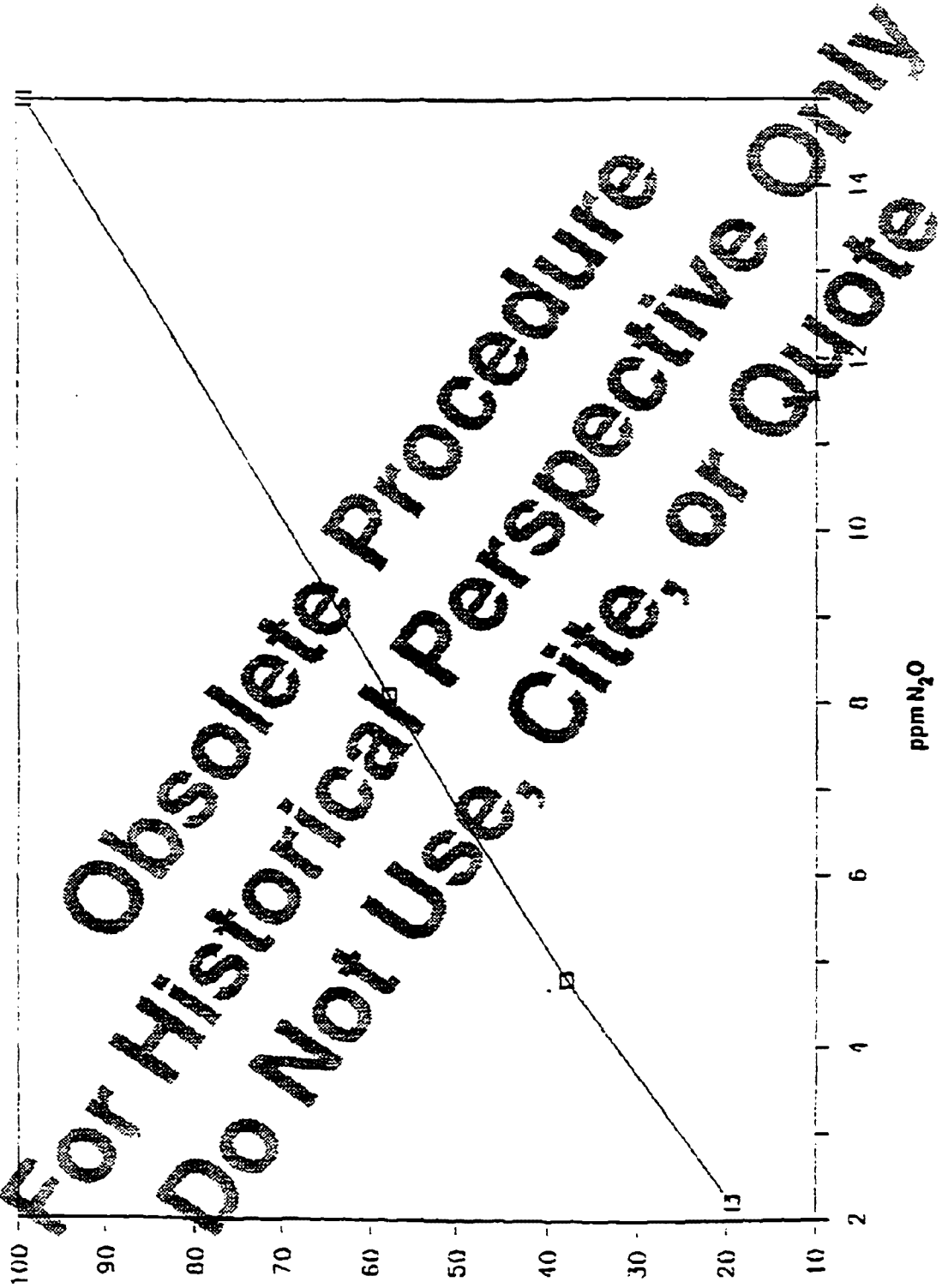Figure 3. N₂O calibration curve for upper range.

Figure 4. N_2O calibration curve for lower range.

- The multipoint calibration shall be repeated if:

  — | D | > 2.5% for any standard

  — the analytical system is subjected to a full shutdown for any reason

  — during analysis the result for any QC sample is greater than ±15% and other corrective action does not resolve the problem.

