



Research and Development

N₂O FIELD STUDY

AP 42 3

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N₂O FIELD STUDY

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ABSTRACT

Nitrous oxide (N_2O) emissions from coal-fired utility boilers were measured at three electric power generating stations. Six units were tested, two at each site, and included sizes ranging from 165 MW to 700 MW. Several manufacturers and boiler firing types (circular, triple cell, and tangential) were represented. Continuous emission monitor (CEM) measurements were made for nitrogen oxide (NO), oxygen (O_2), carbon dioxide (CO_2), and carbon monoxide (CO). On-line N_2O measurements were made using a gas chromatograph with electron capture detection. On-line sulfur dioxide (SO_2) levels were measured on one unit using a gas chromatograph with flame photometric detection. Stainless steel sample containers were used to collect flue gas samples for the evaluation of N_2O formation as a function of time in the presence of NO, SO_2 , and water. The N_2O on-line results were in the range of "not detectable" to 4.6 ppm. The results did not exhibit apparent differences related to different boiler types and load conditions. The stainless steel container results showed a trend of immediate N_2O formation when SO_2 and water are present. The N_2O concentration in all wet samples increased dramatically within the first hour to concentrations ranging from 9 to 120 ppm. The dry sample results showed a much smaller increase in N_2O , ranging from 5-25 ppm over the 2 week time period after sampling.

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SECTION 1

INTRODUCTION

Concern over atmospheric emissions of nitrous oxide (N₂O) has been growing because of increasing ambient concentrations and the suspected connection with stratospheric ozone depletion and expected worldwide climatic changes. Combustion sources, such as coal-fired utility boilers, have been singled out as possible major contributors to overall N₂O emission levels. Analysis of grab stack samples in stainless steel (SS) containers known as "bombs" has shown emission levels as high as hundreds of parts per million of N₂O for these sources. Concerned about these emission values, the Environmental Protection Agency (EPA) has initiated a national and international research program to characterize N₂O emissions. Recent research, however, has cast doubt on the validity of previous measurements of N₂O emissions.

Laboratory results suggest that a rapid reaction occurs with nitrogen oxide (NO) in the presence of water (H₂O) and sulfur dioxide (SO₂) in the sample bombs to form N₂O through an undetermined mechanism. Preliminary results from pilot-scale testing indicate that N₂O levels in SS container samples taken from a coal-burning combustor increase from <10 parts per million (ppm) to >100 ppm within 1 h. These tests suggest that previously reported N₂O emissions may be incorrect. Furthermore, they indicate that drying the flue gas by exposing the flue gas to a desiccant such as P₂O₅ prior to filling the SS sample containers helped to moderate the increase in N₂O concentration, yielding a more representative result.

To test these observations on full-scale combustors, EPA/AEERL proposed a field survey of N₂O emissions from several utility boilers. Several units representing two boiler types (i.e., tangentially fired and wall fired) and various sizes were selected on the basis of availability, location, scheduling, and costs. Schedule constraints limited sampling locations to available ports at a point between the particulate emission control device and the stack.

A two-fold approach to sampling was used. Nitrous oxide levels were determined on-line and compared with samples collected in the SS containers. Both on-line and SS container samples were analyzed by gas chromatography with electron capture detection. The SS container samples were taken before and after moisture removal (by refrigeration and P₂O₅ desiccation) to determine the effect of moisture on N₂O formation. Each SS container sample was taken and analyzed for N₂O and SO₂ at selected intervals to determine and plot the N₂O reaction over time. On-line measurements of carbon monoxide (CO), carbon dioxide (CO₂), nitrogen oxide (NO), and oxygen (O₂), were taken to provide additional operating characteristics of each boiler unit. Initially, SO₂ was also to be measured but was not because of instrument malfunction. On-line SO₂ measurements were performed at Unit F by GC/FPD. Continuous emissions monitors (CEMs), GCs, and associated calibration gases were housed in two self-contained vehicles and transported to the selected sites. Multiple GCs were used to allow simultaneous on-line and SS sample container testing. The test series field work was conducted October 2 through 13, 1988.

By agreement with the utility company the selected sites will be kept confidential. Project organization and data quality assurance requirements may be found in the Quality Assurance Project Plan (Q TRAK No. 88032) for this task.

SECTION 2
PROJECT DESCRIPTION

The EPA Hazardous Air Pollutants (HAP) Van was modified to house three GCs and a dual set of CEMs. These modifications were conducted in conjunction with mechanical service to the van that included exhaust and suspension system repairs. A step van owned by Acurex Corporation was outfitted to house the gas cylinders required for the test.

A representative of a large utility system helped identify a number of potential sites. Samples were taken from six utility boilers on three separate sites. All boilers were burning medium sulfur coal, but the exact sulfur content of coal at each site was not available. An appropriate schedule was developed as shown in the Test Plan (see Appendix A). The six sampled units are as follows:

Unit	Date	Size (MW)	Class	Manufacturer	Firing Type
A	10/05/88	250	Pre-NSPS	B & W	Circular
B	10/07/88	250	Pre-NSPS	B & W	Triple Cell
C	10/08/88	250	Pre-NSPS	Riley	Circular
D	10/10/88	165	Pre-NSPS	CE	Tangential
E	10/11/88	700	Pre-NSPS	CE	Tangential
F	10/12/88	165	Pre-NSPS	CE	Tangential

The first three units were similar in size and represented two manufacturers and two firing types. Units D and F allowed data comparison on two identical units; Unit E was a similar type but was four times larger. This selection of boilers provided sufficient variability to determine whether N₂O emissions from utility boilers are significant and are affected by boiler design criteria.

The original plans called for sampling an 880 MW CE unit rather than the final 165 MW boiler (Unit F), but load conditions and maintenance schedules made that unit unavailable.

Data were collected as proposed in the QAPP. A GC with electron capture detector (GC/ECD) was used for the on-line N₂O measurements, while CEMs were used for measuring the fixed gases.

Samples were also collected in stainless steel containers to evaluate the stability of N₂O in grab samples. The grab samples were analyzed in the field at 1 and 4 h intervals after collection and shipped back to the EPA/RTP laboratory for subsequent analyses at 40, 168, and 336 h periods after collection.

Analytical instrumentation was allowed 24 h to warm up or reach steady-state operating conditions before calibration and testing. A category II QAPP was prepared to ensure proper data quality. Details of the sampling and analytical procedures can be found in subsequent sections of this report.

SECTION 3

SAMPLING PROCEDURES

3.1 PROCESS AND CONTINUOUS MEASUREMENTS

Specific boiler operation data (i.e., firing rate, O₂) were taken from instrumentation already in place. Figure 3-1 illustrates the CEM system. The sampling system was modified slightly from the system proposed in the QAPP. The nitrogen oxides (NO_x) analyzer was moved to the dry side of the system. No heated capillary modules were available in time to configure a wet side NO_x analyzer. A second dryer filled with silica gel was added to the system immediately after the refrigerated dryer. A probe end filter (15 μm) was added to the stainless steel probe. The heated filter was replaced at the beginning of each sampling period as a matter of procedure. All procedures conformed to the methods referenced in Appendix B of the QAPP. Gas was drawn through a heated filter and passed through a heated sample line to a tee. One stream was directed to the SO₂ monitor. Gas was drawn through the SO₂ monitor by an integral ejector. The second flow stream continued to a short-contact-time moisture removal system. The sample passed through a sample pump, silica gel desiccator, and was directed into a distribution manifold. A slipstream of the sample passed through a second pump and into the on-line GC. Individual sample flows were directed to CEMs as required.

A 61-m (200-ft) length of heated 0.95-cm (3/8-in) sample line was used. The heated filter was wrapped with heat tape and set at 177 °C (350 °F) using a variable transformer.

Table 3-1 lists the instruments used. Analyzer signals were continuously recorded and raw data saved with a Compaq Deskpro computer. Sampling periods were generally 4 h as defined in the test plan (Appendix A), but calibration and QC checks required significantly more time.

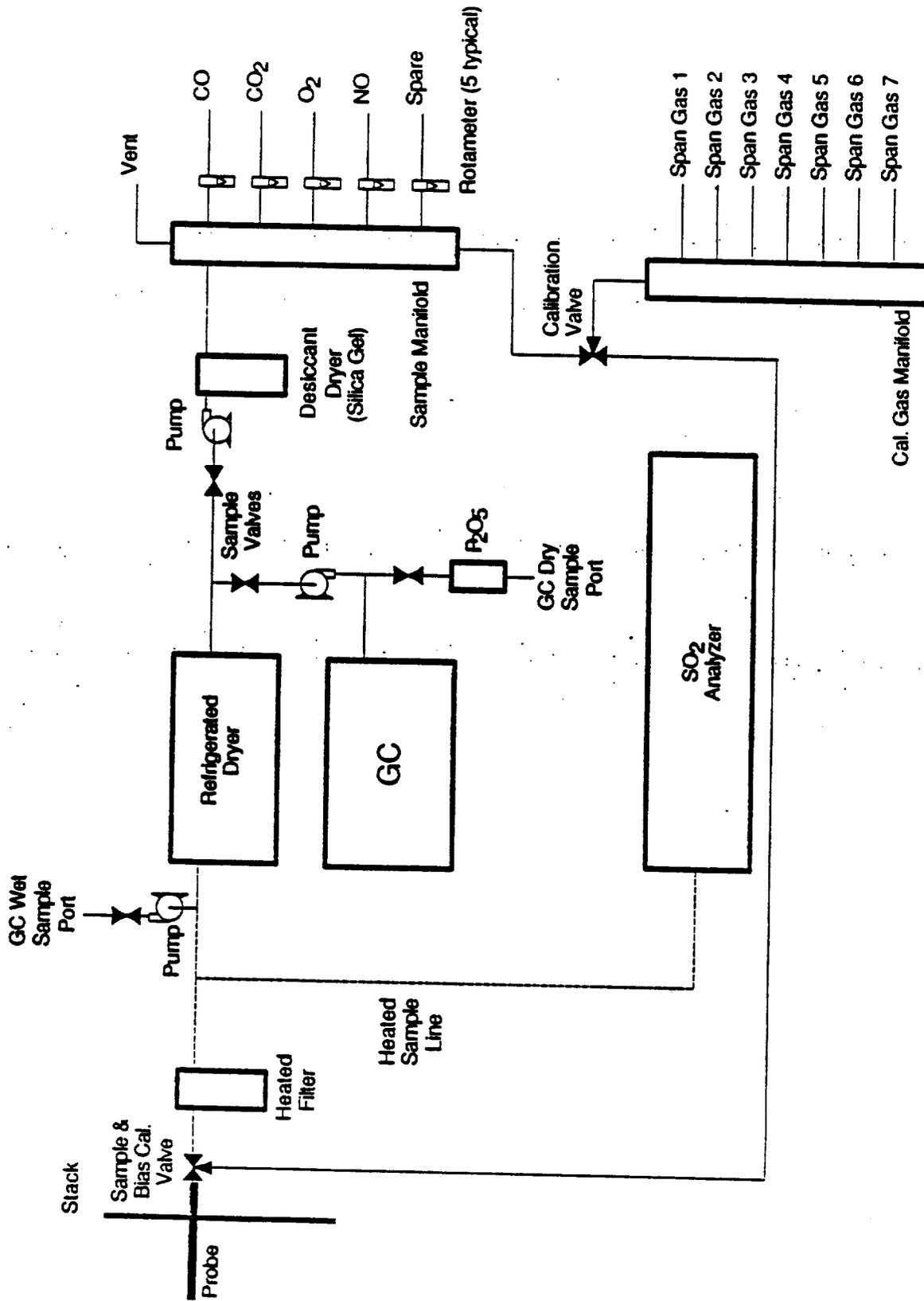


Figure 3-1. Continuous emissions monitoring system.

Table 3-1. Continuous Emissions Monitoring Equipment

Instrument	Principal of operation	Manufacturer	Model No.	Range	Quantity
O ₂	Paramagnetic	MSA	802	0-25%	2
CO ₂	Nondispersive infrared	Beckman	868	0-25%	1
CO ₂	Nondispersive infrared	Beckman	864	0-25%	1
CO	Gas Correlation	TECO	48	0-500 ppm	1
NO _x	Chemiluminescent	TECO	10-AR	0-1,000 ppm	2
*SO _x	UV-Vis	DUPONT	400	0-2,000 ppm	1
*SO _x	Pulsed Fluorescence	TECO	40	0-2,000 ppm	1

* The SO_x instruments were not operational due to malfunctions.

3.2 ON-LINE GC SAMPLING

A particulate-free, dry (refrigerated) sample stream was provided to an on-line GC as shown in Figure 3-1. A description of GC analytical methods particular to this test is included in Section 5.

3.3 N₂O STAINLESS STEEL CONTAINER SAMPLING

The stainless steel containers were dried and checked for leaks prior to use. The SS containers were placed in a 225 °F (107 °C) oven overnight with all valves and ports open. After cooling in a desiccated oven, the SS containers were fitted with septa and then checked for leaks. A high vacuum pump was used to evacuate the SS containers to ~40 mm Hg. The system was closed and the pressure monitored over a 2-5 min period. If a >5 mm Hg increase was detected, the container was deemed unacceptable until the leak was found and repaired. This container was then placed back in the oven for further conditioning. A leak-checked container had all valves closed and ends capped prior to use. The containers were stored and shipped in aluminum cases.

Stainless steel container samples were collected both in a wet and dry gaseous environment for locations shown in Figure 3-1. The wet sample was collected from the heated portion of the sample system, upstream of any water removal device. The dry sample was collected from a point downstream

of the refrigerant condenser but ahead of the silica gel desiccant dryer and passed through a container filled with P_2O_5 before entering the container. A pump operating at a flowrate of greater than 1 L/min was used to draw a sample into the container. This flowrate was maintained through the sample container for at least 5 min before closing the valves on both ends of the container and removing it.

SECTION 4

SAMPLE HANDLING

Data from the CEMs were input directly into a Compaq Deskpro computer, stored, reduced, and output as needed. The on-line N₂O data were generated from a GC with two separate detectors and integrators. Four SS container samples were obtained each sampling day for shipment to the EPA/RTP facility. Sample containers were assigned two identification numbers for tracking: a run number consisting of the year, month, day and sequential number (i.e., 88-10-05-01) and the unique serial number stamped on the container. These numbers were entered into a notebook along with the sampling conditions and the time that the sample was taken. The responsibility for this tracking rested with the sampling technician. Furthermore, the same data were entered on sample custody sheets as shown in Figure 4-1. The responsible technician packaged the samples for shipment and delivered them to an overnight courier service along with the original tracking sheet, a copy of which the technician retained for his records. Upon receipt of the samples in RTP, the samples were logged into a notebook and the tracking sheets were filed.

Samples were analyzed using direct syringe injections using GC/ECD and GC/FPD, following the procedures given in Section 5, at times approximating 1, 4, 48, 168, and 336 h after initial collection. Exact times were recorded in the laboratory notebook. The first two analyses were performed at the field site, and subsequent analyses were conducted in the RTP laboratory after overnight delivery.

Sample identification No. _____ SS Container No. _____

Date Received _____ Time Sample Taken _____

Sample Description _____

Tracking History

Relinquished by	Received by	Date	Time
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____

Figure 4-1. Sample tracking sheets.

SECTION 5

ANALYTICAL PROCEDURES

5.1 CONTINUOUS EMISSIONS MONITORS

The principles of operation for the CEMs used to measure O₂, CO, CO₂, NO_x, and SO₂ are given in Table 3-1. Signals from the CEMs were input directly to a computer. The data acquisition system consisted of a Metralyte Dash-16 A/D card mounted in a Compaq Deskpro 286 computer running Labtech Notebook (LN) software. The LN software converted the raw analyzer signals to engineering units (percent, ppm). Instantaneous data were displayed for the operator. Five-minute averaged data (block average) were stored in ASCII format to a disk file. These data files were imported to LOTUS 1-2-3 for presentation and reporting.

5.2 N₂O MEASUREMENTS

5.2.1 Summary of Method

This method quantifies N₂O in a sample of gas extracted from a combustion source and was intended for use with a GC that is equipped with a packed column connected to an electron capture detector (ECD).

The gaseous sample was introduced via a fixed volume sample loop or gas-tight syringe onto a column for component separation. The ECD response was measured in terms of peak retention times and area counts by a Spectral Physics Integrator. A least squares linear regression equation, generated by a multipoint calibration from known standards covering the expected sample concentration range, was used to determine the relationship between ECD response and N₂O concentration.

5.2.2 Analytical Apparatus and Conditions

- GC: Capable of operating at 35 °C (95 °F) and 220 °C (428 °F), connected to an ECD with Ni⁶³ constant current cell, and capable of operating at 330 °C (626 °F)

- GC Column: 3.7 m (12 ft) by 0.32 cm (0.125 in) O.D. stainless steel, packed with 80/100 mesh support (e.g., Porapak Super Q)
- Carrier Gas: Argon/methane mixture specially prepared for ECD analysis containing 95 percent Ar and 5 percent CH₄
- Pre-Column: 3.8 cm (1.5 in) by 0.64 cm (0.25 in) O.D. Teflon tube containing Aquasorb (P₂O₅-indicating absorbent)
- DAS: Data acquisition system
- Compressed Gas Cylinders: Containing various known concentrations of N₂O in pure N₂
- Valve: 1/8 in 6-port with 1 cc sample loop
- Syringe: 1 cc gas-tight
- Carrier Flow: 20 to 30 cc/min
- Oven Temperature: 35 °C (95 °F)
- Detector Temperature: 330 °C (626 °F)

5.2.3 Calibration

The following multipoint calibration procedure was used for both the on-line and sample container analyses. Differences between the two systems were noted and addressed separately. The nonlinearity of the ECD required generating two calibration curves to determine accurately the N₂O concentrations of combustion gas samples. One standard concentration overlapped the two calibration ranges. Cylinder concentrations used were 4.8 and 16.7 ppm in the low range and 16.7, 125, and 200 ppm in the high range. A 1.0 mL gas-tight syringe was used to construct the calibration curve by introducing 0.25 mL, 0.5 mL, and 1.0 mL of the N₂O. The resulting concentrations in the low range were 1.2 ppm, 2.4 ppm, and 4.8 ppm. A 1.0 mL and a 0.5 mL injection of the 16.7 ppm standard was used to produce 16.7 ppm and 8.4 ppm. The 16.7 ppm standard was originally received from the vendor labeled 21.1 ppm. Further discussion of this problem appears in Section 6.2.

Duplicate injections were made for each calibration point, and the average response of the peak areas was within 10 percent. Two least squares linear regression calibration curves, $Y = mX + b$, were calculated. Zero points were not used as part of the regression equation because this would bias the

calibration curve by forcing it through zero. The regression parameters, slope (m) and intercept (b), were determined by plotting the known N₂O concentration against the average peak area (PA), where:

$$X = \text{N}_2\text{O}$$

$$Y = \text{PA}$$

The correlation coefficient of each curve was determined.

The acceptability of each calibration curve was determined by back-calculating the concentration (X = N₂O) of each calibration standard. The calibration curve was accepted if each point was within 10 percent of its stated concentration.

5.2.4 QC, and System Checks

In addition to the standards used to perform the multipoint calibration, a QC gas was used to verify the accuracy of the calibration and monitor system performance. Two concentrations were required because of the two calibration ranges. The concentration of each QC check was 15 ppm and 104 ppm. Immediately following calibration, each QC gas was introduced in the same manner as the calibration gases. Duplicate analyses with agreement within 10 percent were averaged.

In the on-line analysis, the known value was used to verify the integrity of the sampling system. The QC gas was introduced at the source, run throughout the system as the actual flue gas sample would be, and analyzed. The concentration of the obtained value agreed with the accepted QC limits of 20 percent of the known value. Once system integrity was verified, flue gas sampling began.

5.2.5 Analysis Procedures

On-line Analysis

At the beginning and end of each sample period, a QC or accuracy check was performed on each range. Duplicate analyses with agreement within 10 percent were averaged and used to obtain the measured value. This value, expressed as percent deviation, was used to monitor accuracy. A QC check was also performed every 2 h in the range where the actual sample gases were occurring.

The on-line samples were analyzed by pushing a portion of the gas stream through the sample loop, stopping the flow, allowing the pressure to reach equilibrium, and, finally, injecting the sample into the GC.

Stainless Steel Sample Container Analysis

At the beginning and end of each analytical session, an accuracy check was performed using syringe injection. After a valid operating condition had been confirmed, the sample containers were analyzed in duplicate with agreement within 10 percent. The average was used to obtain the measured value. After two containers had been analyzed, an additional accuracy check was performed in the range where samples were found.

5.2.6 Calculations

The following calculations were used to quantify N₂O concentrations in each unknown gas sample:

- N₂O concentration for QC sample and field sample

$$\text{N}_2\text{O measured} = (\text{PA} - b) / m$$

where:

N₂O measured = N₂O concentration calculated from calibration curve

PA = average integrated peak area

b = intercept of regression

m = slope of regression

5.3 SO₂ ANALYSIS

5.3.1 Summary of Method (Sample Container Analysis)

This method quantifies SO₂ in a combustion gas sample that was extracted from the sample container or an on-line sample manifold and introduced via syringe injection to a GC that was equipped with a packed column connected to a flame photometric detector (FPD). The FPD response was measured in terms of peak retention time and area counts. The relationship between FPD response and SO₂ concentration was determined by a least squares linear regression equation generated by a multipoint calibration from known standards covering the expected sample concentration range.

5.3.2 Analytical Apparatus and Conditions

- GC: Capable of operating at 100 °C and equipped with a FPD

- Column: 1.8 m (6 ft) by 0.32-cm (1/8-in) O.D. Teflon packed with Chromosorb 107 80/100 mesh
- DAS: Data acquisition system
- Compressed Gas Cylinders: Containing known concentrations of SO₂ in N₂
- Syringe: 1 cc gas-tight
- Carrier Gas: Helium
- Carrier Flow: 20 to 30 cc/min
- Oven Temperature: 100 °C (212 °F)
- Detector/Injector Temperature: 120 °C (248 °F)

5.3.3 Calibration

The sensitivity of the detector required more than one operating range to cover the expected SO₂ gas levels. Each range required a separate calibration. Nominally, a 3-point calibration was performed on each range. The average of duplicate syringe injections having 10 percent agreement was used for each point. Least squares linear regression calibration curves were calculated and the correlation coefficient determined. The acceptability of the calibration curves was based on recalculating each point from the curve, with results within 10 percent of the stated value.

5.4 QUALITY CONTROL ELEMENTS

5.4.1 QC Checks

- The integrity of the multipoint calibration was monitored with verified QC samples as outlined in the analytical procedures section. When the results of the QC check deviated from the primary curve by more than 20 percent, the problem was corrected and/or a full multipoint calibration was conducted.
- Gas cylinders containing less than 7.03 kg/cm² (100 psi) were not used.
- Calculations for precision were based on daily accuracy checks.

5.4.2 QC Controls

- **Documentation**

- Laboratory Notebook**—All test results, calibration data, and quality control data were kept in a bound laboratory notebook that was signed and dated at time of data entry.

- Control Charts**—Control charts were used to track daily response to QC samples.

- Instrument manuals**—Operator manuals for all components of the analytical system were kept available and easily accessible.

- **Raw Data**

- All measurement data (storage diskettes, printouts) were retained on file in a secure area.

SECTION 6 OPERATION

Testing throughout the period generally went according to plan (see Appendix A), with a few exceptions. An 880 MW unit at the first test site could not be tested because of scheduling constraints and a lack of available power for the sampling system. The temporary power transformer adjacent to the sampling site had to be secured for maintenance during the time scheduled for testing. Ensuing difficulties reestablishing reliable power allowed only an abbreviated sampling schedule at a second unit (Unit A) at that site. The analyzers were warmed up for approximately 2 h prior to sampling. Four hundred feet of sample line was used for this unit, double that used for the remaining units.

Table 6-1 summarizes the load conditions and control room O₂ average for each site visited during the test period. Although efforts were made to maintain the load on each unit at full capacity and at steady state, some fluctuations in operating parameters were evident. All sampling was done downstream of the economizer and cleanup equipment. Table 6-2 lists the sample port location relative to the induced draft (ID) fan.

