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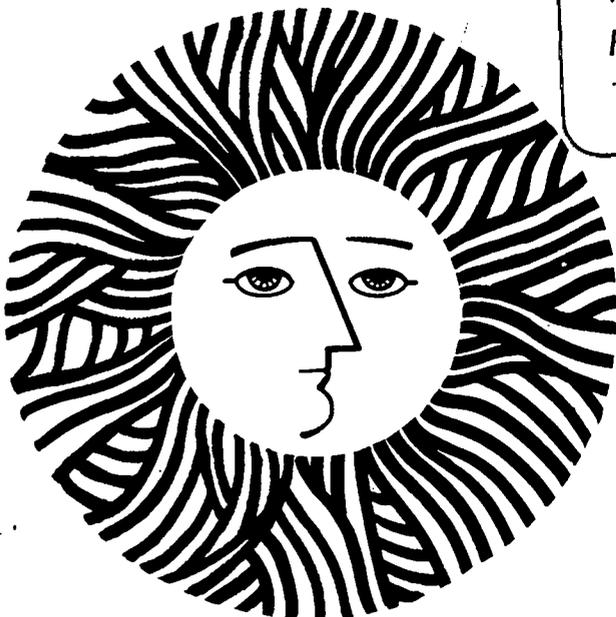
A COMPARATIVE STUDY OF NO MEASUREMENT IN
METHANE/AIR FLAMES

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A COMPARATIVE STUDY OF NO MEASUREMENT IN METHANE/AIR FLAMES

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I. INTRODUCTION

Characterization of nitrogenous emissions from combustion sources and determination of the atmospheric fate of nitrogen compounds are crucial for an assessment of air quality. Generic sources of nitrogen oxides are classified according to how emissions are generated and released to the environment. On a global basis 90% of the oxides of nitrogen emissions are attributable to natural sources, and these are emissions from the nitrogen cycle and lightning. The most preponderate compound associated with the natural source emissions is N_2O . The second source type of oxides of nitrogen is anthropogenic, and the major contribution is due to combustion with mobil and stationary sources contributing equally. In urban environments the distribution between natural and anthropogenic sources is reversed with anthropogenic (and mainly combustion) sources responsible for 90% of the emissions of oxides of nitrogen, mainly as nitric oxide.

Two mechanistic paths are responsible for nitric oxide production during combustion, one involves the oxidation of atmospheric nitrogen (thermal NO) and the other results from NO production from the oxidation of nitrogen chemically bound to fuel molecules (fuel NO). In order to understand mechanistic details of NO formation and destruction mechanisms, it is necessary to have reliable methods for NO quantification in combustion mixtures.

The most frequently utilized technique for NO quantification in combustion environments is chemiluminescent analysis following sample extraction with a probe. There are intrinsic errors associated with such a technique. Since the method is intrusive, it is important that the disturbance to the flow field and temperature field in the vicinity of the microprobe be small to prevent sampling biases. Additional sources of error are homogeneous and heterogeneous reactions in the sampling system

which alter the concentration of NO and NO₂. Furthermore, there are some potential errors associated with the analyzer, namely those attributable to quenching effects which have been described by Matthews et al.¹ and those associated with changes in sample viscosity with sample composition as described by Zabielski et al.²

Non-intrusive optical techniques for NO quantification are highly desirable since they eliminate the potential errors associated with chemiluminescent analysis. Optical methods are not without problems of their own; for instance, problems associated with high temperature calibration require a great deal of ingenuity to solve. A uniform temperature field is required along a line-of-sight absorption measurement which is difficult to achieve for most burner systems. For some optical techniques, (e.g. laser fluorescence) proper accounting for deactivation of the excited state by collisions with chaperone gases is necessary and difficult to quantify experimentally.

In this paper we report on a comparative study of NO measurement in the post combustion environment of atmospheric pressure, premixed methane/air stoichiometric flames. One of the analytical techniques used is probe extraction with uncooled quartz microprobes followed by chemiluminescent analysis in an analyzer specially constructed to eliminate most of the errors associated with viscosity and third body quenching effects. The other technique utilized is a non-intrusive spectroscopic technique called tunable atomic line molecular spectroscopy (TALMS).