1.7.3 Calibration Checks

- Obtain three commercially prepared compressed gas cylinders certified to contain N₂O concentrations at 5 to 15 ppm and 100 ppm. The background gas composition may be similar to that expected in combustion flue gas samples (consisting of N₂, CO₂, and O₂) or pure nitrogen. These gases will be used as QC samples during the analysis of unknowns.

- Verify the accuracy and stability of the certified N₂O concentration for each cylinder against the multipoint calibration from Section 1.7.

  1) Conduct triplicate measurements of the ECD response to each QC sample. The agreement between each run must be within 5 percent of the previous run.

  2) Calculate the average integrated peak area and the N₂O concentration of each standard as outlined in Section 1.7.2, where:

  $$[N_2O]_{QC\ initial} = PA - b/m$$

  - If $[N_2O]_{QC\ initial}$ is $\geq \pm 25\%$ of certified ppm, this value must be used as the uncorrected concentration during the analysis of unknowns.

  - Correct each N₂O concentration to standard pressure and temperature using the following equation:

  $$[N_2O]_{QC\ cor} = [N_2O]_{QC\ initial} \times \frac{P_{mmHg}}{760} \times \frac{293.16}{T°C - 273.16}$$

- Fill three 25 mL sample container with a portion of each QC sample gas.

  1) Place a two-stage, ultra high purity, flow regulator on the gas cylinder.

  2) Attach one end of a 0.64 cm (0.25 inches) O.D. sample line with Swagelock™ fittings to the regulator outlet.

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3) Open valves located at each end of the sample container.

4) Attach the other end of the sample line connected to the cylinder regulator to the sample container inlet.

5) Open the cylinder and regulator outlet valves. Set the cylinder regulator delivery pressure to 0.35 kg/cm^2 (5 psi).

6) Purge the sample container with the QC sample for sufficient time to allow at least 10 liters of gas flow through the container.

7) Close the valve on the sample container inlet, turn off the cylinder at the regulator outlet valve, and allow the sample container to equilibrate to ambient pressure.

8) Close the valve on the sample container outlet.

- Verify the N_2O concentration for each transferred portion of the QC samples as outlined in the analytical procedures section.

- Calculate the percent difference (D) between the initial concentration calculated in section 1.7.3 ($[N_2O]_{initial}$) and the concentration calculated after the transfer ($[N_2O]_{QC\ final}$), for each QC sample, where:

$$D = \frac{[N_2O]_{QC\ final} - [N_2O]_{QC\ initial}}{[N_2O]_{QC\ initial}} \times 100 \ .$$

- If $|D|$ is $\leq$ 15%, the transferred QC sample is acceptable for use as a calibration check sample during the analysis of combustion flue gas samples.

- Conduct a calibration check as outlined in the analytical procedures section, at least once for every two samples analyzed.

1.8 Analysis Procedures

- Verify the integrity of the multipoint calibration by duplicate analysis of two QC samples that are in the mid-range of each calibration curve.

- Connect the sample container to the analytical system.

- Evacuate the sample loop to approximately 100 mmHg on the mercury manometer.

- Close the pump line valve.

Figure 5. Chromatogram for N_2O analysis.

- Open the sample container outlet valve and fill the sample loop by allowing the manometer to return to approximately 400 mmHg. Record the actual manometer reading for calculating the total corrected volume of the sample in the sample loop.

- Direct the sample flow from the sample loop into the carrier gas stream and onto the GC column.

- Three constituents will be eluted in the following order and at these approximated times: O_2 at ~1.5 minutes, CO_2 at 4.5 minutes, and N_2O at ~6.0 minutes. The sample run will be terminated at 10 minutes. The response of the ECD is recorded by the DAS. Figure 5 shows a chromatogram for N_2O analysis.

- Conduct the triplicate analysis of unknowns as outlined above.

- The analysis sequence is QC sample (duplicate), unknown (triplicate), unknown (triplicate), and QC sample.

- Determine the concentration of N_2O in each unknown using the result of the QC sample analyzed immediately before or immediately after the sample in question, as described in the calculations section.

1.9 Calculations

The following calculations are used to quantify nitrous oxide concentrations in each unknown gas sample:

- Uncorrected N_2O concentration for QC sample and field sample.

$$[N_2O] \text{ obtained} = \overline{PA} \ (b/m)$$

where:

$[N_2O]_{obtained}$ = N_2O concentration calculated from calibration curve.