6.1 CEM OPERATIONS

The CEM data were taken to monitor the boiler combustion conditions and to characterize other emissions. All the units tested operated at expected emissions levels for the gases measured. The analyzers used and the ranges for which they were calibrated are summarized in Table 3-1. CEM data taken during each test period are presented in Appendix B.

At Unit A the CO analyzer would not calibrate. Front panel checks indicated internal problems. Later disassembly of the sample cell showed some minor deposits. Cleaning, reassembly, and realignment of the optics brought the analyzer to specification. In addition, the UV-Vis SO₂ monitor would not hold calibration. The TECO SO₂ monitor was not started due to the abbreviated schedule. The

Table 6-1. Conditions at Unit Control Room

Unit	Date	Load (MW)	O ₂ (%) (average for day)	Load Management	Comments
A	10/05/88	230	4.2	—	
B	10/07/88	273	4.0	No	
C	10/08/88	271	3.8	No	
D	10/10/88	92	4.0	Yes	
E	10/11/88	542-685	3.8	Yes	Load @ -550 most of day 685 @ 1730 until end of run
F	10/12/88	90	3.8	Yes	

Table 6-2. Sampling Location

Unit	Sample Date	Sample Port Location
A	10/05/88	Before ID fan
B	10/07/88	After ID fan
C	10/08/88	After ID fan
D	10/10/88	Before ID fan
E	10/11/88	Before ID fan
F	10/12/88	Before ID fan

cause of the problem with the Dupont SO₂ monitor was not immediately evident. Valid O₂, CO₂ and NO data were taken at Unit A.

Efforts were made to repair the DuPont SO₂ monitor to correct signal drift after calibration and zero checks. The problem was traced to oil (probably from an unfiltered compressed air line at a previous installation) that had soaked into the insulation surrounding the inside of the sample cell chamber. The oil volatilized as the monitor heated up and then condensed on the quartz separator glasses. The oil film apparently provided an excellent filter at the measurement wavelengths. Repeated cleaning helped for only about 30 min at a time.

The flow control for the SO₂ analyzer was very sensitive. As the probe end filter began to plug, this flow required continuous attention. This problem became irrelevant because the SO₂ analyzer could not be operated within QA limits.

At the second site, checking the analyzers showed the CO analyzer failed front panel tests. Realignment of the optics solved the problem. The Dupont SO₂ monitor was cleaned out and turned on. Initial checks indicated that it might operate correctly. However, the signal from the analyzer began to

degrade within 1 h. Oil was again found in the instrument. The TECO SO₂ monitor (brought along as a dry SO₂ backup instrument) had an internal electrical problem. This difficulty was traced to a circuit card connector loosened during transport. A second difficulty surfaced during calibration. The SO₂ in N₂ calibration gas mixtures required the use of a bleed orifice in the instrument. Leaks in this system and flow imbalances could not be repaired or resolved in the field. No CEM SO₂ data were obtained for any of the sampled units because of the inability to eliminate the oil from the instrument.

Loads on both Units B and C were constant for the duration of testing. All operating CEMs performed adequately. Zero and span drift and bias check were within limits. A probe plug occurred during testing on Unit B. Calibration checks were made after replacing the probe end filter and found to meet the criteria.

After transport to the third site, the CO analyzer again required realignment of the optics. This analyzer seems to be very susceptible to shocks during transport. The Unit E test was extended to get 2 h of sampling at nearly full load. The O₂ level indicated that Unit E was operated at low excess air during the middle of the day. The increase in CO reflected this trend.

6.2 GC OPERATIONS

Two ECDs were calibrated each day and were used to analyze the on-line samples. The detection limits varied for each detector, which was due to an unknown interfering peak in the sample stream that affected the signal to noise ratio. The unknown peak eluted after 70 min from the initial injection and subsequently every 10 min afterwards for approximately 1 h. At that time, on-line analysis was switched to the other ECD for another 70 min of analyses. When the interfering peaks began masking N₂O analysis again, the first ECD was ready for further analysis but required recalibration. After recalibration, the ECD had less noise and a lower detection limit.

The on-line SO₂ was analyzed by GC/FPD with gas-tight syringe injections of 1.0 mL. The SO₂ results were obtained for Unit F (October 12, 1988). The GC/FPD on the previous days could not be used because all available integrators were required on the three ECDs for the N₂O analyses. Unit F did not have stainless steel container samples collected because the GC/FPD integrator was being used for the SO₂ on-line analysis. The decision was made because the SO₂ CEM instruments had not been

operational and no on-line SO₂ data had been gathered up to that time. An additional problem occurred during the calibration of the GCs for N₂O analysis. One of the span gases procured just prior to the test was determined to be incorrectly labeled. Results showed that the 21.1-ppm N₂O in the N₂ gas was actually 16.7 ppm. This caused unacceptable calibration data that adversely affected the schedule prior to its discovery. The gas has been returned to the supplier for re-analysis and is not available at this time.

SECTION 7

QUALITY ASSURANCE

7.1 QUALITY CONTROL CHECKS AND RTI AUDIT SAMPLE

Table 7-1 lists all N₂O QC check samples that were analyzed during the field test. During each test a QC check sample was analyzed to verify instrument calibration. The QC check sample was not a calibration point. Two levels of QC checks were used, 15.1 ppm and 104 ppm. All QC check results were within the ± 20 percent acceptable limits of the QA plan, including the sample line check. The highest deviation was 10.5 percent. Table 7-2 lists the CEM QC checks.

An independent audit was conducted by Research Triangle Institute. RTI supplied a cylinder of N₂O in N₂. The concentration of N₂O in this cylinder gas was not known to the sampling team. The cylinder was analyzed by direct injection into the GC and also through the sample loop connected to the sample conditioning system. The sampling location is given in Figure 3-1. The measured concentration for both injection methods was 38.7 ppm, indicating no sampling system bias.

Daily calibration curves for the N₂O analysis by GC/ECD are contained in Appendix C.

Table 7-1. Nitrous Oxide Quality Control Check Results

Unit	Date	Detector	Challenge concentration (ppm)	Injection location	Percent deviation
A	10/5/88	On-line B	15.1	GC	7.3
			15.1	Sample port	3.0
B	10/7/88	On-line A	15.1	GC	0.5
		On-line B	15.1	GC	0.0
			15.1	Sample port	3.7
		RTI Audit Result	38.7		
C	10/8/88	On-line A	15.1	GC	4.4
		On-line B	15.1	GC	8.9
			15.1	Sample port	1.6
		Bomb	15.1	GC	2.2
		Bomb	104	GC	4.1
D	10/10/88	On-line A	15.1	GC	9.4
		On-line B	15.1	GC	2.2
			15.1	Sample port	9.2
E	10/11/88	On-line A	15.1	GC	0.8
			15.1	Sample port	1.5
		On-line B	15.1	GC	2.7
		Bomb	15.1	GC	10.5
		Bomb	104	GC	2.7
		Bomb	4.8	GC	6.4
F	10/12/88	On-line A	15.1	GC	2.0
		On-line B	15.1	Sample port	0.02

Table 7-2. CEM QC Checks

Gas	Analyzer calibration error, percent			Zero drift	Span drift	Percent bias error
	Cal.	Midpoint	Zero			
<u>Unit A</u>						
O ₂	0.2	0.5	0.0	0.3	0.8	0.0
CO ₂	1.0		0.0	1.4	1.0	0.5
NO	0.5		0.5	1.2	1.4	0.2
CO		Not operating				
SO ₂		Not operating				
<u>Unit B</u>						
O ₂	1.2	0.8	0.4	0.8	1.2	2.4
CO ₂	0.0	2.5	0.5	1.0	1.5	1.0
NO	0.0	0.4	0.4	0.5	1.0	1.0
CO	0.4	0.2	0.2	1.0	0.6	0.2
SO ₂		Not operating				
<u>Unit C</u>						
O ₂	1.0	0.0	1.0	2.0	0.8	1.0
CO ₂	1.3	4.0	0.0	1.5	2.5	3.0
NO	0.5	0.5	0.0	1.2	1.3	0.5
CO	1.0	1.4	1.0	0.2	2.0	2.0
SO ₂		Not operating				

(continued)

Table 7-2. CEM QC Checks (continued)

Gas	Analyzer calibration error, percent			Zero drift	Span drift	Percent bias error
	Cal.	Midpoint	Zero			
<u>Unit D</u>						
O ₂	0.8		0.8	0.0	1.2	0.0
CO ₂	0.0		0.5	0.5	0.5	0.5
NO	0.7	1.0	0.7	0.3	1.2	0.3
CO		0.6	0.0	0.4	0.8	0.0
SO ₂	Not operating					
<u>Unit E</u>						
O ₂	1.6		0.4	0.0	1.2	0.0
CO ₂	0.5		0.0	1.5	0.5	1.5
NO	0.2	0.3	0.2	0.3	1.3	0.0
CO		0.0	0.3	0.4	0.2	0.3
SO ₂	Not operating					
<u>Unit F</u>						
O ₂	1.2	1.6	0.4	0.0	2.0	0.0
CO ₂	1.5	0.5	0.0	1.0	0.4	1.0
NO	0.8	0.6	0.5	0.1	4.0	0.2
CO		1.4	0.2	0.4	0.8	0.8
SO ₂	Not operating					

SECTION 8

DATA

The on-line N₂O data are presented in summary form as Table 8-1. Individual data points are shown in Table 8-2. Stainless steel container sampling N₂O and SO₂ results are presented in Table 8-3. Table 8-3 wet and dry samples are identified as #1-4, only to differentiate between samples. Time zero concentrations were determined from the on-line results. Appendix D graphically presents the SS container results in concentration vs. time of N₂O and SO₂ data. Table 8-4 contains the CEM data summary.

As discussed in Section 6.2 under GC operation, two GC/ECDs were used to analyze the N₂O on-line samples. Each ECD was calibrated prior to sample analysis. The N₂O low range calibration points were used to determine the practical quantitation limit. Each lower calibration points in descending order was injected until that point could not be detected. The lowest point that was detected was selected as the practical quantitation limit (PQL), which is expressed as a less than value. The selected PQL varied according to the ECD used and also according to affects of the sample, which contained an unknown interfering peak. The interfering peak affected the ECDs in a manner that reduced the signal to noise ratios, allowing a smaller signal response to be detected and quantitated. Many data points determined were below the PQL or the calibration curve. These points have been included in Tables 8-1 and 8-2 with asterisks.

Table 8-1. Nitrous Oxide On-Line GC Data Summary

Site	Date	Time, h	No. of Data Points	On-Line N ₂ O, ppm
A	10/5/88	1533-1649	9	1.3 ± 0.5
B	10/7/88	1732-1911	9	<3.6
C	10/8/88	1146-1225	4	<2.4
		1241	1	4.6
		1251-1802	20	<3.6
D	10/10/88	1001-1045	7	<1.2
		1050	1	*0.6
		1057-1104	2	<1.2
		1111	1	*0.4
		1116-1305	11	<1.2
		1316-1324	2	*0.5
		1349-1526	15	<1.2
E	10/11/88	1150-1226	5	<1.2
		1232	1	2.3
		1304-1740	21	*0.7 ± 0.2
F	10/12/88	1147-1230	9	<1.2
		1245-1311	5	*0.6 ± 0.3
		1507-1540	8	<1.2

* Values determined below the calibration curve

Table 8-2. Nitrous Oxide On-Line GC Data

Date	Unit	Time, h	N ₂ O, ppm	Date	Unit	Time, h	N ₂ O, ppm	SO ₂ , ppm
10/5/88	A	1533	1.8	10/7/88	B	1732	<2.4	
		1541	2.1			1742	<2.4	
		1550	2.0			1752	<2.4	
		1559	1.4			1804	<2.4	
		1612	1.1			1814	<2.4	
		1621	0.7			1836	<3.6	
		1628	0.8			1856	<3.6	
		1636	0.9			1903	<3.6	
		1649	0.9			1911	<3.6	
10/8/88	C	1146	<2.4	10/10/88	D	1001	<1.2	
		1154	<2.4			1007	<1.2	
		1204	0.7			1013	<1.2	
		1225	<2.4			1020	<1.2	
		1241	4.6			1028	<1.2	
		1251	<3.6			1037	<1.2	
		1256	<3.6			1045	<1.2	
		1304	<3.6			1050	0.6	
		1310	<3.6			1057	<1.2	
		1317	<3.6			1104	<1.2	
		1335	<3.6			1111	0.4	
		1523	<2.4			1116	<1.2	
		1532	<2.4			1122	<1.2	
		1545	<2.4			1154	<1.2	
		1550	<2.4			1200	<1.2	
		1557	<2.4			1206	<1.2	
		1613	<3.6			1212	<1.2	
		1619	2.1			1218	<1.2	
		1626	<3.6			1224	<1.2	
		1633	<3.6			1230	<1.2	
1640	3.0	1254	<1.2					
1729	<2.4	1305	<1.2					
1740	<2.4	1316	0.5					
1746	<2.4	1324	0.6					
1802	<2.4	15 points 1349 - 1526		<1.2				

(continued)

Table 8-2. Nitrous Oxide On-Line GC Data (concluded)

Date	Unit	Time, h	N ₂ O, ppm	Date	Unit	Time, h	N ₂ O, ppm	SO ₂ , ppm
10/11/88	E	1150	<1.2	10/12/88	F	1147	<1.2	
		1209	<1.2			1154	*0.2	778
		1214	<1.2			1200	<1.2	870
		1220	<1.2			1206	<1.2	918
		1226	<1.2			1211	<1.2	920
		1232	**2.3			1216	<1.2	884
		1245	<1.2			1221	<1.2	942
		1304	*0.8			1227	<1.2	929
		1309	*0.7			1230	<1.2	954
		1314	*0.5			1232		954
		1319	*0.4			1239		922
		1507	*0.4			1245	*1.1	972
		1512	*0.4			1254	*0.3	960
		1525	*0.5			1258	*0.4	945
		1530	*0.5			1304	*0.7	953
		1535	*0.4			1311	*0.6	967
		1540	*0.4			1318		813
		1546	*0.5			1326		901
		1556	*0.7			1334		897
		1601	*0.8			1338		904
		1613	*0.9			1347		906
		1620	*0.7			1352		969
		1625	*0.7			1400		996
		1632	*0.7			1407		947
		1714	*0.9			1412		945
		1721	1.2			1433		913
		1730	*0.8			1446		1004
		1740	*0.9			1507	<1.2	
						1511	*0.7	
						1516	<1.2	
						1521	<1.2	
						1526	<1.2	
						1531	<1.2	
						1536	<1.2	
						1540	<1.2	
						1548		1036

* Value determined is below the calibration curve.

** The stainless steel container sample was taken at this time, possibly contributing to the increased N₂O value by allowing water to enter the sample line.

Table 8-3. Nitrous Oxide and Sulfur Dioxide SS Container GC Data

Date	Unit	Wet or Dry	Time, h	N ₂ O, ppm	SO ₂ , ppm
10/5/88	A	Wet #1	0	2.0	1195
			1	23.0	1056
			4	—	—
			48	45.3	ND
			168	58.7	ND
			336	41.0	ND
10/5/88	A	Wet #3	0	1.3	—
			1	59.3	—
			4	—	—
			48	104.8	ND
			168	113.2	ND
			336	83.9	—
10/5/88	A	Dry #2	0	1.3	1180
			1	—	1555
			4	—	—
			48	7.5	1342
			168	20.8	783
			336	16.2	670
10/7/88	B	Wet #1	0	<3.6	—
			1	120.8	—
			4	142.0	—
			48	127.5	ND
			168	126.0	ND
			336	132.0	—
10/7/88	B	Wet #3	0	<3.6	—
			1	78.5	—
			4	—	—
			48	94.3	ND
			168	165.0	ND
			336	100.0	—
10/7/88	B	Dry #2	0	<3.6	—
			1	1.6	—
			4	—	—
			48	4.7	935
			168	12.5	57
			336	14.6	ND
10/7/88	B	Dry #4	0	<3.6	—
			1	2.1	—
			4	—	—
			48	6.8	923
			168	17.5	674
			336	24.6	434

(continued)

Table 8-3. Nitrous Oxide and Sulfur Dioxide SS Container GC Data (continued)

Date	Unit	Wet or Dry	Time, h	N ₂ O, ppm	SO ₂ , ppm
10/8/88	C	Wet #1	0	<2.4	—
			1	83.1	—
			4	92.4	—
			48	110.3	ND
			168	115.1	ND
			336	95.3	—
10/8/88	C	Wet #3	0	<2.4	—
			1	50.2	—
			4	59.5	—
			48	78.2	ND
			168	83.4	ND
			336	65.5	—
10/8/88	C	Dry #2	0	<2.4	—
			1	—	—
			4	3.6	—
			48	8.5	1146
			168	17.3	844
			336	25.8	155
10/8/88	C	Dry #4	0	<2.4	—
			1	2.2	—
			4	3.2	—
			48	7.2	1132
			168	12.7	884
			336	17.4	687
10/10/88	D	Wet #1	0	<1.2	—
			1	35.2	—
			4	58.2	—
			48	76.5	ND
			168	70.7	ND
			336	59.3	—
10/10/88	D	Wet #3	0	<1.2	—
			1	33.5	—
			4	47.5	—
			48	63.0	ND
			168	65.3	ND
			336	48.8	—
10/10/88	D	Dry #2	0	<1.2	—
			1	—	—
			4	1.4	—
			48	4.5	622
			168	9.3	509
			336	6.8	378

(continued)

Table 8-3. Nitrous Oxide and Sulfur Dioxide SS Container GC Data (concluded)

Date	Unit	Wet or Dry	Time, h	N2O, ppm	SO2, ppm
10/10/88	D	Dry #4	0	<1.2	—
			1	—	—
			4	1.4	—
			48	3.2	639
			168	7.1	522
			336	5.8	356
10/11/88	E	Wet #1	0	<1.2	—
			1	10.4	—
			4	20.1	—
			48	28.8	ND
			168	28.5	ND
			336	20.5	—
10/11/88	E	Wet #3	0	<1.2	—
			1	9.2	—
			4	15.0	—
			48	31.7	ND
			168	35.5	ND
			336	27.4	—
10/11/88	E	Dry #2	0	<1.2	—
			1	2.1	—
			4	3.1	—
			48	5.3	921
			168	7.1	590
			336	18.5	356
10/11/88	E	Dry #4	0	<1.2	—
			1	2.0	—
			4	2.6	—
			48	5.2	970
			168	7.3	720
			336	10.1	522

Note: Time zero data determined from on-line results.
 ND = Not detected above 15 ppm

Table 8-4. CEM Summary - Average Concentrations

Unit	CO ₂ (%)	NO (ppm)	CO (ppm)	O ₂ (%)
A	14.8	386	*	4.6
B	13.5	513	13.3	7.1
C	14.3	559	8.6	6.1
D	11.7	354	2.2	8.3
E	13.1	374	30.7	6.0
F	11.9	319	3.1	8.1

(*) Missing data.

SECTION 9 RESULTS AND CONCLUSIONS

9.1 ON-LINE RESULTS

The N₂O on-line results were in the range of "not detectable" to 4.6 ppm. The results showed no trends according to boiler type, operating, and load conditions. The detection limits for N₂O varied depending on the specific ECD used. Two separate ECDs were required for each unit tested. Each individual detector exhibited different detection limits that varied throughout the test. The variability was due to sample effects and signal/noise ratio changes. These data agree with recent in-house studies that show N₂O levels ranging from 1.2 to 5.4 ppm from the combustion of various coal types.

Because very little on-line SO₂ data were obtained, no conclusions can be made. Data were collected only on Unit F between the hours of 11:54 and 14:46. The concentration was initially measured at 778 ppm and gradually increased to 1004 ppm. A total of 25 injections were made, with an average concentration of 924 ppm.

9.2 SS CONTAINER RESULTS

Stainless steel container N₂O wet sample results demonstrate that N₂O formation with SO₂ present is immediate. All wet samples increased (Appendix D) in N₂O concentration dramatically within the first hour to concentrations ranging from 9 to 120 ppm. The N₂O dry sample results show a much smaller increase to 5-25 ppm over the 336 h time period. This smaller increase is likely due to traces (<15 ppm) of SO₂ and water in the containers. These results verify the same phenomena observed in the laboratory studies for both the wet and dry samples for all fuels (coal, fuel oil, natural gas). The SO₂ concentration in the wet sample decreased dramatically from time zero (on-line results) to <15 ppm at the 48 h interval. SO₂ and N₂O were not determined at the 4 h interval because the samples had been shipped to the Research Triangle Park laboratory for further analysis. The dry sample SO₂ remained high (between 500 and 1,500 ppm) through the 168 h time period and dropped to a range of

150-700 ppm at the 336 h time period. An exception was Unit B 10/7/88, which decreased to 57 ppm at the 168 h period. This may have been due to a sample handling problem, because the duplicate was consistent with other results.

REFERENCES

1. Code of Federal Regulations, Title 40, Part 60, EPA Method 3A; "Determination of O₂ and CO₂ Concentrations in Emissions from Stationary Sources."
2. Code of Federal Regulations, Title 40, Part 60, EPA Method 6C-Rev. 3; 4/88; "Determination of SO₂ Emissions from Stationary Sources."
3. Code of Federal Regulations, Title 40, Part 60, EPA Method 7E-Rev. 2; 7/86; "Determination of Nitrogen Oxides from Stationary Sources."
4. Code of Federal Regulations, Title 40, Part 60, EPA Method 10-Rev. 1; 7/85; "Determination of CO Emissions from Stationary Sources."
5. Code of Federal Regulations, Title 40, Part 60, EPA Method 18-Rev. 2; 6/87; "Determination of Gaseous Organic Compound Emissions by Gas Chromatography."

APPENDIX A

TEST PLAN

TEST PLAN

To obtain field data on N₂O emissions from coal-fired utility boilers, a test program will be conducted at three electric power generating stations. The test plan has been designed to provide continuous, real-time data on N₂O emissions from as many types and sizes of boilers as schedule and budgetary constraints permit. Six units at three sites will be visited within a 9-day sampling period. Table A-1 shows the proposed test schedule. A gas chromatograph (GC) will be used for the on-line N₂O measurements, while continuous emissions monitors (CEMs) will be used for measuring NO_x, O₂, CO₂, SO₂, and CO levels in the flue gas. As a stainless steel container objective, canister samples will also be collected to evaluate the stability of N₂O in grab samples. The concentration of N₂O and SO₂ in the sample containers will be measured at specified intervals after collection to determine the buildup or breakdown of the target compounds. Samples will be extracted from the containers by a syringe (through an integral system) and injected into a GC/ECD for N₂O and a GC/FPD for SO₂. A description of the sampling system and all sampling and analytical procedures are presented in the QAPP for this task.

At each site, the host utility is providing 4-in pipe nipple ports downstream of an ESP and air preheater. Therefore, each sample stream should be relatively clean (low particulate loading) and cool (250-300 °F). The monitoring van containing all the instrumentation will be able to locate within 100 ft of most sampling ports. The host utility will also provide a 220 volt, 100 amp electrical service to the monitoring van. In some cases, it may be necessary to park the van at a central location where a longer heated sample line will be needed to reach both ports.

It is hoped that each sampled unit will be operating at nearly full load, but that may not be possible at this season of the year. The utilities will, however, try to operate at a steady-state condition with minor variances in load or flue gas O₂ levels. Each 4-h sampling period should produce relatively stable CEM and on-line GC data. If unsteady conditions occur, the test period may be extended at the discretion of the sampling team leader.

Table A-1. Test Schedule for Nitrous Oxide Emissions Project

Unit	Task	Date	Time	Duration (h)	Preferred load (Mw)
	Acurex team travels to first site	10/2			
A	Connect power to van	10/3	8:00 am		
	Set up instrumentation	10/3	8:00 am	4	
	Perform pretest QA	10/4	9:00 am	2	
	Conduct emissions tests	10/4	11:00 am	4	Full
	Perform post-test QA	10/4	3:00 pm	2	
B	Relocate van and connect power	10/4	5:00 pm	1	
	Perform pretest QA	10/5	8:00 am	2	
	Conduct emissions tests	10/5	11:00 am	4	Full
	Perform post-test QA	10/5	3:00 pm	2	
C	Relocate van and connect power	10/6	8:00 am	1	
	Set up instrumentation	10/6	8:00 am	4	
	Perform pretest QA	10/7	8:00 am	2	
	Conduct emissions tests	10/7	11:00 am	4	Full
	Perform post-test QA	10/7	3:00 pm	2	
D	Relocate van and connect power	10/7	5:00 pm	1	
	Perform pretest QA	10/8	8:00 am	2	
	Conduct emissions tests	10/8	11:00 am	4	Full
	Perform post-test QA	10/8	3:00 pm	2	
E	Relocate van and connect power	10/9	8:00 am	1	
	Set up instrumentation	10/9	8:00 am	4	
	Perform pretest QA	10/10	8:00 am	2	
	Conduct emissions tests	10/10	11:00 am	4	Full
	Perform post-test QA	10/10	3:00 pm	2	
F	Relocate van and connect power	10/10	5:00 pm	1	
	Perform pretest QA	10/11	8:00 am	2	
	Conduct emissions tests	10/11	11:00 am	4	Full
	Perform post-test QA	10/11	3:00 pm	2	
	Make-up test day	10/12			
	Acurex team returns to RTP	10/13			

The probe will be a 4-ft-long, .5-in O.D. stainless steel tube inserted through a modified 4-in pipe cap. A heated Perma-Pure spun glass filter will remove the particulate prior to the .25-in-diameter heated sample line. A temperature controlled sample will be delivered to the sampling van. The schematic for the sampling system is provided in Section 4 of the QAPP.

The typical sampling day includes a 2-h pretest calibration, a 4-h sampling period, and a 2-h post-test calibration. Data collection will begin as soon as all instrumentation is calibrated. Approximately 1 h after on-line data collection begins, the first of four stainless steel container samples will be collected. Two samples will be collected upstream of the dryer (wet), and two will be collected downstream of the dryers (dry). The schedule as shown in Table A-2 will be followed, which requires 6.5 h per day of syringe injection sampling from the containers. All samples will be shipped back to RTP after on-site analyses are completed. If boiler conditions are not steady, a canister pair (wet and dry sample) will be taken simultaneously.

Validated on-line data will be tabulated and submitted to EPA prior to October 14, 1988, with a final report completed by month's end.

Table A-2. Canister Sampling and Analysis Schedule^a

Collect 4 samples/day (2 wet, 2 dry)			
Sample no.	Type	Collection time	Analysis time ^b
1	wet	11:00	12:00, 15:00
2	dry	11:30	12:30, 15:30
3	wet	12:30	13:30, 16:30
4	dry	13:00	14:00, 17:00

Total elapsed time: 6.5 h

^a Instrument calibration will be conducted at 1.5-h intervals beginning at 11:30.

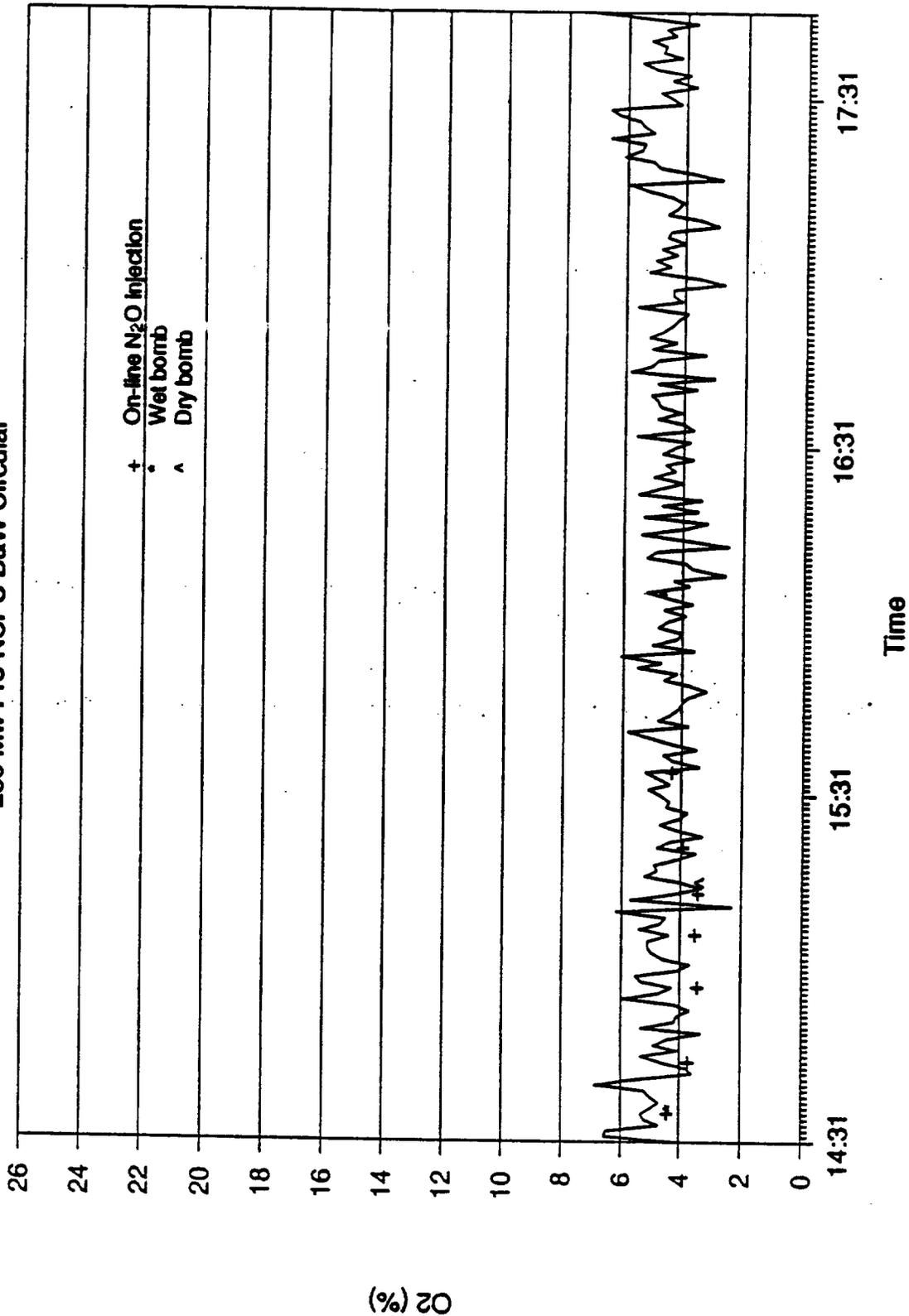
^b Samples will be analyzed at 1 h and 4 h after collection. Ship back 4 samples/day to EPA/RTP.