$\overline{PA}$ = average integrated peak area
b = intercept of regression
m = slope of regression

- N_2O concentration in field sample corrected for instrument drift and sample loop pressure ($[N_2O]_{final}$).

$$[N_2O]_{final} = [N_2O]_{obt.} \times (760/P_{loop}) \times (293.16/T^\circ C - 273.16).$$

where:

$[N_2O]_{obt.}$ = N_2O concentration in field samples, calculated from calibration curve.

P_{loop} = absolute pressure in sample loop as indicated by mercury manometer prior to injection.

$T°C$ = ambient temperature in degrees Celcius.

- Accuracy expressed as percent deviation.

$$100 \cdot (\overline{X}-T)/T$$

where:

$$X = \text{average measured value} = \frac{\sum\limits_{i=1}^{n} X_i}{n}$$

T = true value

- Precision expressed as relative standard deviation (RSD) or coefficient of variation (CV).

$$P = \frac{S}{\overline{X}} \cdot 100$$

where:

$$S = \text{Standard deviation} = \left[\frac{1}{n-1}\left(\sum_{i=1}^{n} (X_i - \overline{X})^2\right)\right]^{1/2}$$

2.0 QUALITY CONTROL (QC) ELEMENTS

2.1 QC Checks

- The integrity of the multipoint calibration will be monitored with verified QC samples as outlined in the analytical procedures section. When the results of the QC check deviate from the primary curve by more than 15 percent, steps will be taken to correct the problem and/or a full multipoint calibration will be conducted.

- Gas cylinders containing less than 7.03 kg/cm^2 (100 psi) will not be used.

- Calculations for precision will be based on triplicate analysis of each sample.

2.2 QC Controls

- Documentation

  1) Laboratory Notebook—Keep all test results, calibration data, and quality control data in a bound laboratory notebook. Sign and date the notebook at time of data entry.

2) Instrument Notebook—Assign a logbook to the GC to maintain a record of all calibrations, maintenance, and repairs.

3) Control Charts—Use control charts to track daily response to QC samples.

4) Certification/Verifications—In a secure area, maintain a file containing manufacturer's certifications and laboratory verification of standards.

5) Instrument Manuals—Keep operator manuals for all components of the analytical system available and easily accessible.

- Raw Data

  Maintain all measurement data (storage diskettes, printouts) on file in a secure area.

3.0 REFERENCES

The following were referenced for discussion of N$_2$O measurement.

Cicerone, R.J., et al. *Journal of Geophysical Research.* Vol. 83, No. C6, 3042-3050, June 1978.

EPA Workshop on N$_2$O Emission from Combustion. EPA-600/8-86-035.

Quality Assurance Handbook for Air Pollution Measurement Systems. Vol. III. EPA-600/4-77-027b.

Sykes, A.L. Radian Corporation, personal communication.

Weiss, R.F. *Journal of Chromatographic Science.* Vol. 19, 611-616. December 1981.

16. ABSTRACT The report documents the technical approach and results achieved while developing a grab sampling method and an automated, on-line gas chromatography method suitable to characterize nitrous oxide (N_2O) emissions from fossil fuel combustion sources. The two methods developed have been documented in the form of U.S. EPA/AEERL Recommended Operating Procedures. The combustion of fossil fuels is suspected to contribute to measured increases in ambient concentrations of N_2O. Accurate and reliable measurement techniques would help to assess the relative contribution of fossil fuel combustion N_2O emissions to the increase in ambient concentrations. The characterization of N_2O emissions from fossil fuel combustion sources has been hindered by the lack of suitable and acceptable grab sampling and on-line monitoring methodologies. Grab samples have been shown to be compromised by a sampling artifact in which N_2O is actually generated in the sample container in the presence of sulfur dioxide (SO_2), nitrogen oxides (NO_x), and moisture. On-line monitoring techniques are limited and, of those available, instrument costs are often prohibitive, detection levels are often insufficient, and the techniques are often susceptible to interferences present in combustion process effluents.

17.	KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution Nitrogen Oxide (N_2O) Fossil Fuels Combustion Measurement Sampling	Analyzing Gas Chromatography	Pollution Control Stationary Sources	13B 07B 21D 07D 21B 14G 14B

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