APPENDIX B

CEM DATA

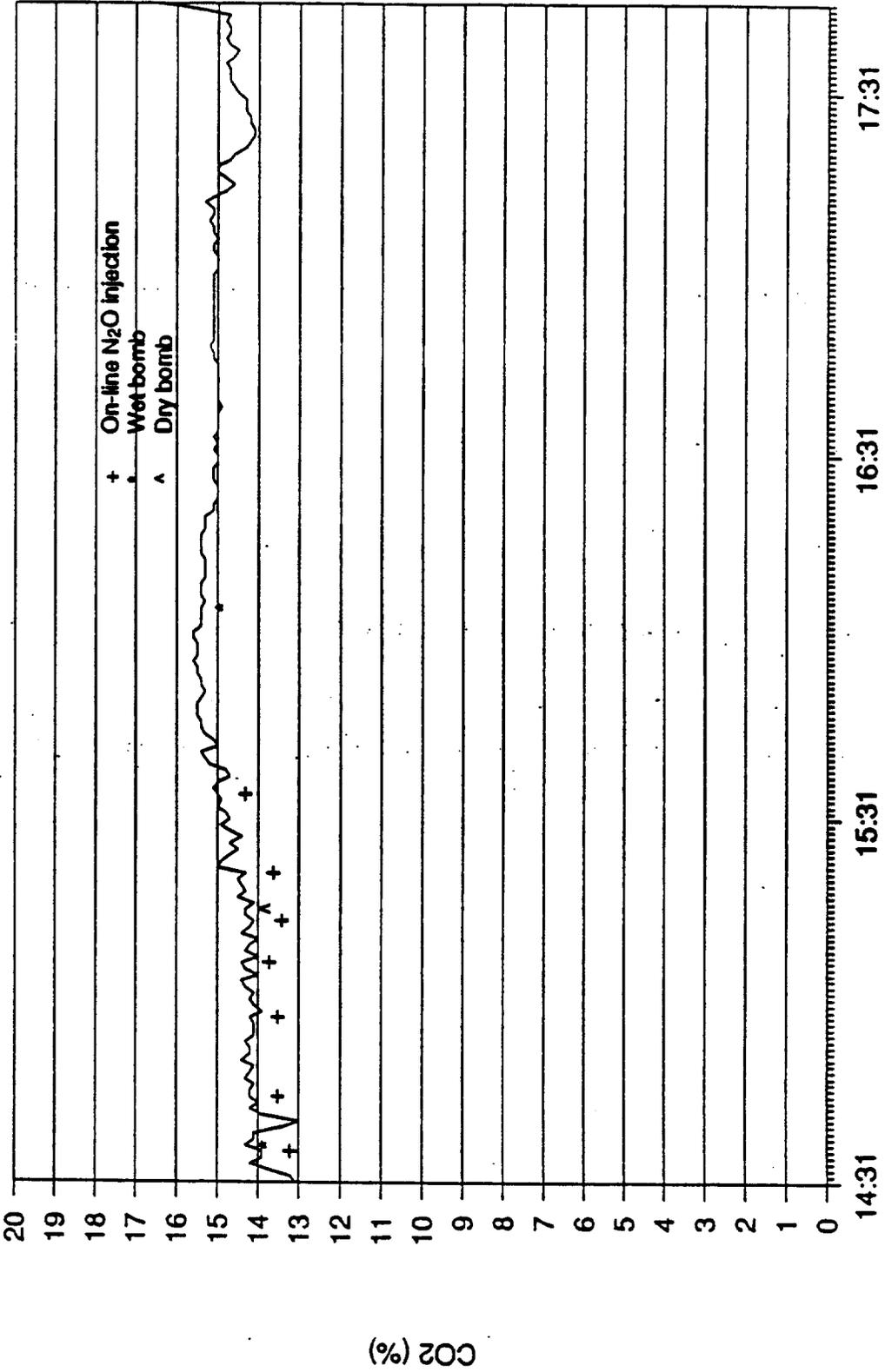
Unit A O2--5 Oct 88

250 Mw Pre-NSPS B&W Circular



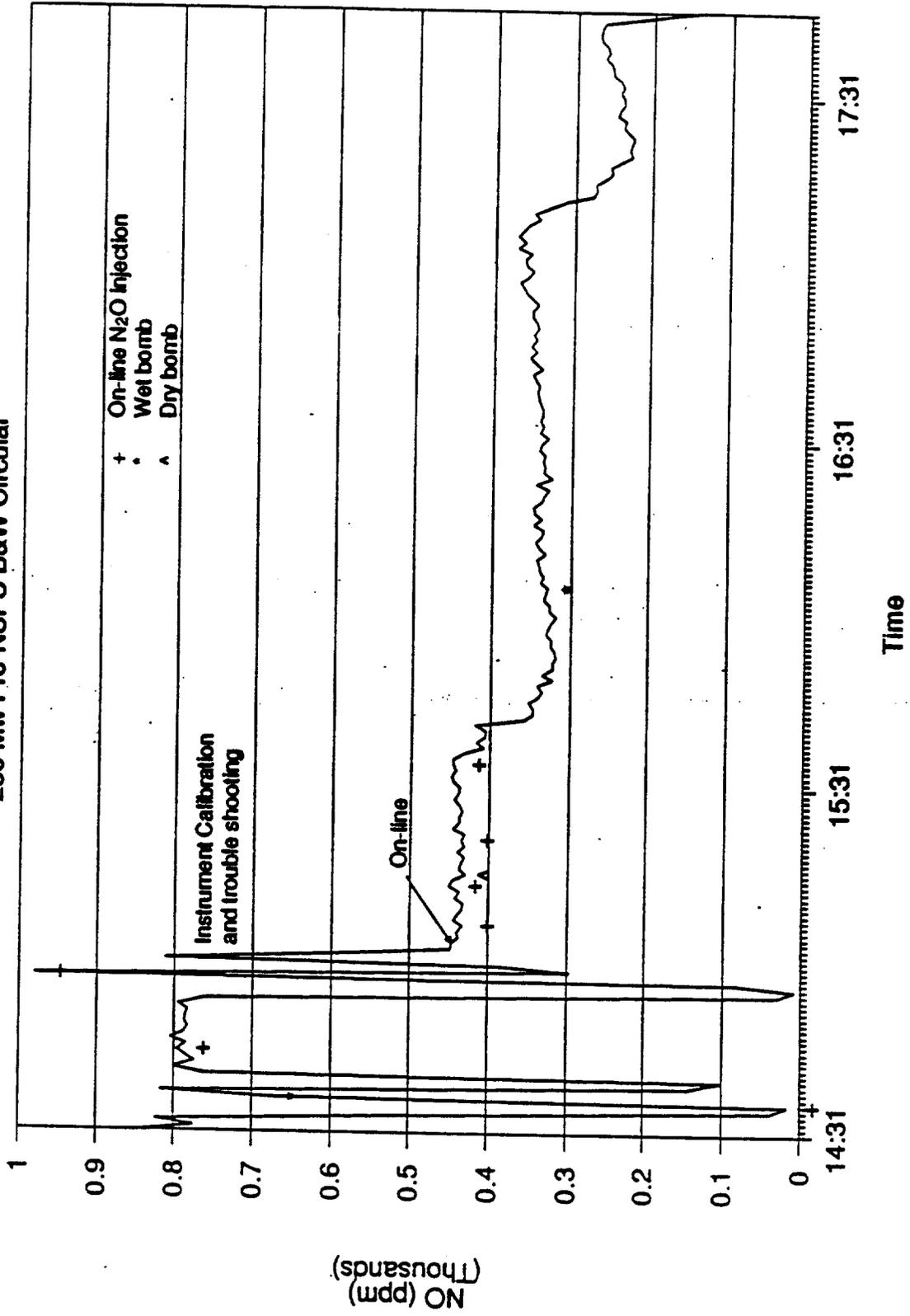
Unit A CO2--5 Oct 88

250 Mw Pre-NSPS B&W Circular



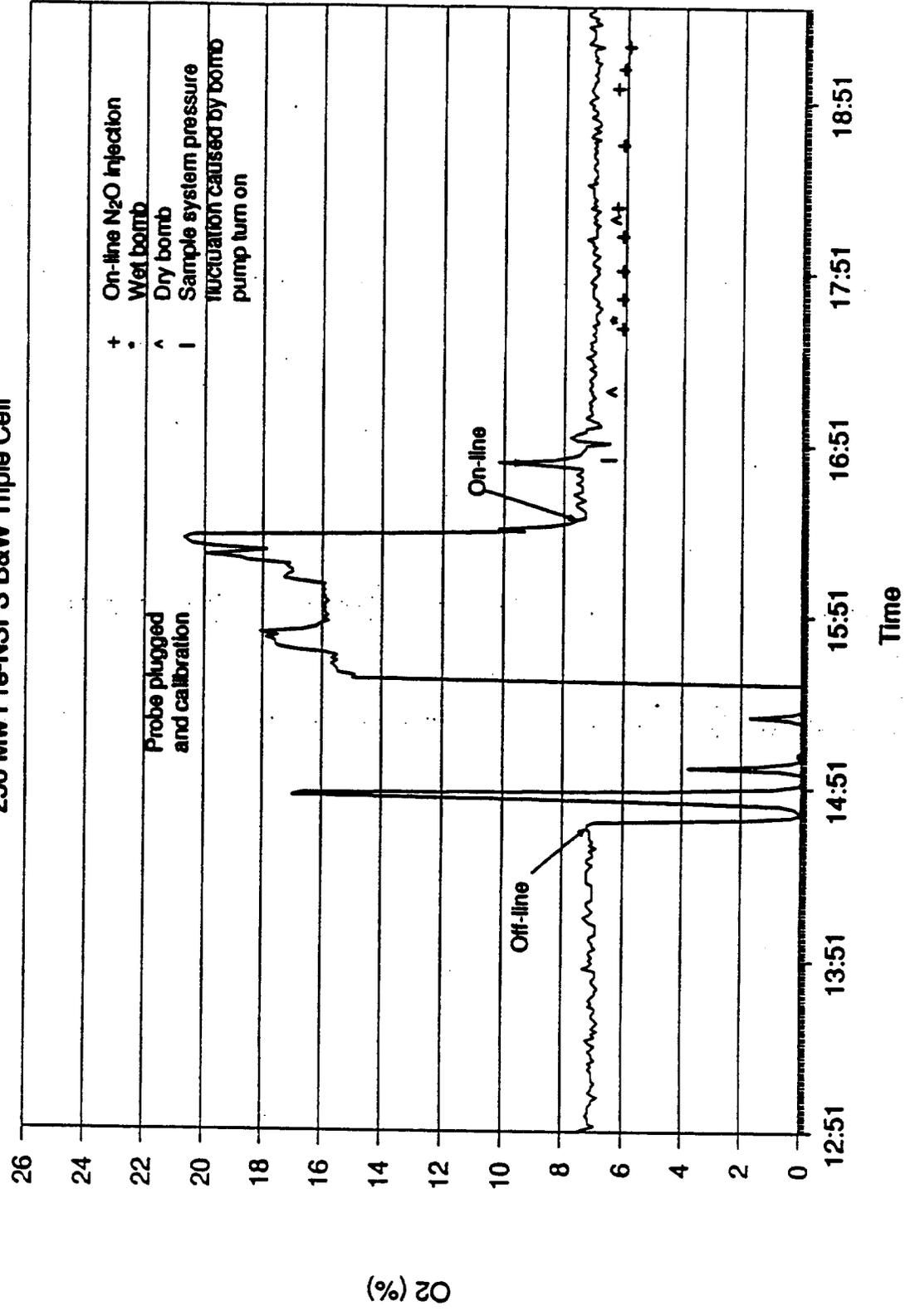
Unit A NO--5 Oct 88

250 Mw Pre-NSPS B&W Circular



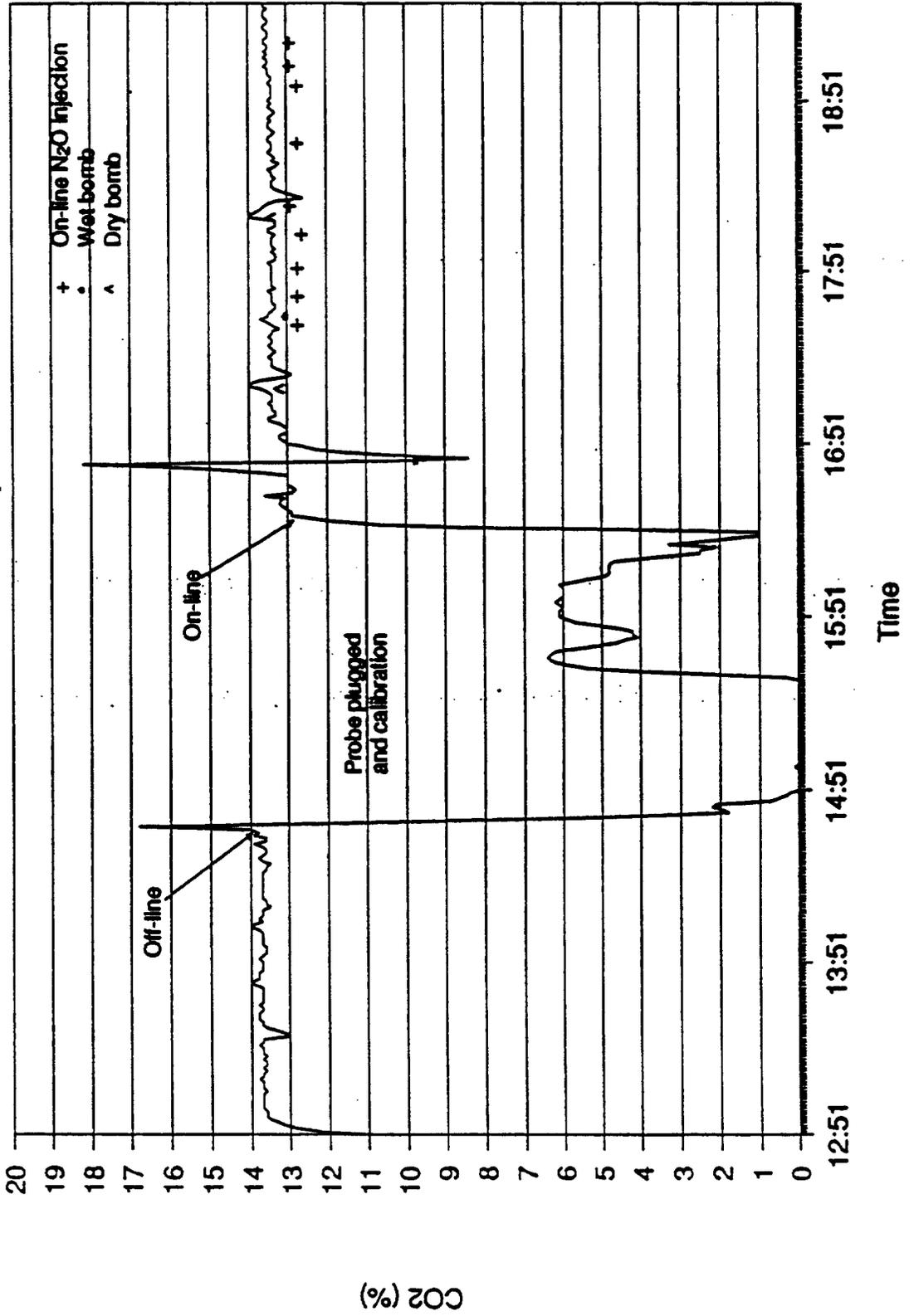
Unit B O2--7 Oct 88

250 Mw Pre-NSPS B&W Triple Cell



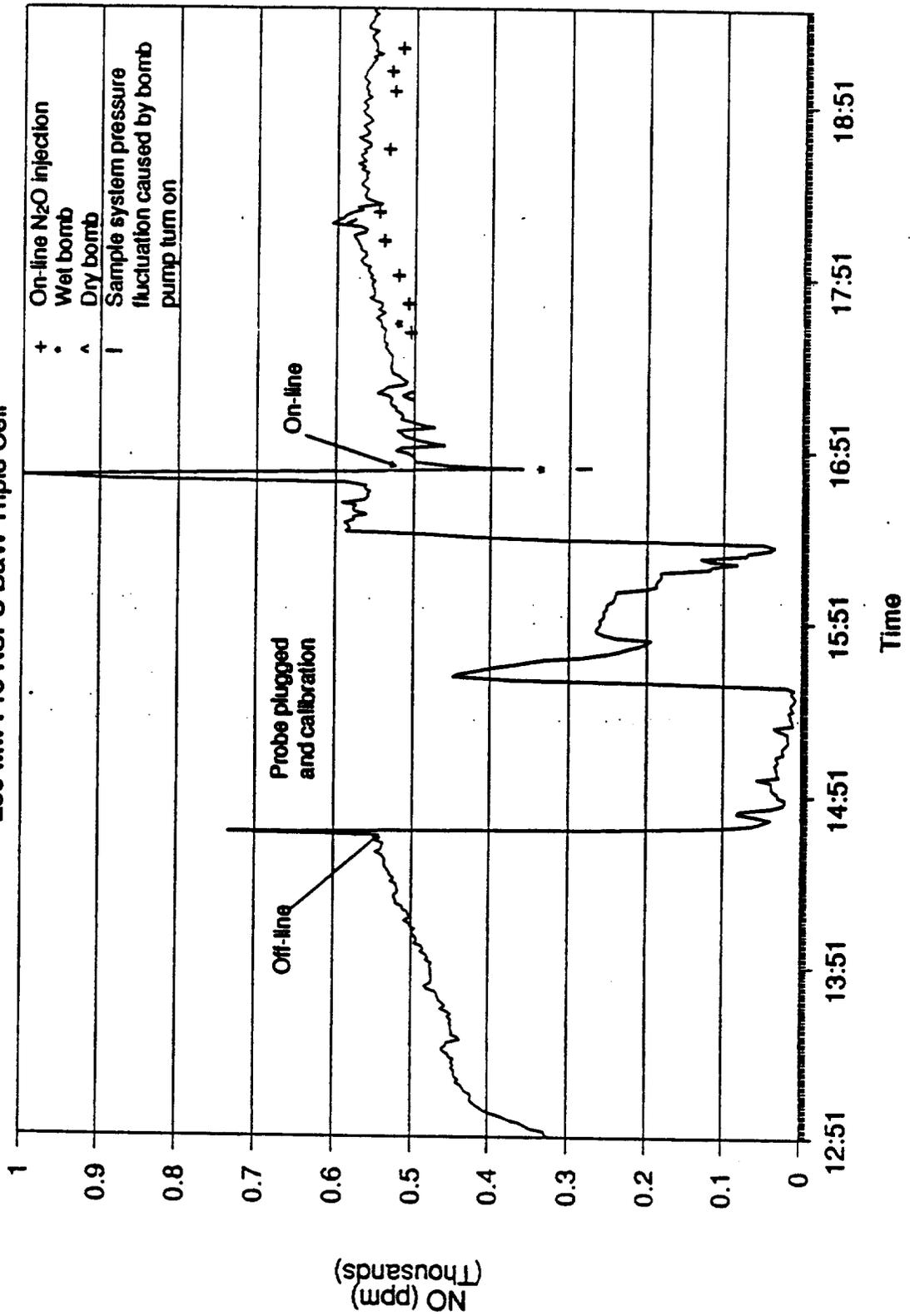
Unit B CO2--7 Oct 88

250 Mw Pre-NSPS B&W Triple Cell



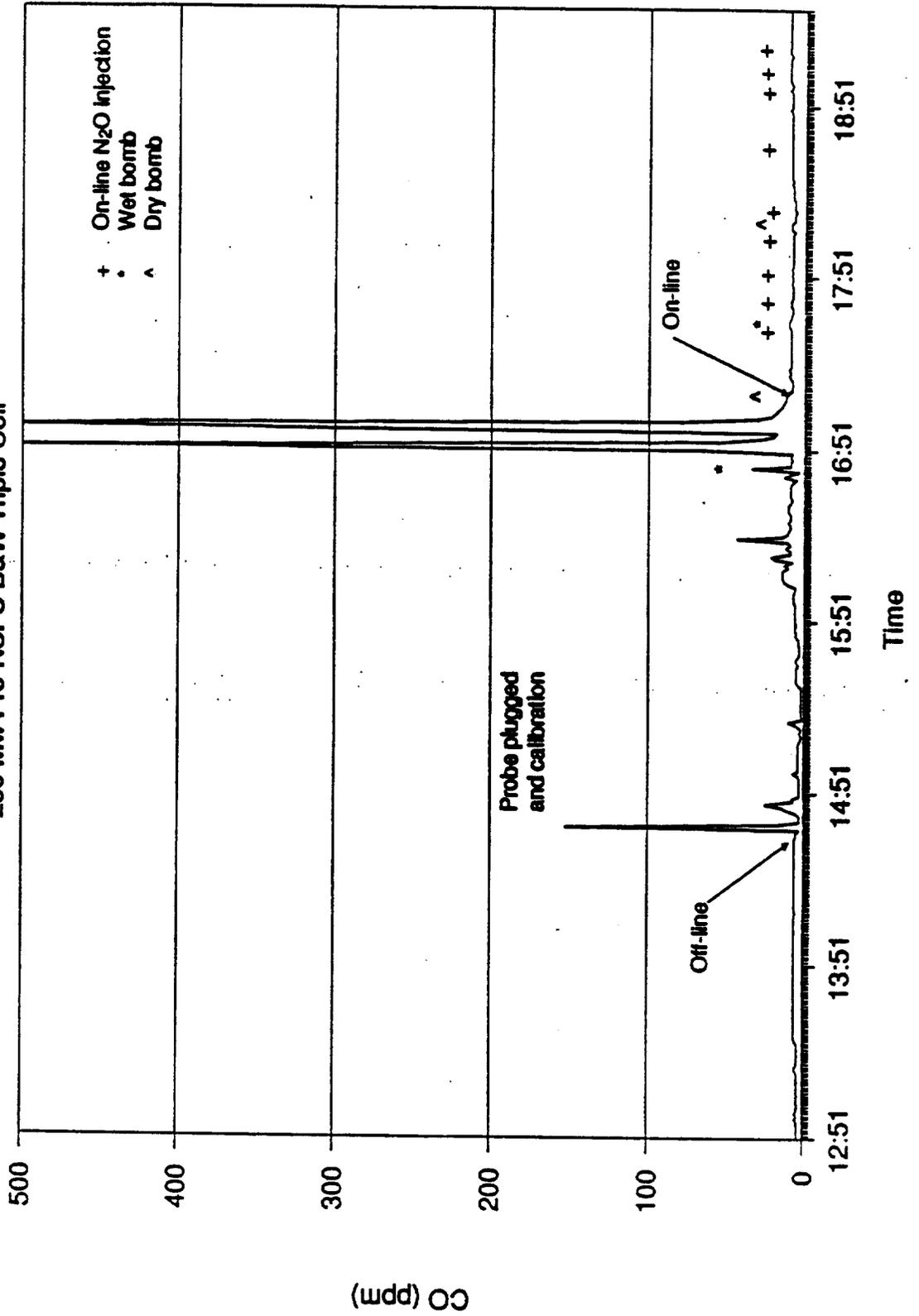
Unit B NO--7 Oct 88

250 Mw Pre-NSPS B&W Triple Cell



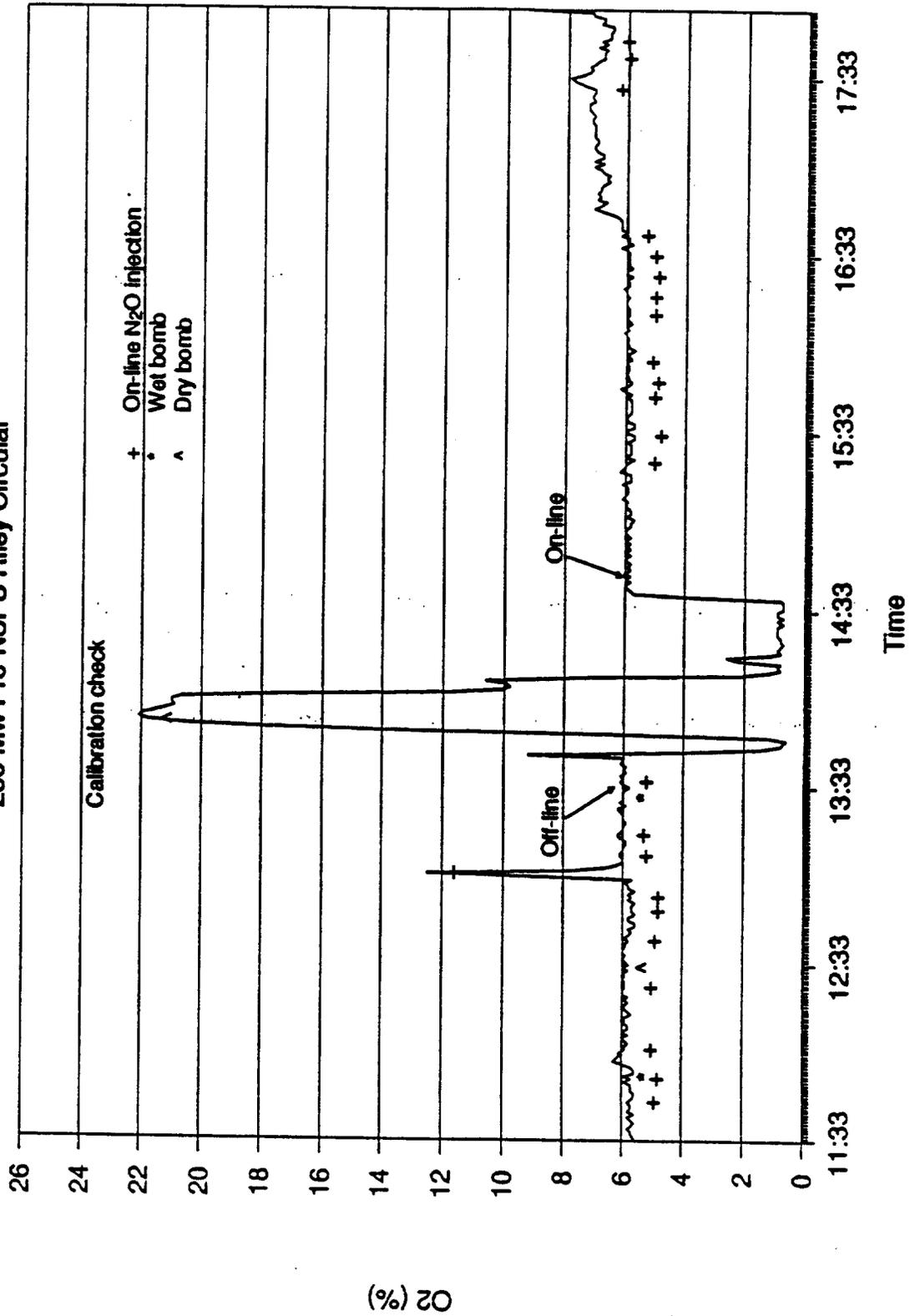
Unit B CO--7 Oct 88

250 Mw Pre-NSPS B&W Triple Cell



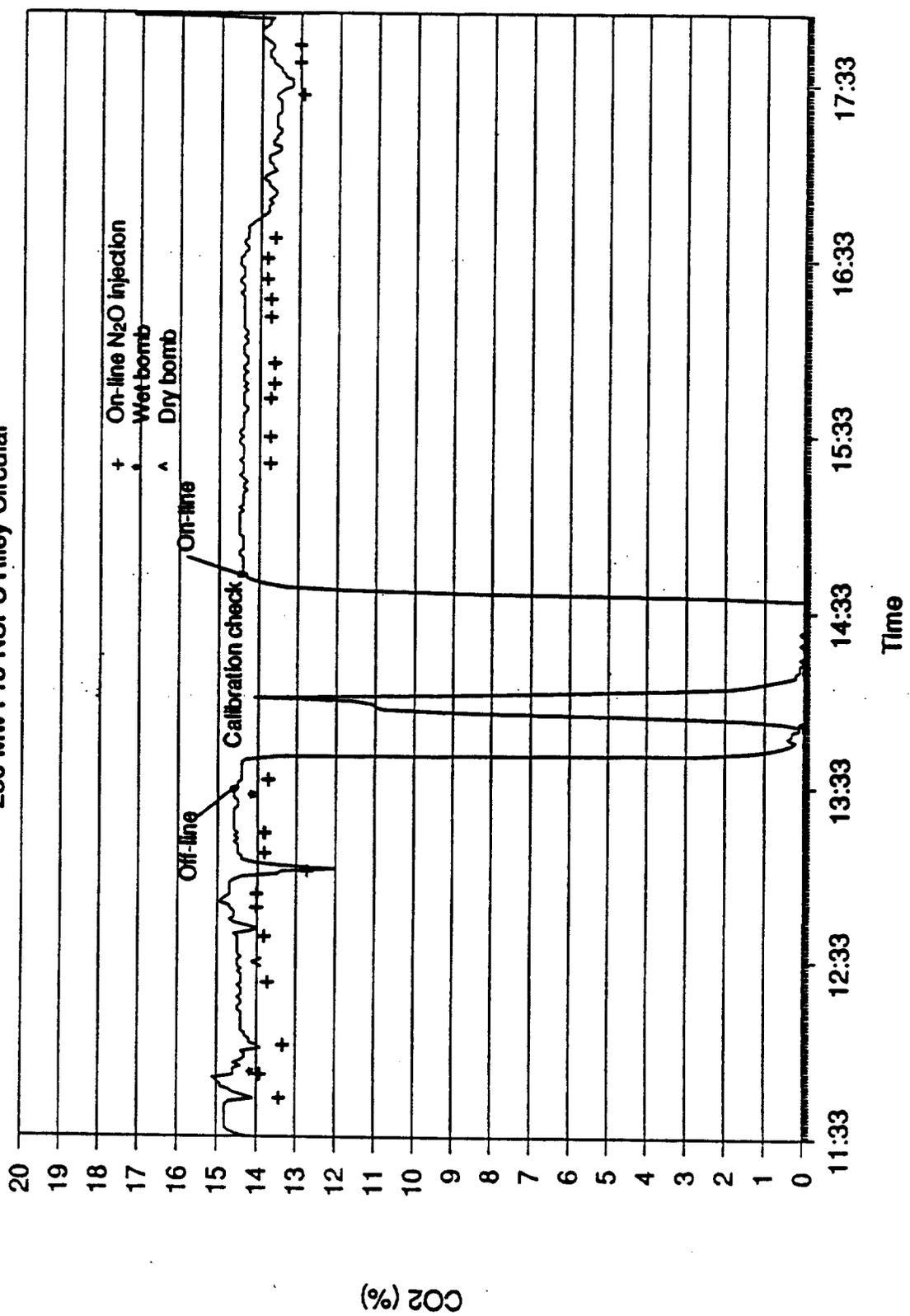
Unit C O2--8 Oct 88

250 Mw Pre-NSPS Riley Circular



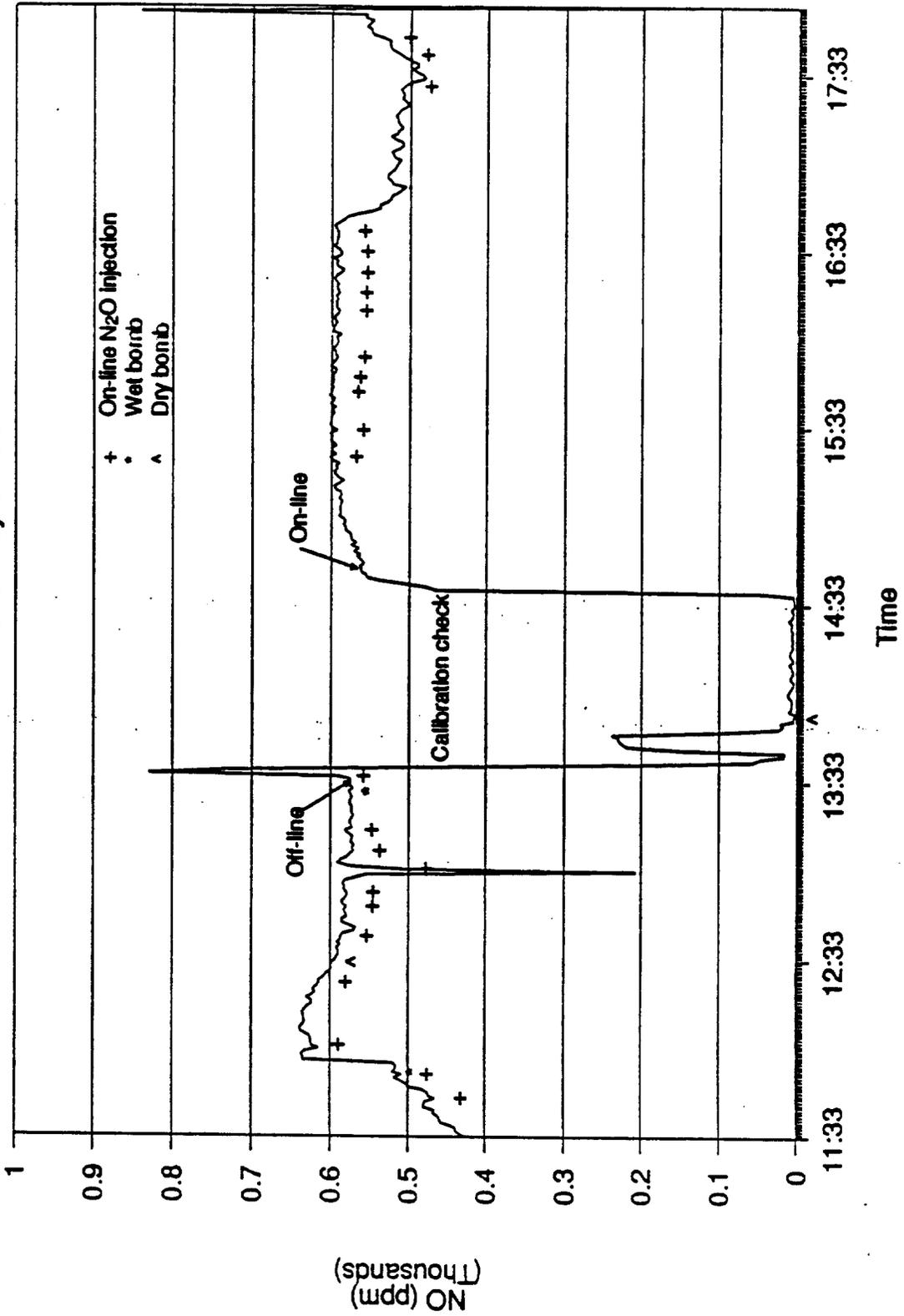
Unit C CO2--8 Oct 88

250 Mw Pre-NSPS Riley Circular



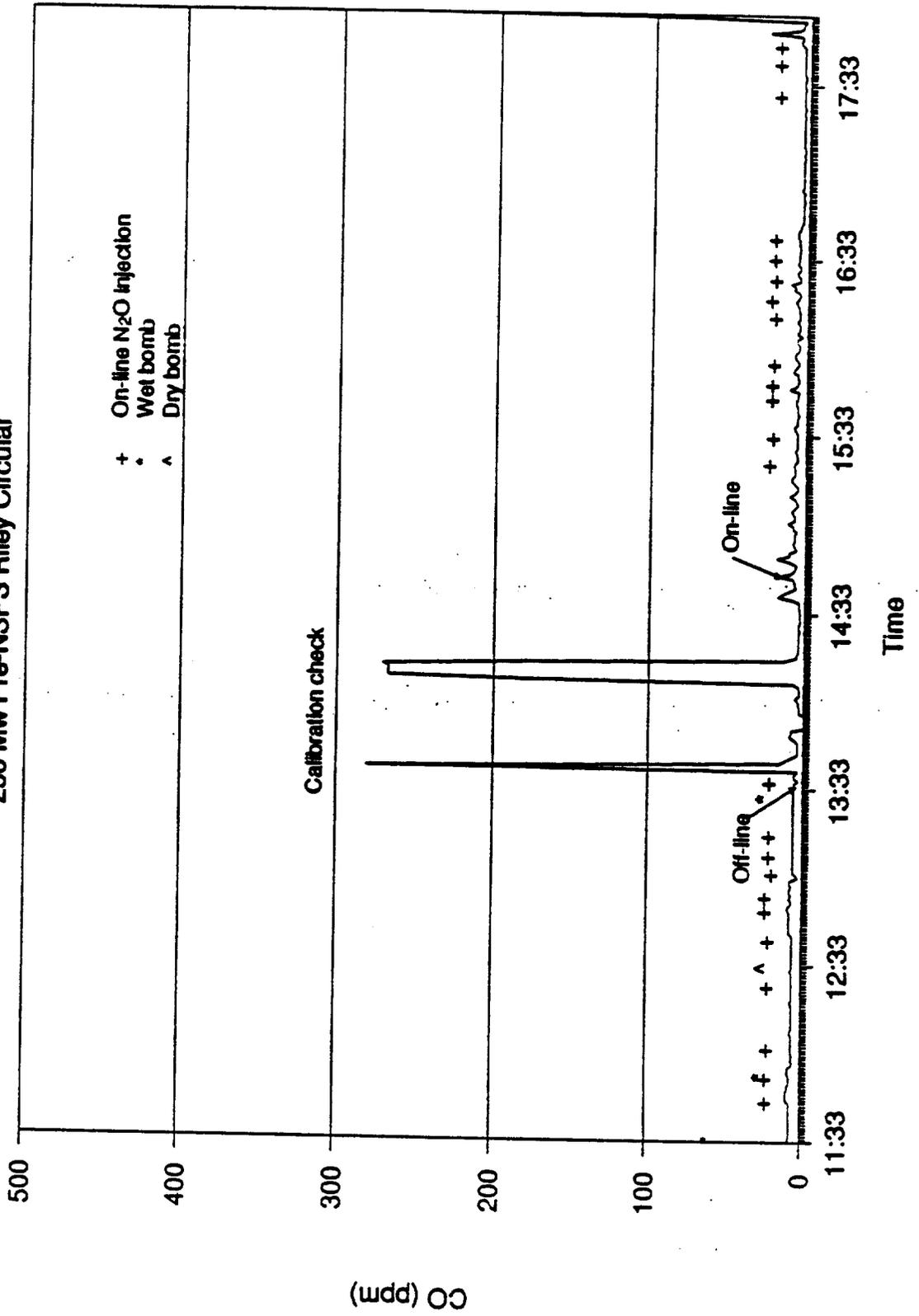
Unit C NO--8 Oct 88

250 Mw Pre-NSPS Riley Circular



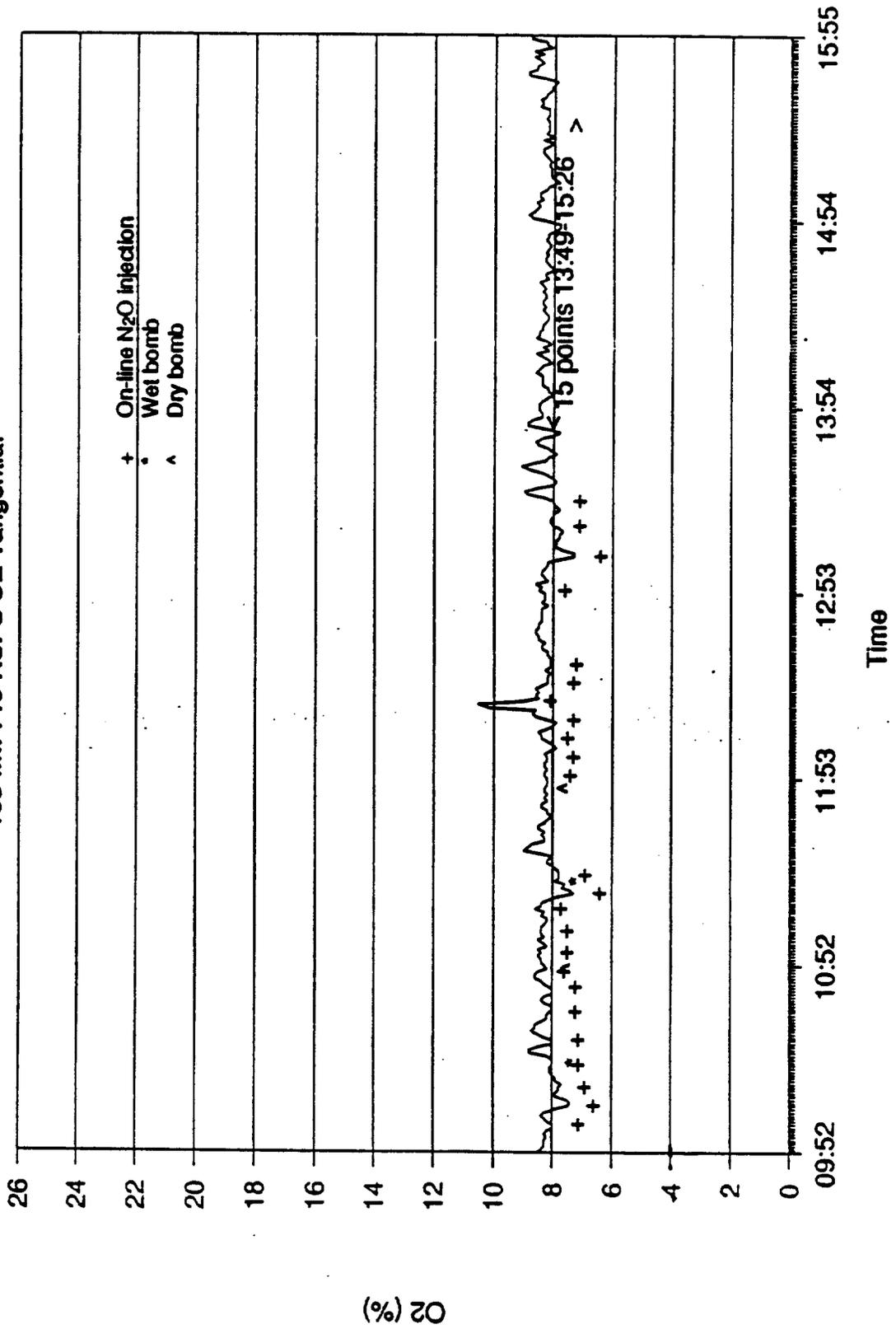
Unit C CO--8 Oct 88

250 Mw Pre-NSPS Riley Circular



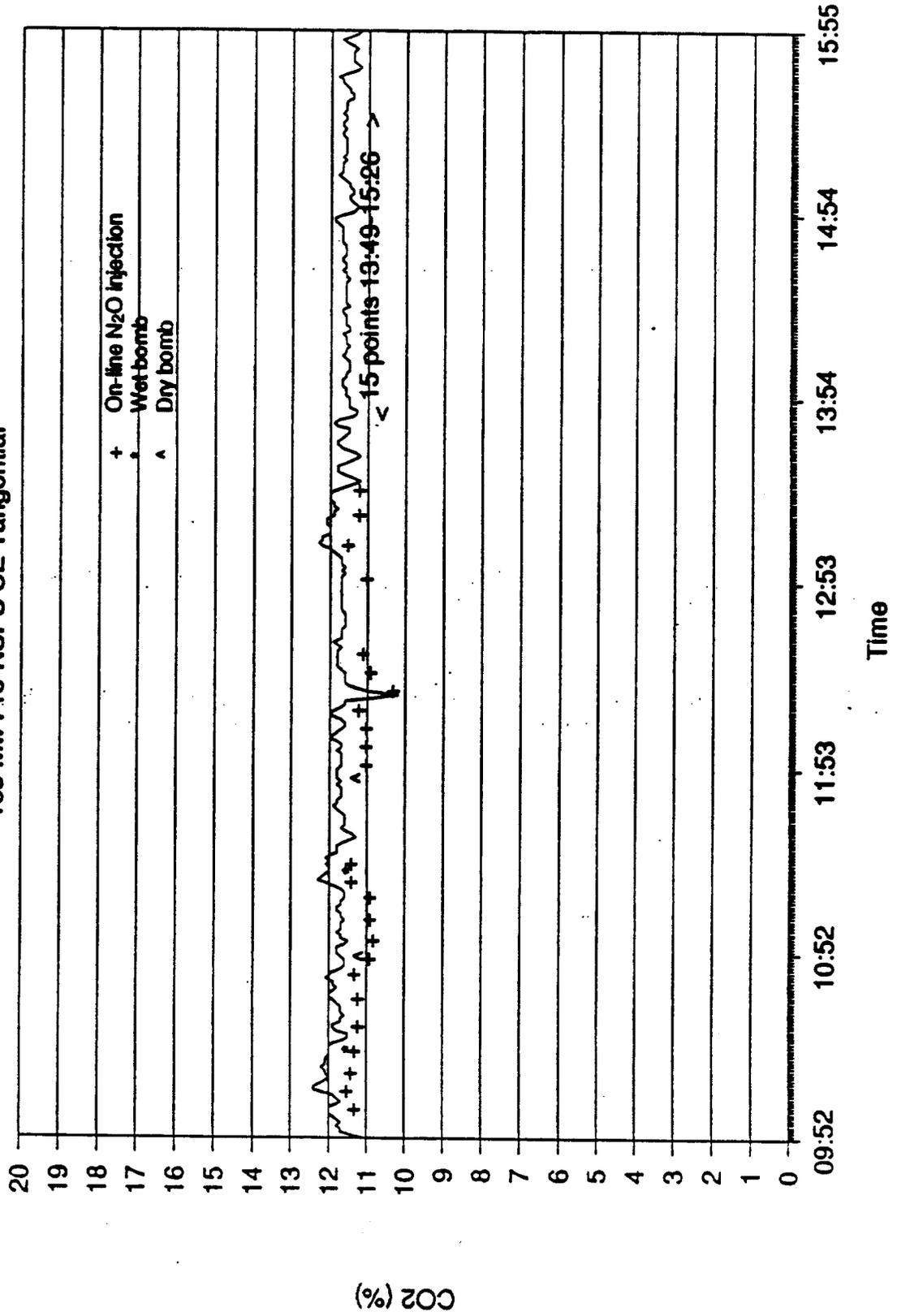
Unit D O2--10 Oct 88

165 Mw Pre-NSPS CE Tangential



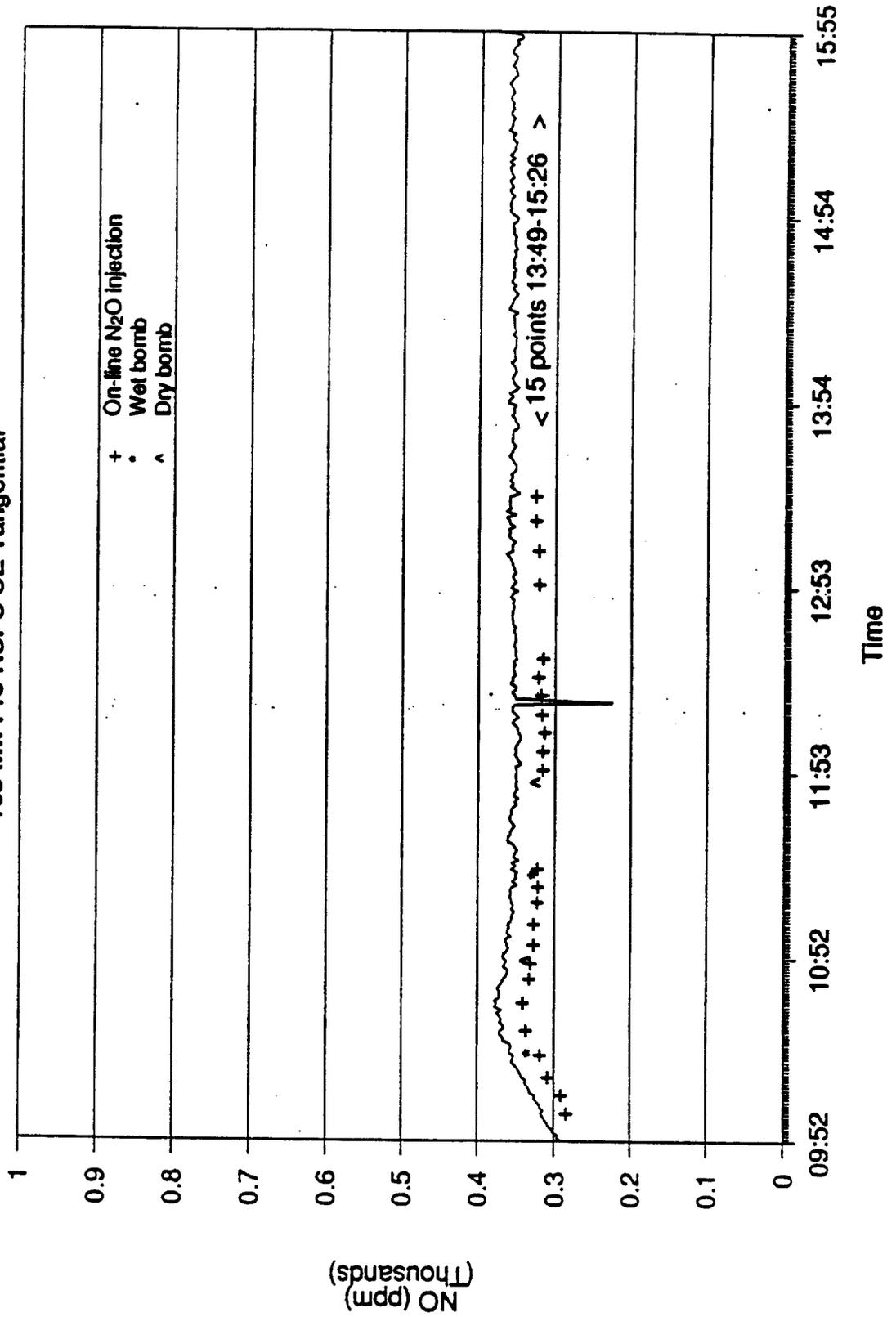
Unit D CO2--10 Oct 88

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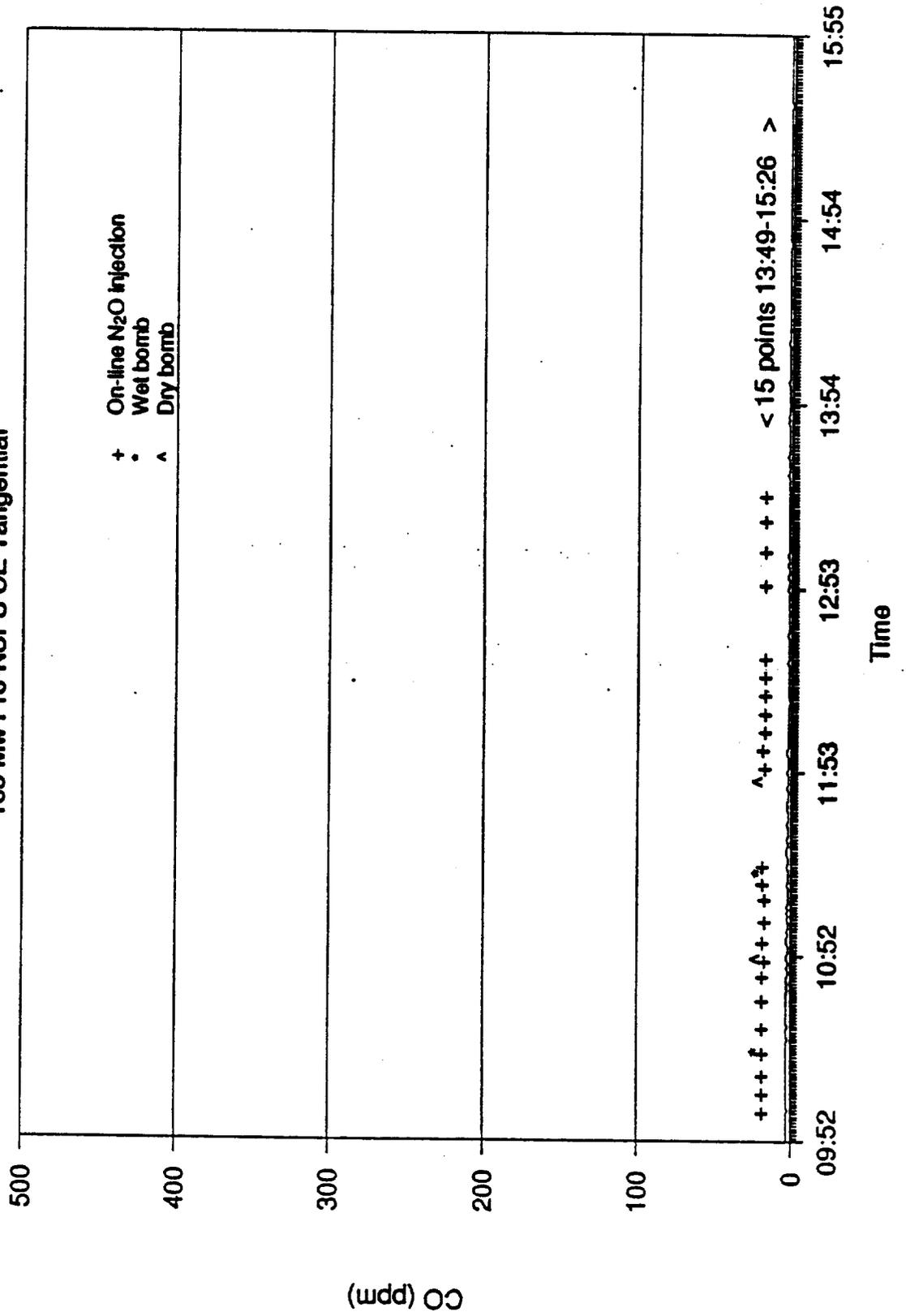
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165 Mw Pre-NSPS CE Tangential



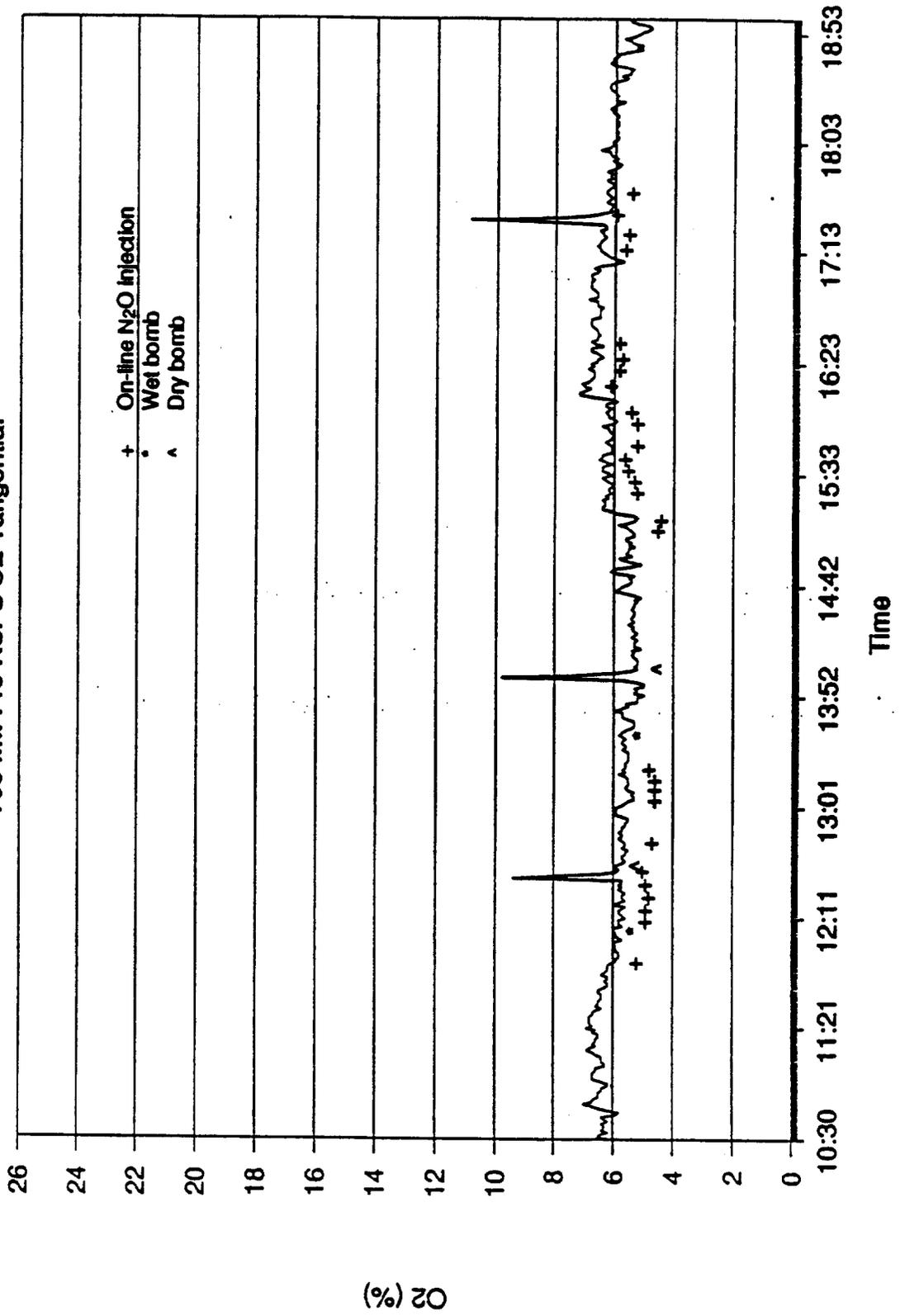
Unit D CO--10 Oct 88

165 Mw Pre-NSPS CE Tangential



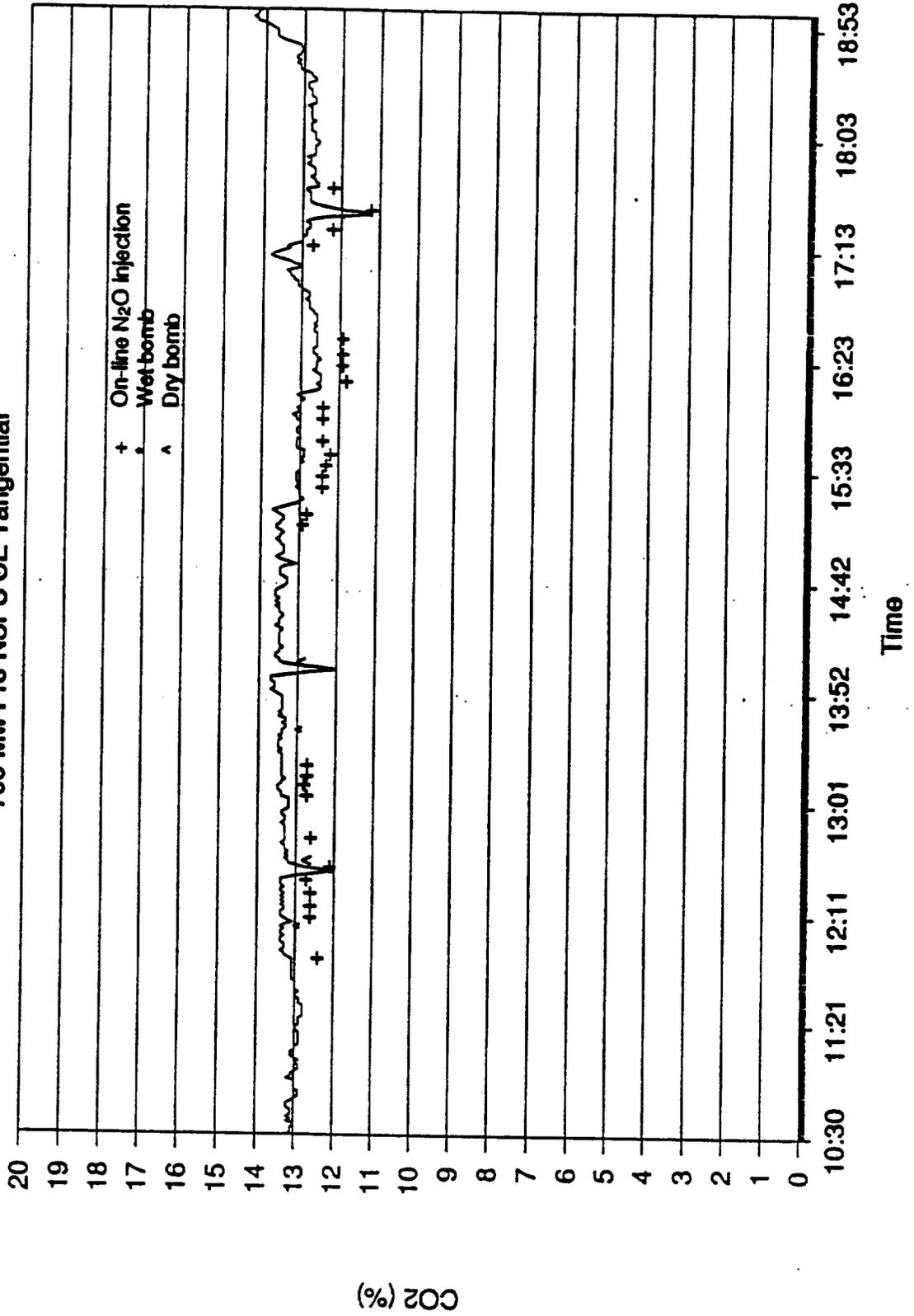
Unit E O2--11 Oct 88

700 Mw Pre-NSPS CE Tangential



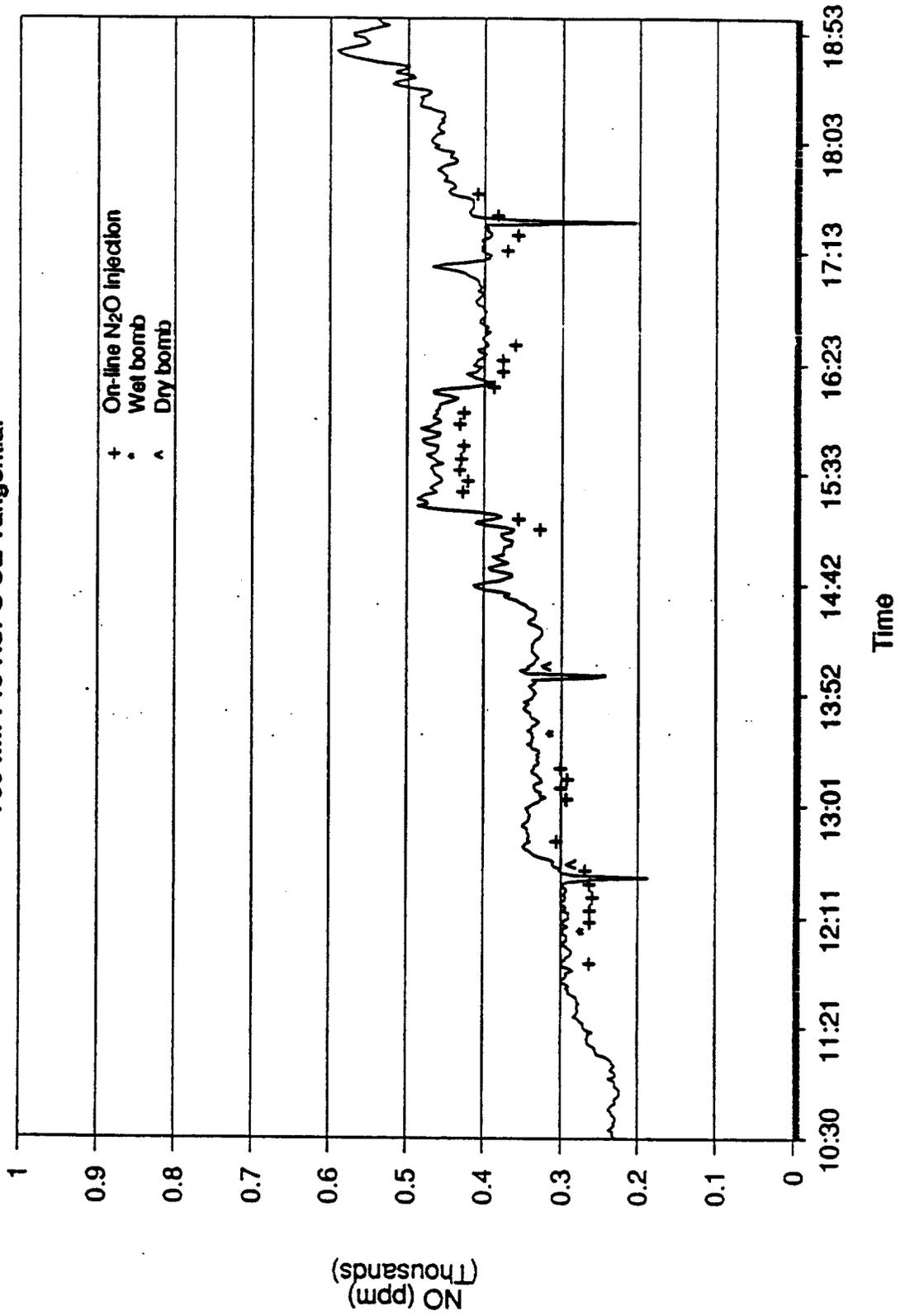
Unit E CO2--11 Oct 88

700 Mw Pre-NSPS CE Tangential



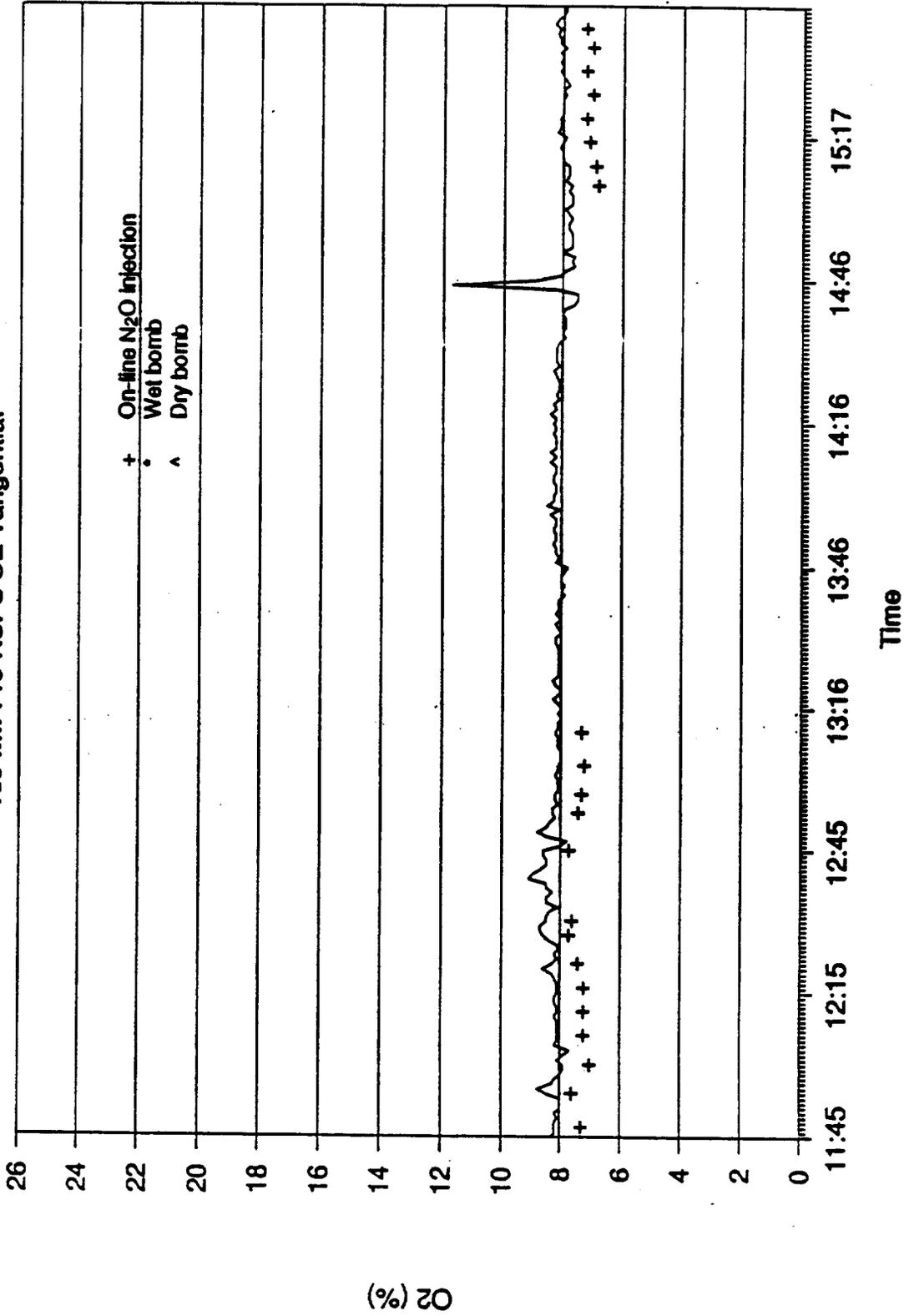
Unit E NO--11 Oct 88

700 Mw Pre-NSPS CE Tangential



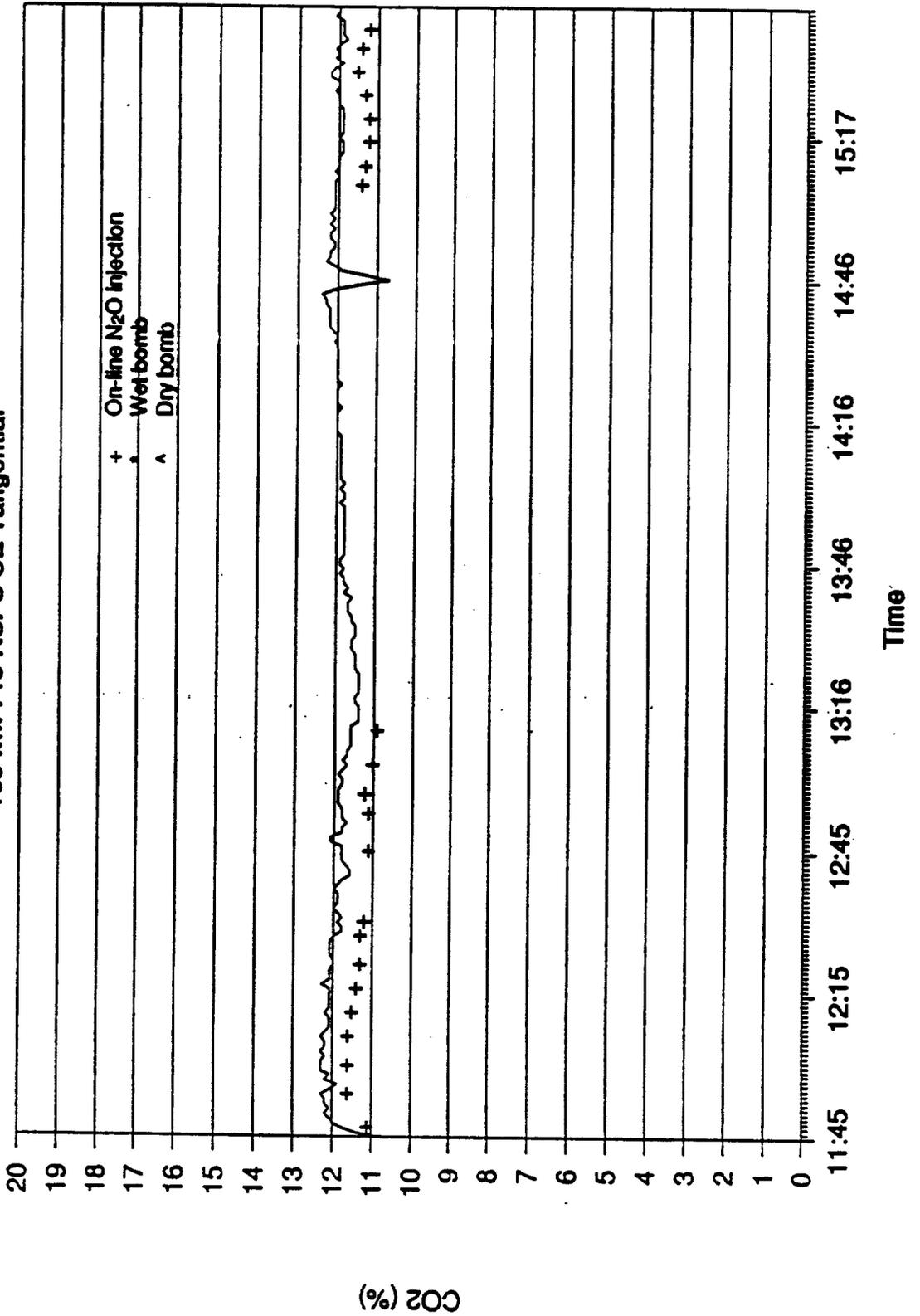
Unit F O2--12 Oct 88

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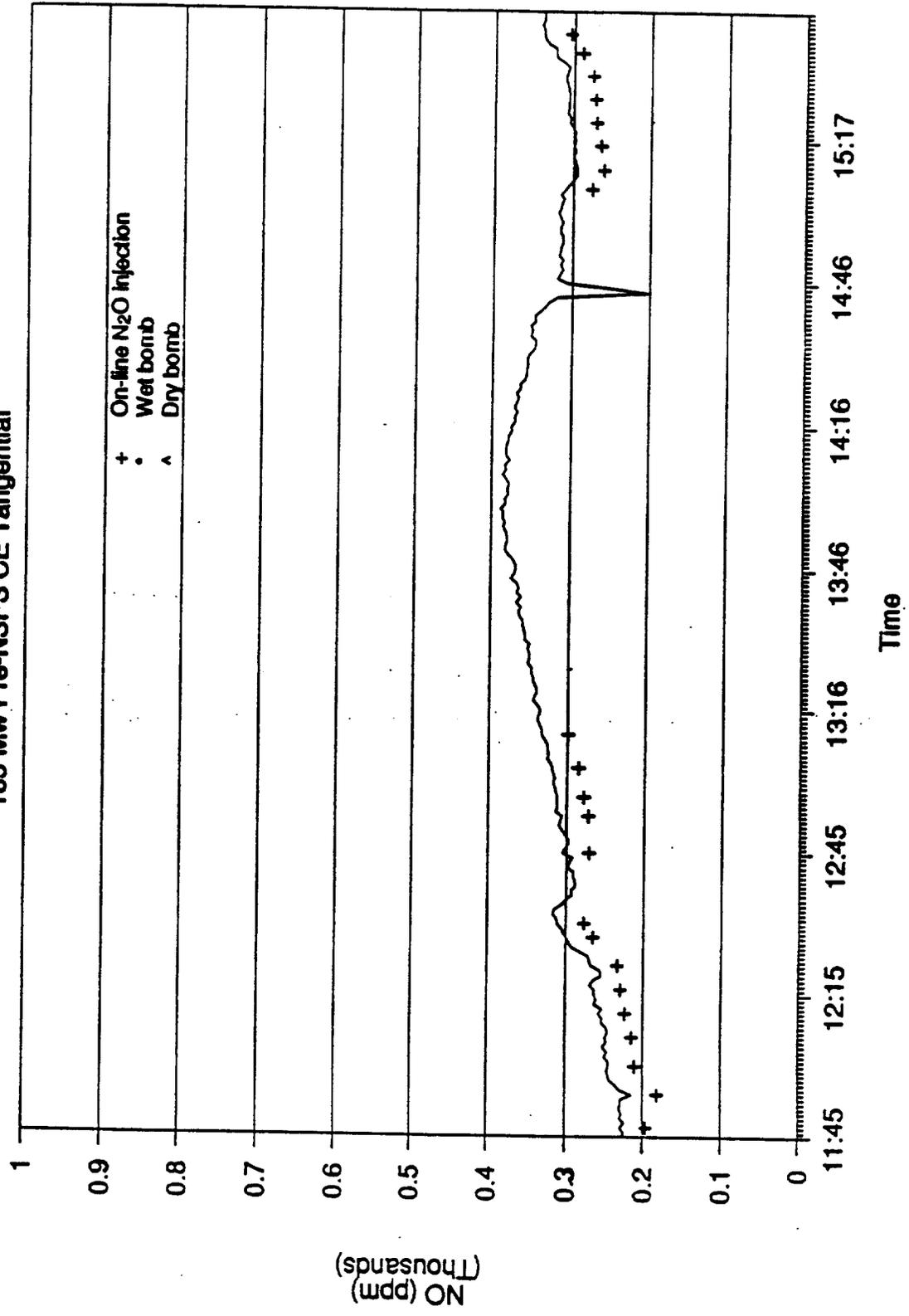
Unit F CO2--12 Oct 88

165 Mw Pre-NSPS CE Tangential



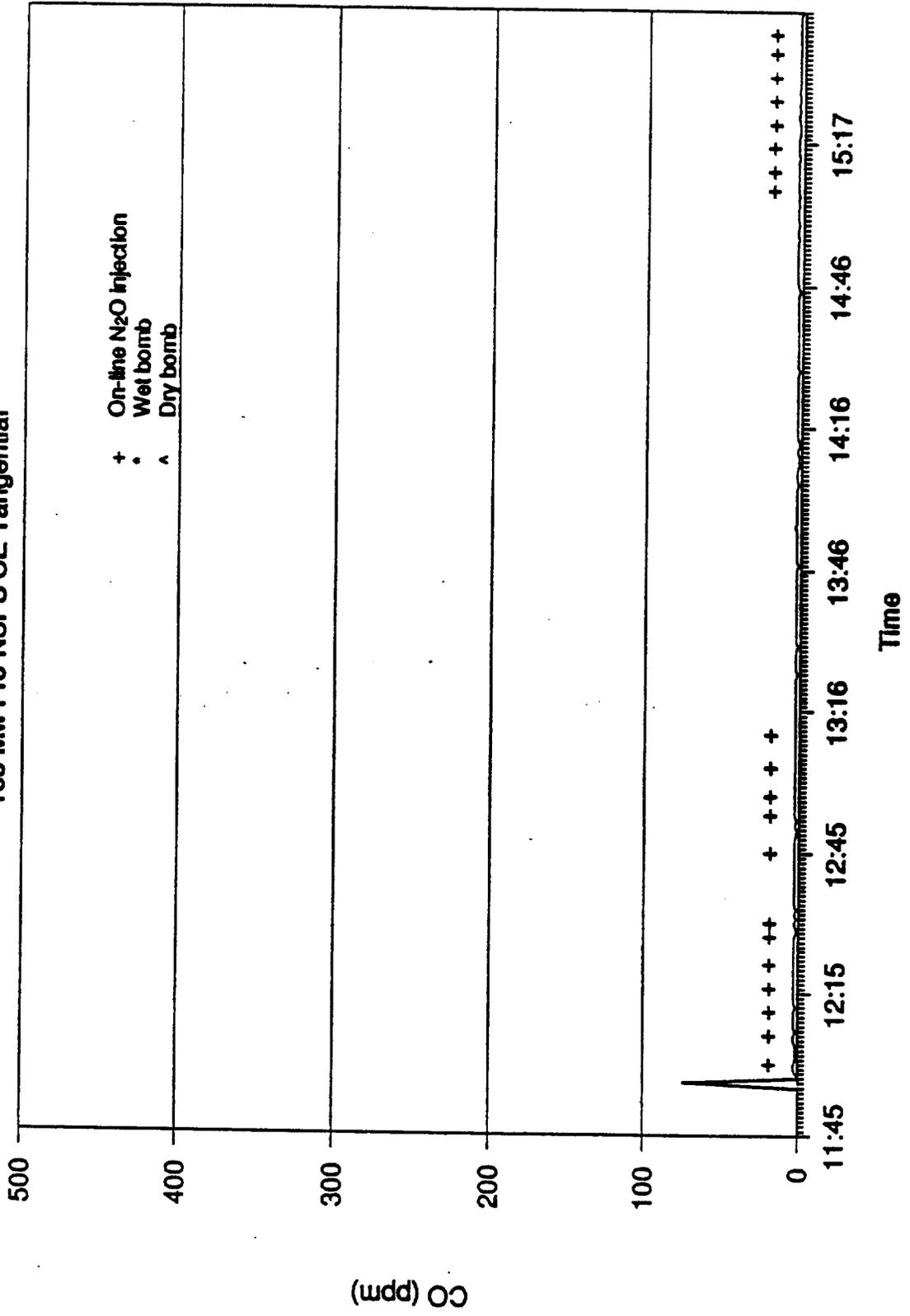
Unit F NO--12 Oct 88

165 Mw Pre-NSPS CE Tangential



Unit F CO--12 Oct 88

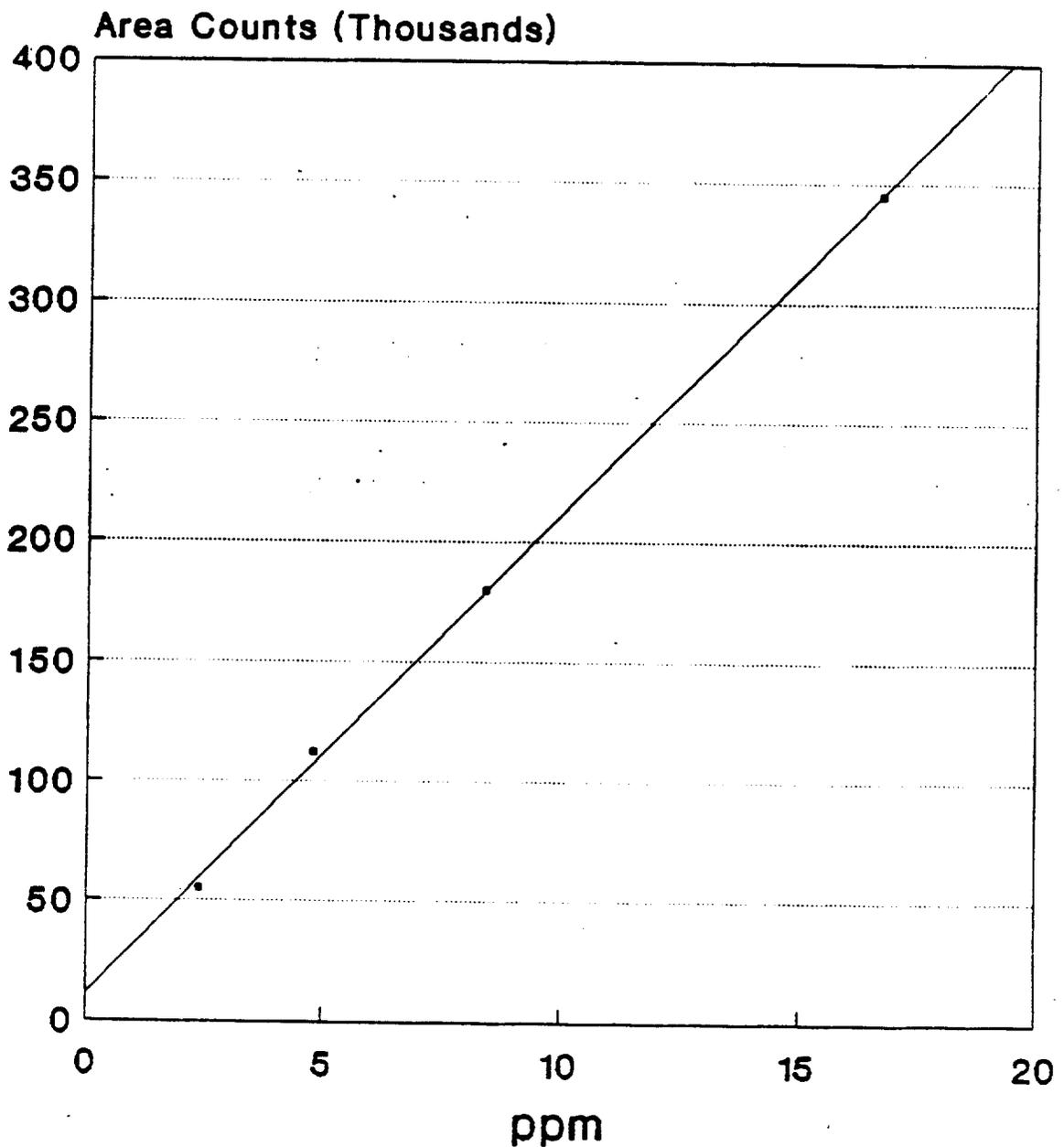
165 Mw Pre-NSPS CE Tangential



APPENDIX C
GC CALIBRATION CURVES

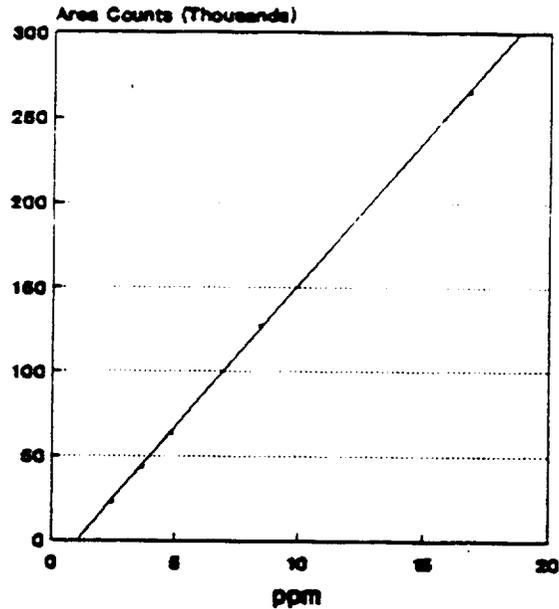
N2O Calibration Curve

GC/ECD Side "B" On-Line



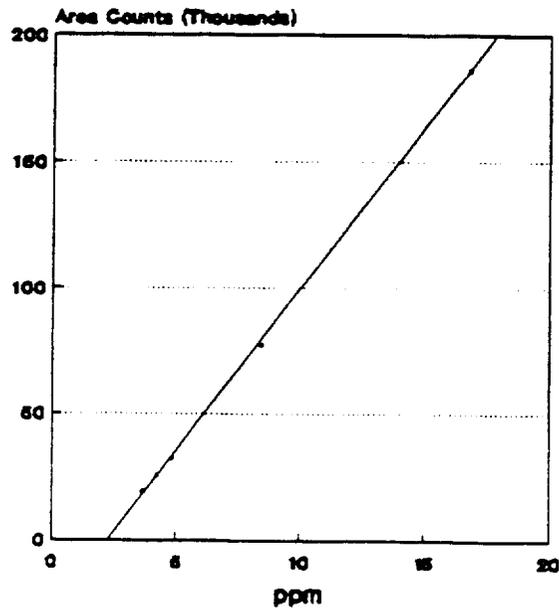
10/5/88 Curve Not Forced Thru Zero

N2O Calibration Curve GC/ECD Side "A" On-Line



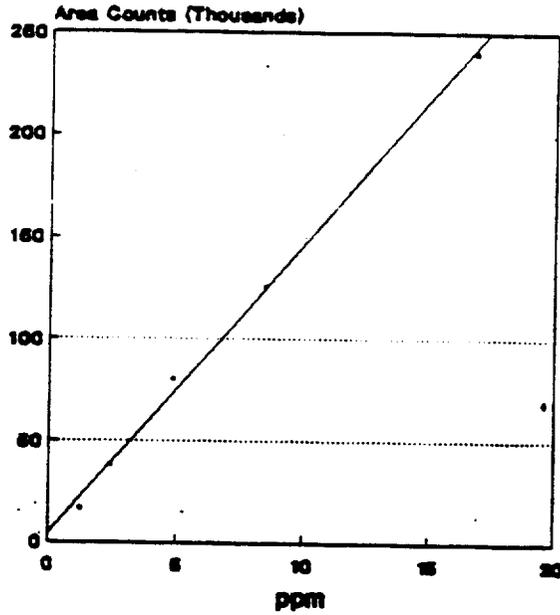
12/7/88 Curve Not Forced Thru Zero

N2O Calibration Curve GC/ECD Side "B" On-Line



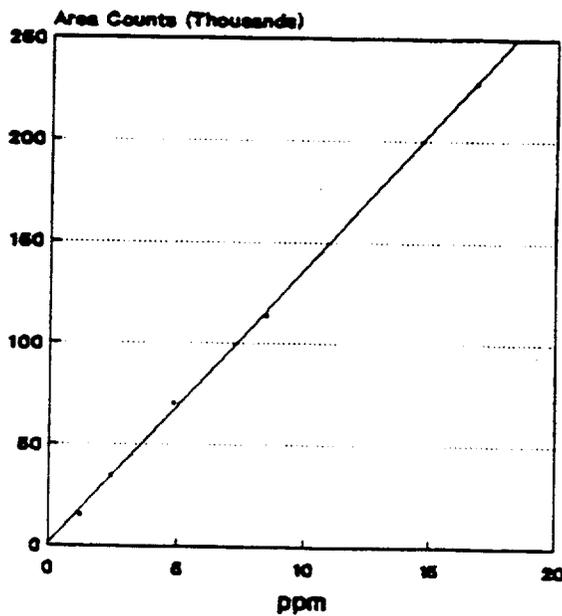
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N2O Calibration Curve GC/ECD Side "A" On-Line



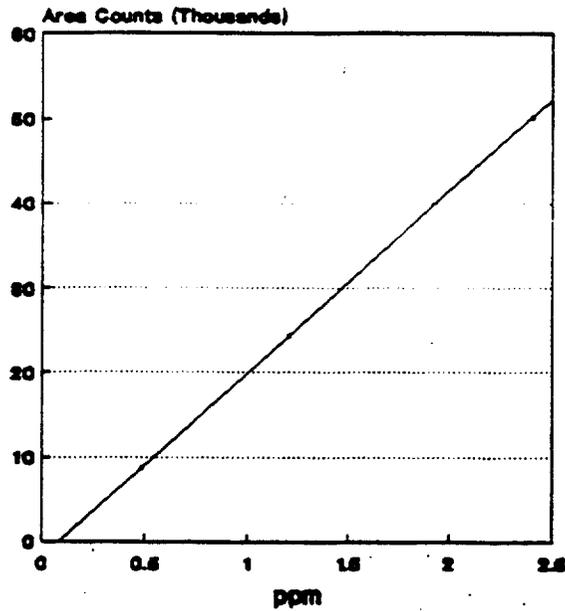
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N2O Calibration Curve GC/ECD Side "B" On-Line



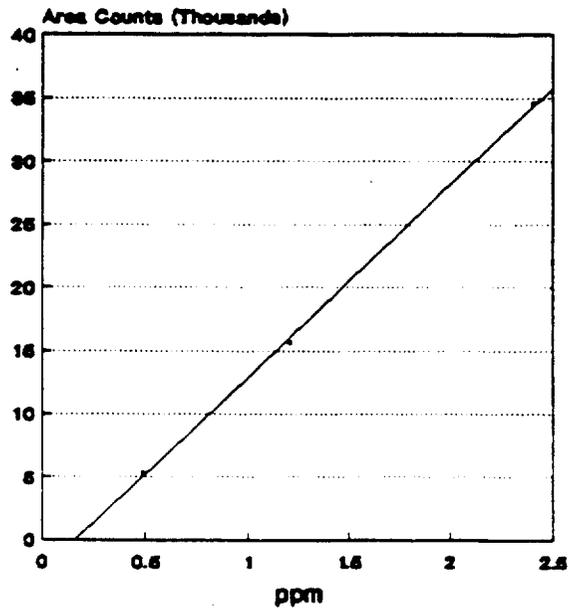
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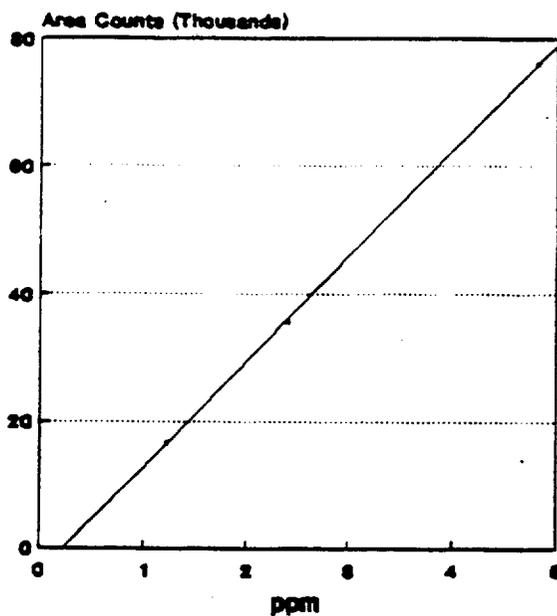
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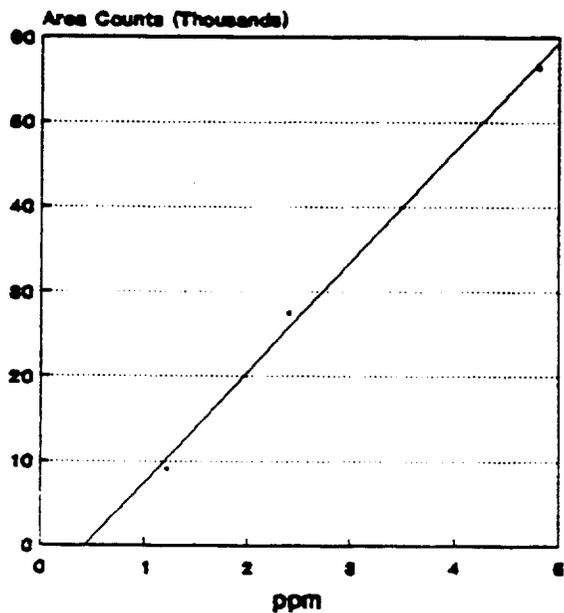
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N2O Calibration Curve GC/ECD Side "A" On-Line



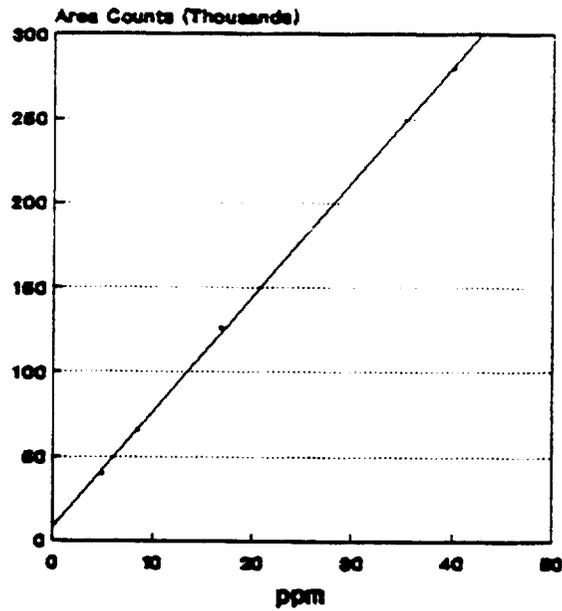
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N2O Calibration Curve GC/ECD Side "B" On-Line



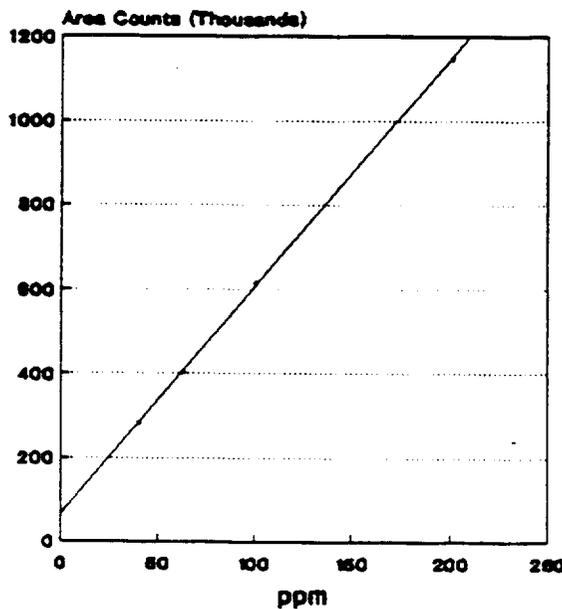
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N2O Calibration Curve GC/ECD SS Container



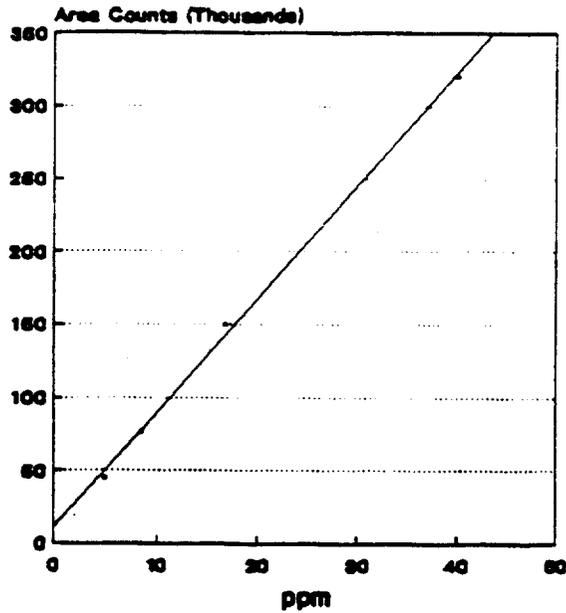
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N2O Calibration Curve GC/ECD SS Container



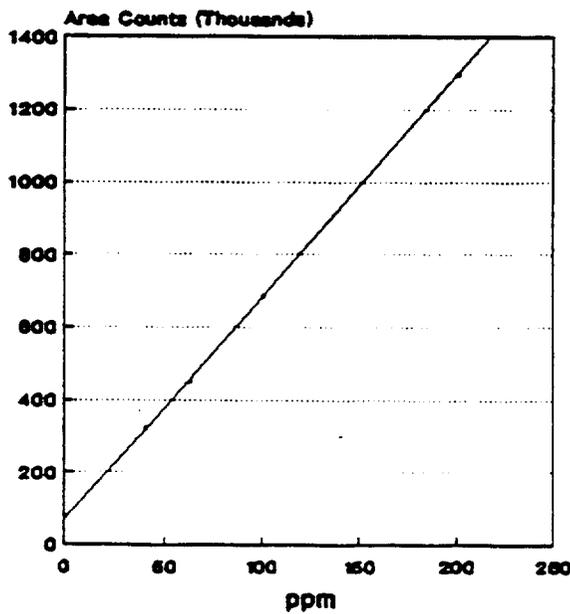
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N2O Calibration Curve GC/ECD SS Container



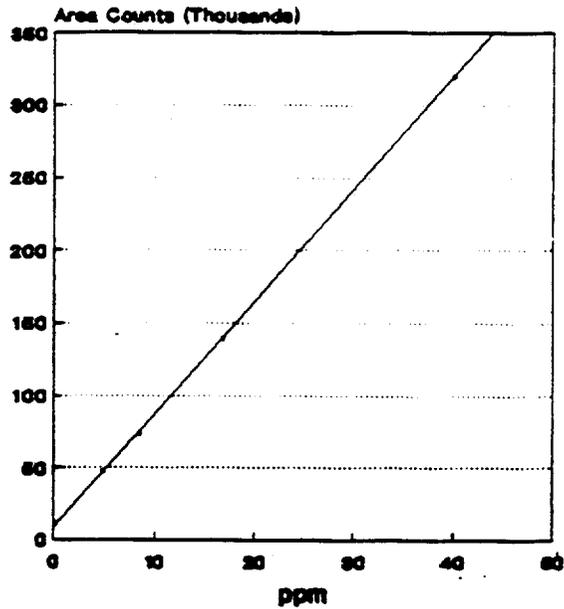
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N2O Calibration Curve GC/ECD SS Container



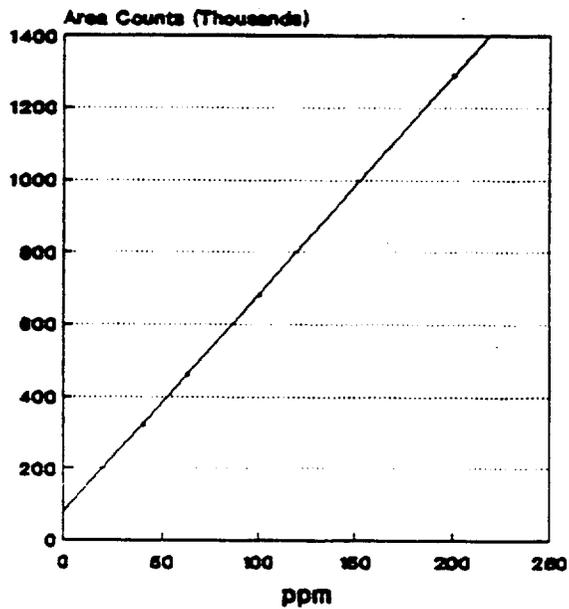
10/7/88 Curve Not Forced Thru Zero

N2O Calibration Curve GC/ECD SS. Container



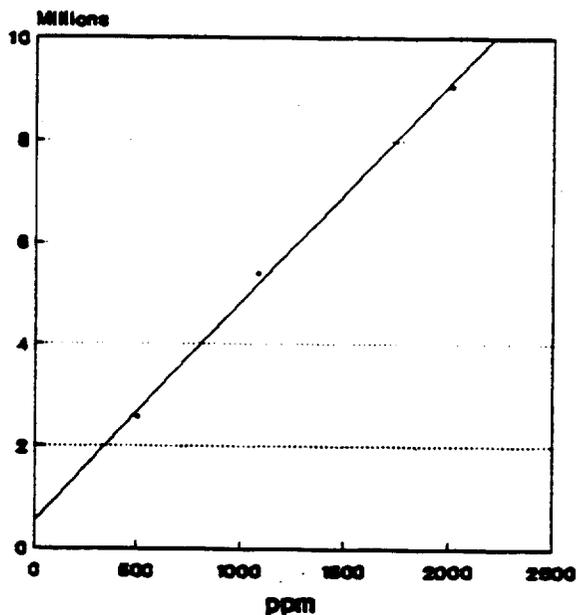
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N2O Calibration Curve GC/ECD SS Container



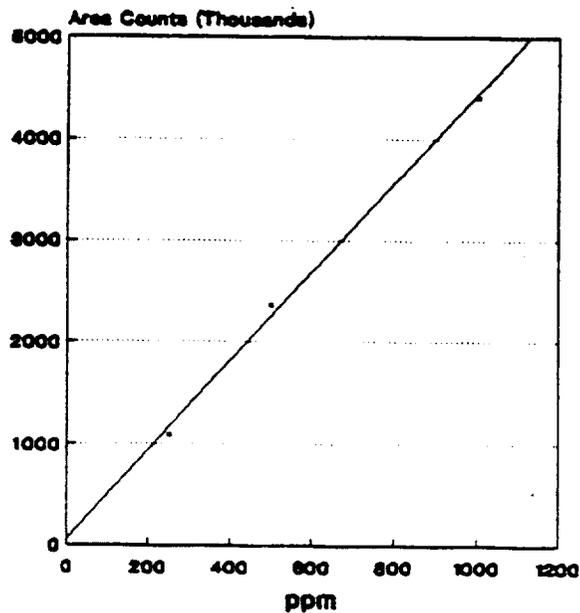
10/10/88 Curve Not Forced Thru Zero

SO2 Calibration Curve GC/FPD



10/6/88 Curve Not Forced Thru Zero

SO2 Calibration Curve GC/FPD

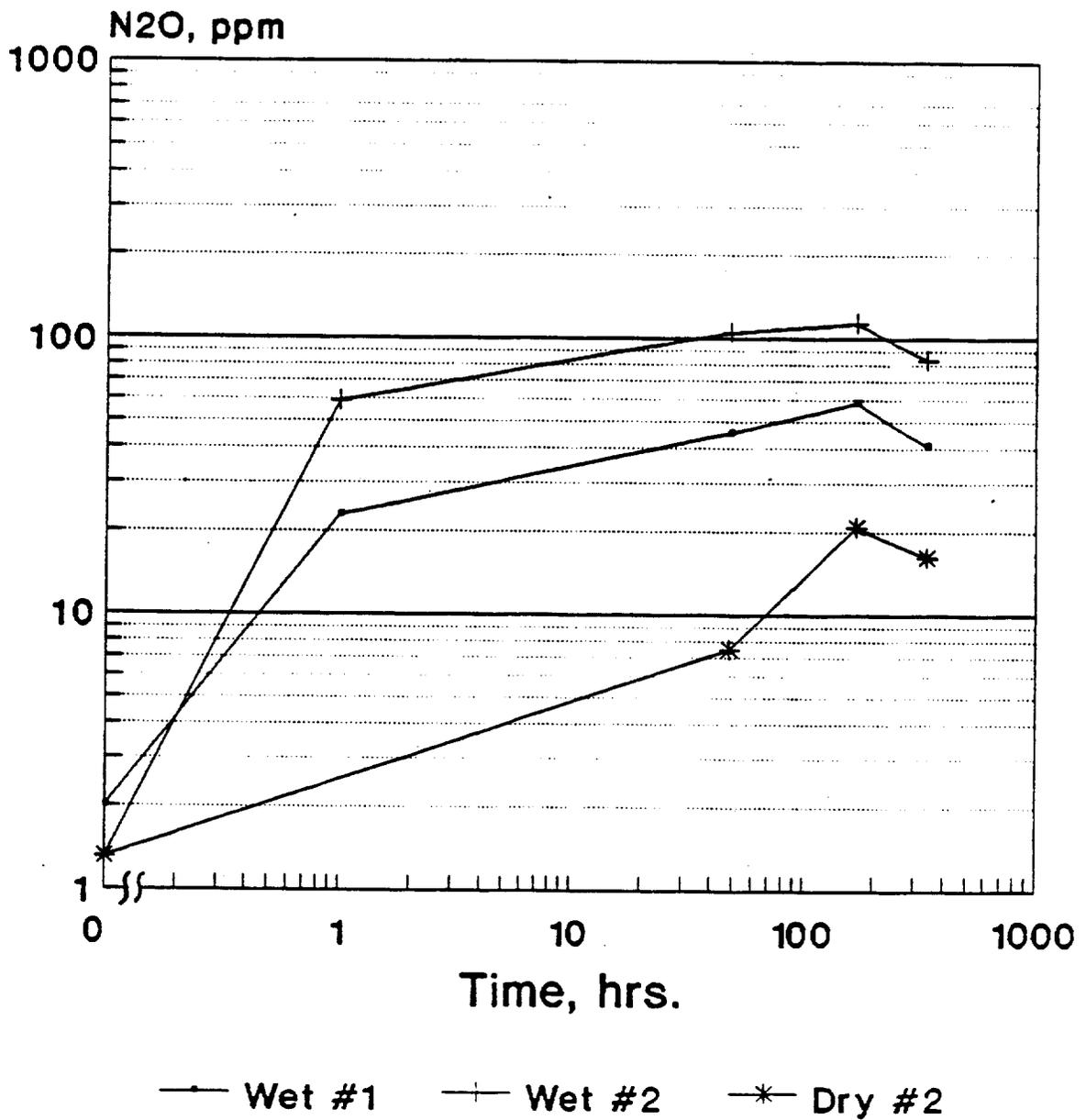


10/12/88 Curve Not Forced thru Zero

APPENDIX D

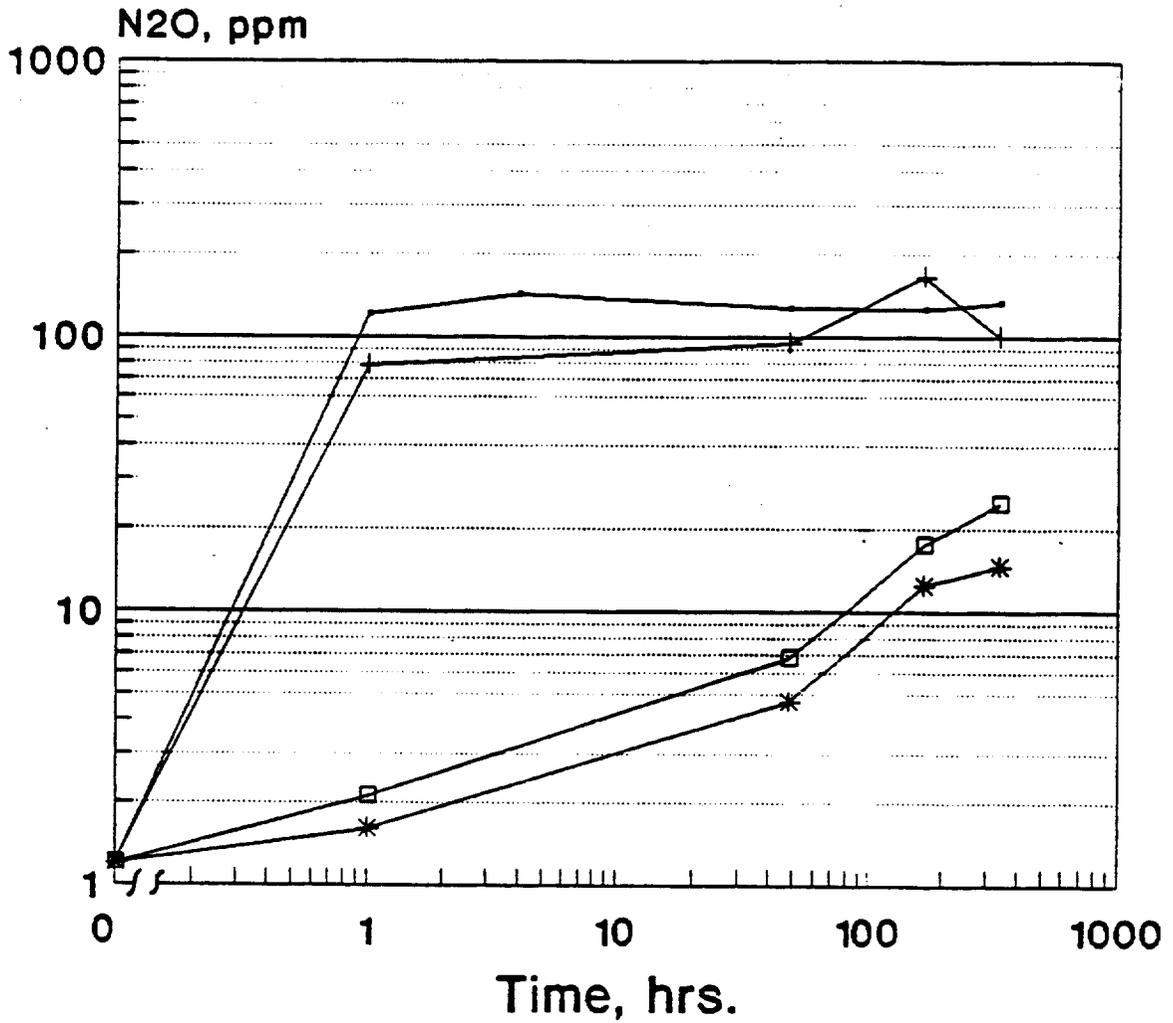
STAINLESS STEEL CONTAINER RESULT PLOTS OF N₂O AND SO₂ CONCENTRATION VS. TIME

Nitrous Oxide Field Test Unit A SS Containers



10/5/88

Nitrous Oxide Field Test Unit B SS Containers



— Wet #1

+ Wet #3

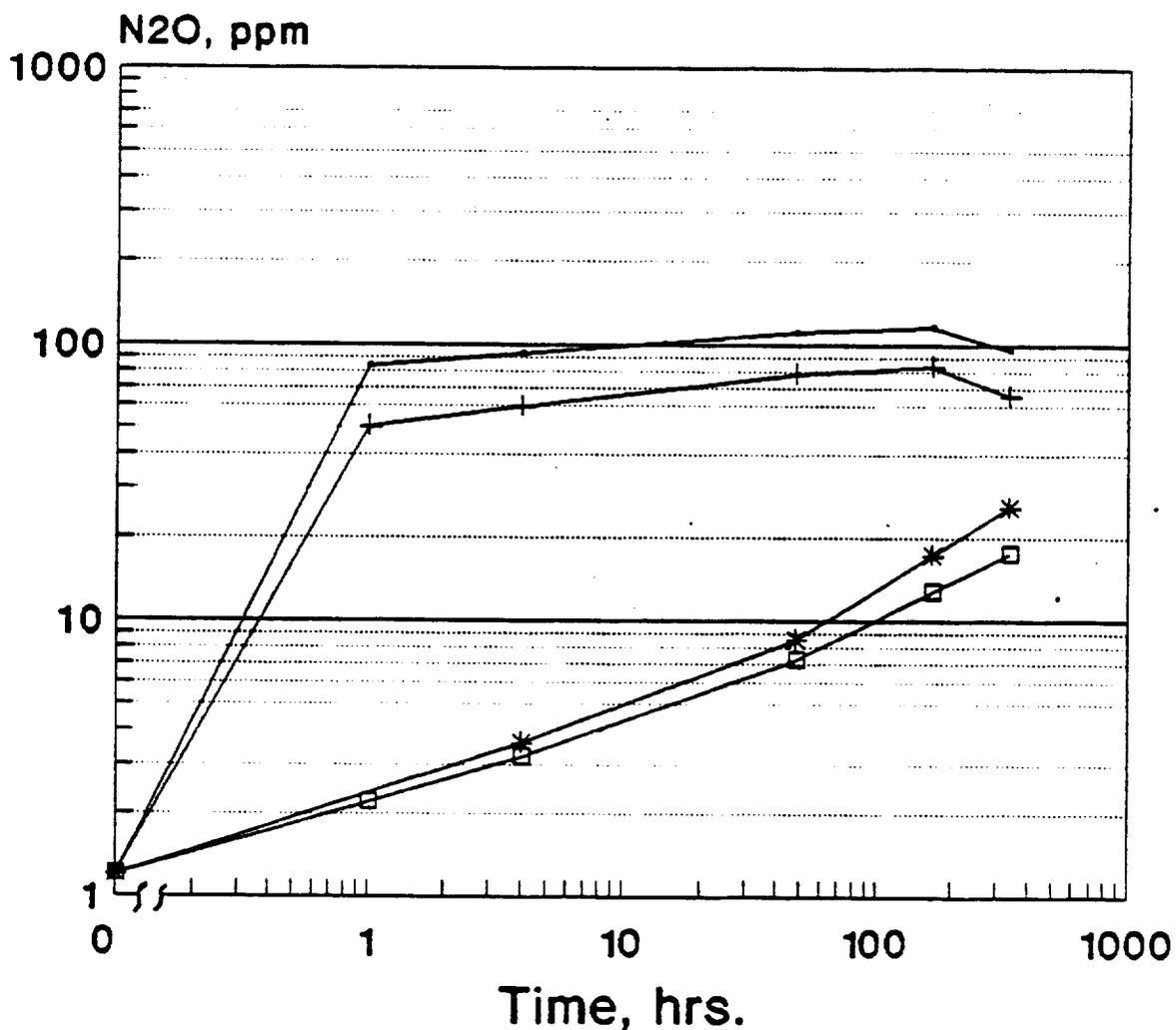
* Dry #2

□ Dry #4

10/7/88

Nitrous Oxide Field Test

Unit C SS Containers



— Wet #1

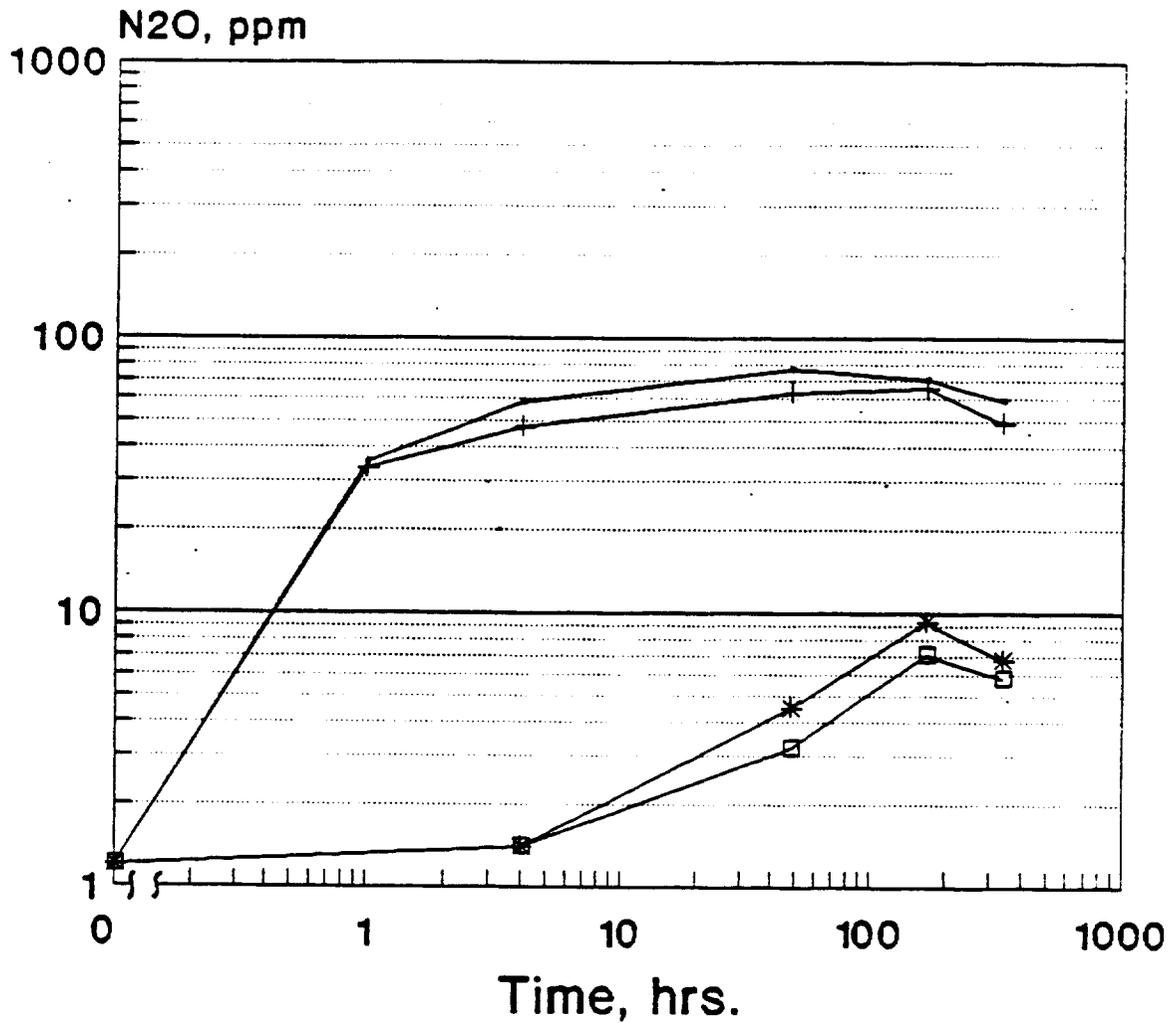
+ Wet #3

* Dry #2

□ Dry #4

10/8/88

Nitrous Oxide Field Test Unit D SS Containers



— Wet #1

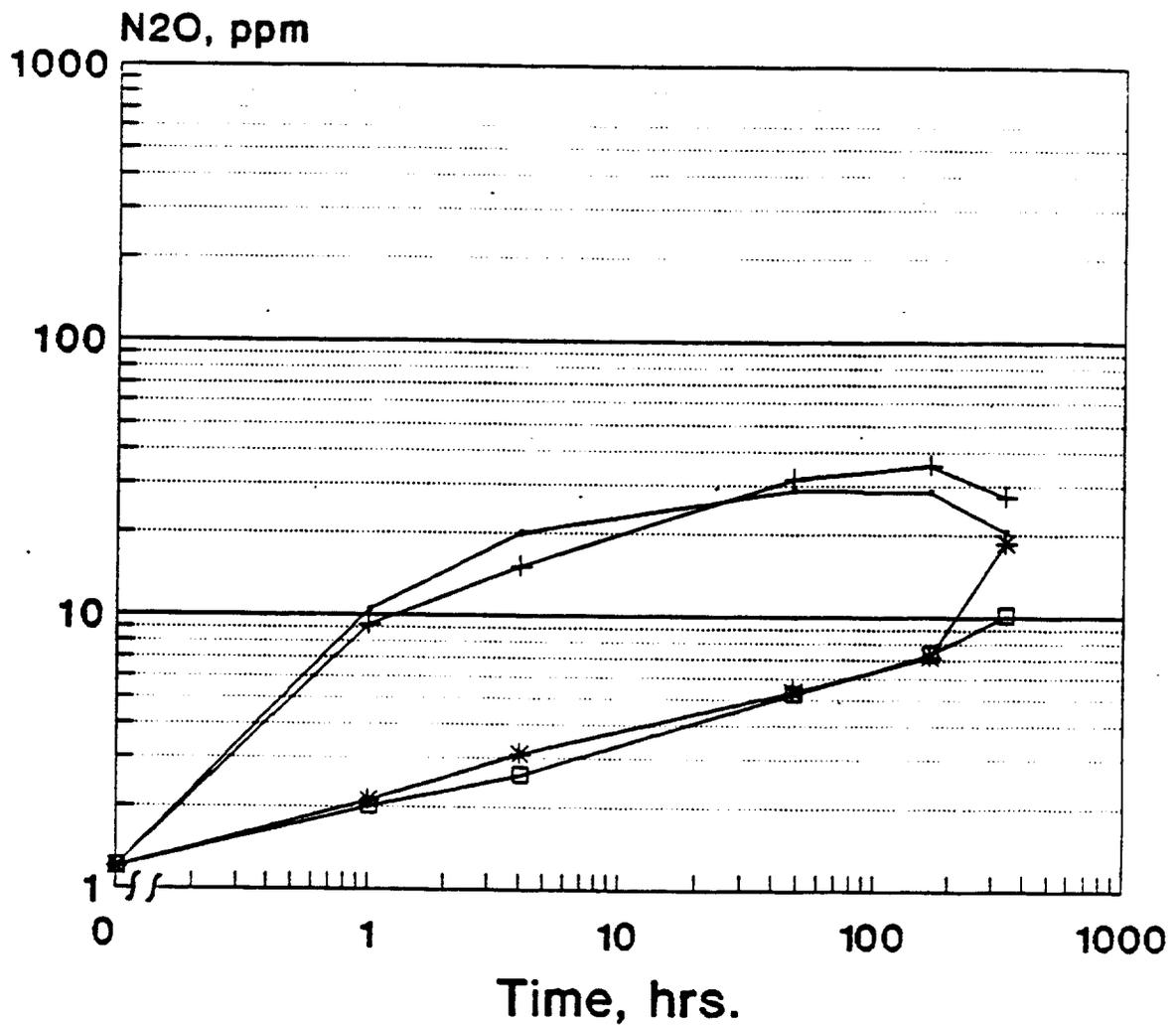
—+ Wet #3

—* Dry #2

—□ Dry #4

10/10/88

Nitrous Oxide Field Test Unit E SS Containers



— Wet #1

—+ Wet #3

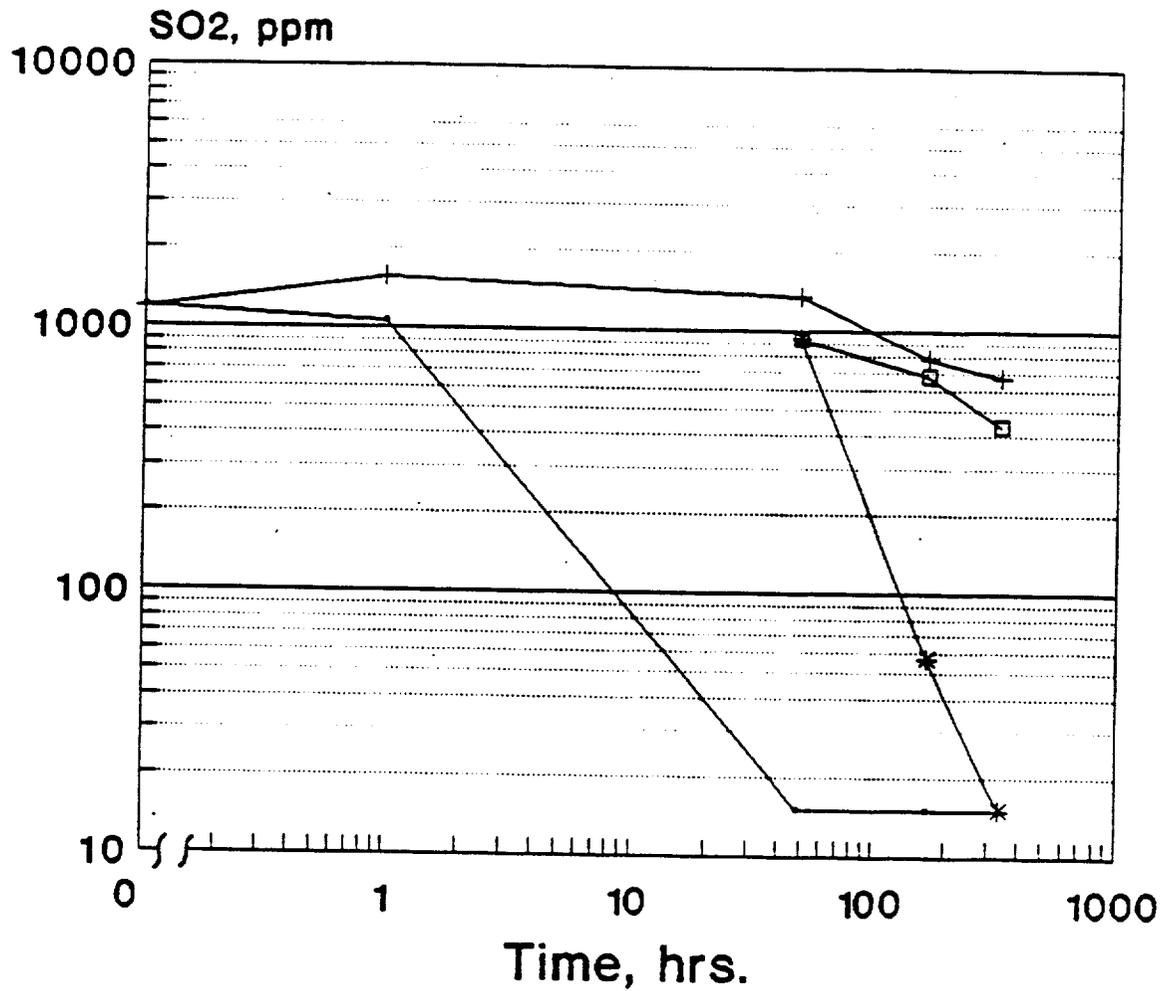
—* Dry #2

—□ Dry #4

10/11/88

N2O Field Test

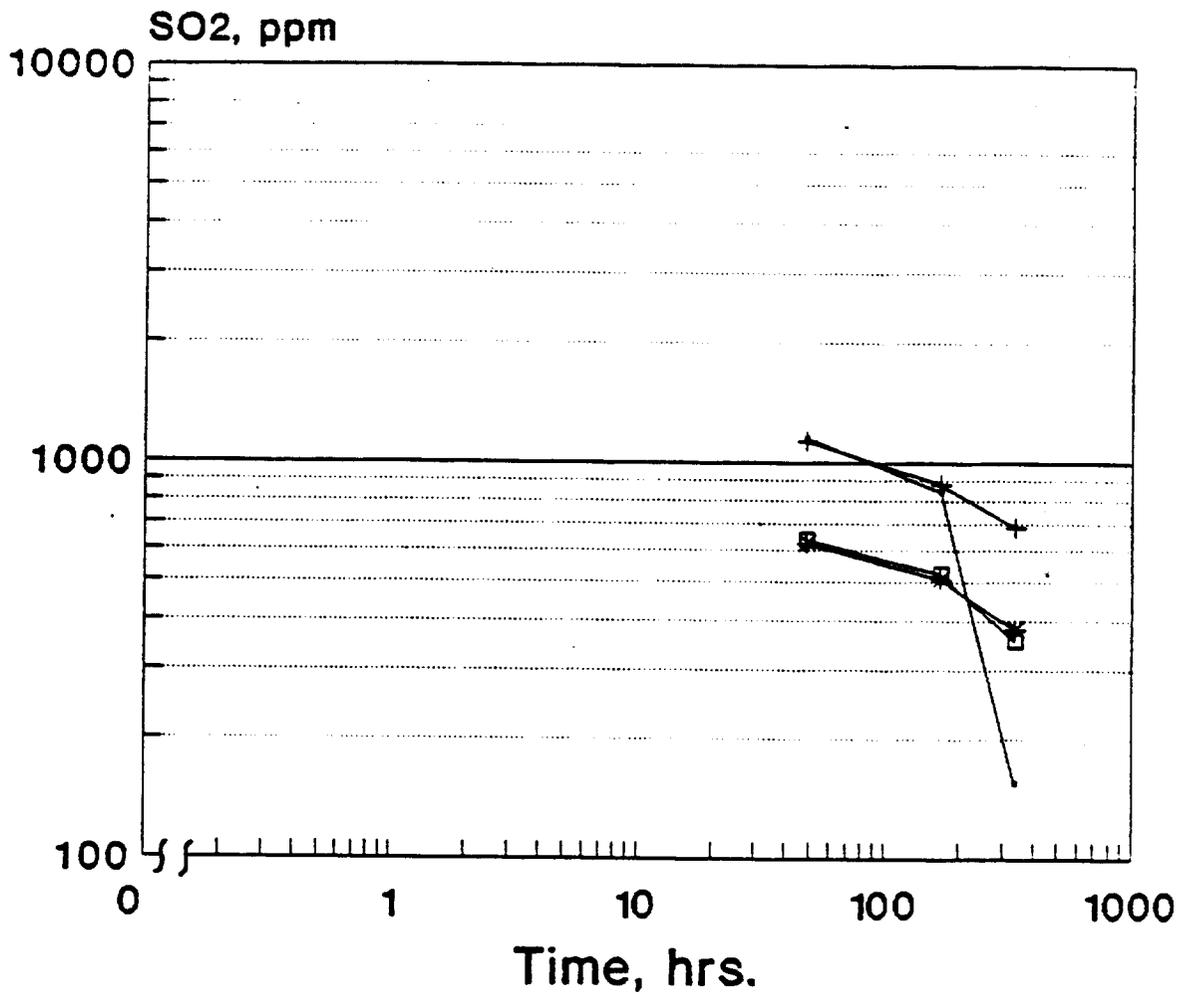
SO2 in SS Containers



— Wet #1 Unit A + Dry #2 Unit A
 * Dry #2 Unit B □ Dry #4 Unit B

10/5/88 Unit A
 10/7/88 Unit B

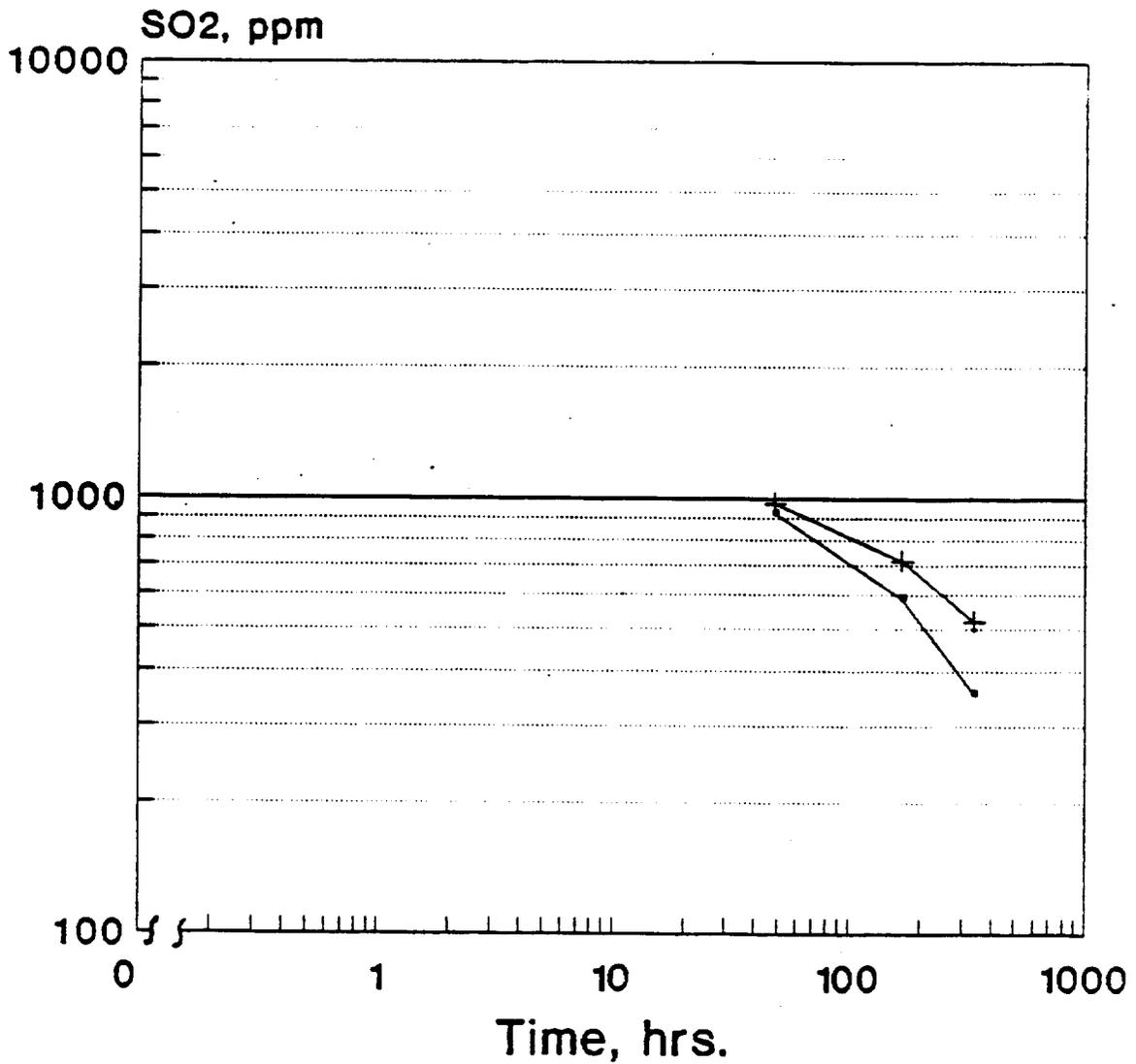
N2O Field Test SO2 in SS Containers



— Dry #2 Unit C	+ Dry #4 Unit C
* Dry #2 Unit D	□ Dry #4 Unit D

10/8/88 Unit C
10/10/88 Unit D

N2O Field Test SO2 in SS Containers



—●— Dry #2 Unit E —+— Dry #4 Unit E

10/11/88 Unit E

TECHNICAL REPORT DATA
(Please read instructions on the reverse before completing)

1. REPORT NO. EPA-600/2-89-006		2.	3. RECIPIENT'S ACCESSION NO.	
4. TITLE AND SUBTITLE N ₂ O Field Study		5. REPORT DATE February 1989		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) R. Clayton, A. Sykes, R. Machilek, K. Krebs, and J. Ryan		8. PERFORMING ORGANIZATION REPORT NO.		
9. PERFORMING ORGANIZATION NAME AND ADDRESS Acurex Corporation P. O. Box 13109 Research Triangle Park, North Carolina 27709		10. PROGRAM ELEMENT NO.		11. CONTRACT/GRANT NO. 68-02-4285, Task 1-015
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development Air and Energy Engineering Research Laboratory Research Triangle Park, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED Task Final: 9-12/88		14. SPONSORING AGENCY CODE EPA/600/13
15. SUPPLEMENTARY NOTES AEERL project officer is William P. Linak, Mail Drop 65, 919/541-5792.				
16. ABSTRACT The report gives results of measurements of nitrous oxide (N ₂ O) emissions from coal-fired utility boilers at three electric power generating stations. Six units were tested, two at each site, including sizes ranging from 165 to 700 MW. Several manufacturers and boiler firing types were represented. Continuous emissions monitor measurements were made for nitrogen oxide (NO), O ₂ , CO ₂ , and CO. On-line N ₂ O measurements were made using a gas chromatograph (GC) with electron capture detection. On-line SO ₂ levels were measured on one unit using a GC with flame photometric detection. Stainless steel (SS) sample containers were used to collect flue gas samples for the evaluation of N ₂ O formation as a function of time in the presence of NO, SO ₂ , and water. The N ₂ O on-line results were in the range from "not detectable" to 4.6 ppm. The results did not exhibit apparent differences related to different boiler types and load conditions. The SS container results showed a trend of immediate N ₂ O formation when SO ₂ and water are present. The N ₂ O concentration in all wet samples increased dramatically within the first hour to concentrations ranging from 9 to 120 ppm. The dry sample results showed a much smaller increase in N ₂ O, ranging from 5 to 25 ppm over the 2 weeks after sampling.				
17. KEY WORDS AND DOCUMENT ANALYSIS				
a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS		c. COSATI Field/Group
Pollution	Gas Chromatography	Pollution Control	13B	
Nitrogen Oxide (N ₂ O)	graphy	Stationary Sources	07B	07D
Emission	Electron Capture	Continuous Emission	14G	20H
Measurement	Flame Photometry	Monitors	14G	14B
Electric Power Plants			10B	
Coal	Combustion		21D	21B
18. DISTRIBUTION STATEMENT Release to Public		19. SECURITY CLASS (This Report) Unclassified		21. NO. OF PAGES 88
		20. SECURITY CLASS (This page) Unclassified		22. PRICE

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