Although the TALMS technique is relatively new for combustion applications, utilization of the Zeeman effect to achieve differential absorption measurements has been available for some time. The magnetic scanning of a single Zeeman component of an atomic emission line was first

used by Bitter and co-workers³ for investigating the hyperfine structure and isotope shift of the resonance radiation of mercury. This technique was utilized by Hadeishi and McLaughlin⁴ to develop a new type of atomic absorption spectrometer to detect trace mercury, and utilizing the Zeeman effect for background correction. The technique has been extended to the detection of small molecules which exhibit sharp rotational structure⁵, and has been used to detect NO, NO₂, SO₂ and HCHO⁶. Cuellar and Brown^{7,8} have recently used the technique to detect S₂ in the presence of SO₂ and to resolve several closely spaced lines belonging to different branches which result from the triplet splitting in the (7,2) band of the B³Σ_u⁻ - X³Σ_g⁻ system of S₂.

II. EXPERIMENTAL

A. Flat Flame Burner

A schematic diagram of the experimental system is shown in Figure 1. Methane-air flames were stabilized at atmospheric pressure on a water cooled porous plug flat flame burner. The burner was constructed from a 6.0 cm diameter sintered bronze disk with a porosity of 100 microns. Water cooling was provided by a copper coil imbedded in the sintered disk with the plane of the coil parallel to the burner surface. The burner was mounted below the optical path of the tunable atomic line molecular spectrometer (see below) through an opening in the optical bench. A micrometer driven x-y-z translation stage permitted motion of the burner relative to the fixed focused optical beam.

Methane (Matheson C.P. grade, 99.0% minimum purity) and air were supplied in high pressure gas cylinders. Calibration gases consisting of various concentrations of NO in N₂ were obtained from AIRCO (97 ppm, 511 ppm, and 4.41% NO in N₂). The calibration gases were checked against NBS standards by the Air and Industrial Hygiene Laboratory of the State of California Department of Health. The 97 and 511 ppm NO/N₂ gas mixtures were used to calibrate the chemiluminescent gas analyzer. The 4.41% NO/N₂ gas was used to dope the CH₄/air flows with varying amounts of NO while keeping the total flow constant.

Gas flows were metered separately using rotameters (Matheson, 600 Series) which were calibrated using a wet test meter. These calibrations were checked against calibrations obtained using a rotating vane dry test meter (Singer American Meter Division, Model DTM-325), and Brooks Vol-U-Meter gas calibrators.

A cylindrical stainless steel mixing chamber 30 cm long and 4.8 cm

i.d. was packed with glass beads to provide adequate mixing of the gases prior to flowing into the flat flame burner. Methane and air were introduced near the top of the chamber through two 3/8-inch ports placed opposite to each other and perpendicular to the axis of the mixing chamber. The NO/N₂ dopant was introduced via a 1/8-inch stainless steel tubing penetrating through the top flange of the chamber and terminating midway between the CH₄/air ports. Gases exiting from the chamber then flowed into the burner, or alternatively, a portion of the cold flow could be diverted directly into the chemiluminescent analyzer.

The chemiluminescent gas analyzer (CLA) and the gas mixing system were tested by introducing known amounts of NO/N₂ into a N₂ stream (metered through calibrated rotameters). Part of this flow was sampled by the CLA and quantified using the 97 and 511 ppm NO/N₂ calibration gases. No significant differences were found between the two measurements: in the range tested from 50 to 2500 ppm NO, the concentration of NO measured by the CLA was an average of 3.2 ± 1.8% higher than the concentration of NO determined from the rotameter calibrations of the NO/N₂ and N₂ flows.

Stable CH₄/air flat flames were obtained over a wide range of equivalence ratios and total gas flows. We selected to operate the burner at a total flow $\dot{Q}_T = 30,000$ sccm, corresponding to a linear velocity of 17.7 cm/sec. At this flow, stable flames could be obtained at equivalence ratios ϕ ranging from 0.75 to 1.5.

Temperature profiles were obtained using a Pt/Pt-13% Rh thermocouple. The thermocouple was constructed from 0.076 mm diameter wire which was butt welded to form a junction whose diameter (0.102 mm) was only slightly larger than that of the wire. The thermocouple wire was 12 mm long and was supported between two 0.254 mm support wires with the junction at the

center. In the determination of temperature profiles above the burner the thermocouple junction lead wires were placed parallel to the burner surface to minimize heat conduction losses to the support wires. Vertical and radial temperature profiles are shown in Figures 2 and 3. Temperatures reported here are not corrected for radiative losses.

B. Chemiluminescent Gas Analyzer

Gas samples were withdrawn from the flame through a 10 cm long, 1 mm i.d. uncooled quartz probe. The orifice diameter at the tip of the probe was 314 microns. The probe was mounted on a x-y-z micrometer driven translation stage which allowed for reproducible positioning of the tip of the probe relative to the burner surface. The probe itself was located at a 65° angle with respect to the normal to the burner surface. A heated teflon sampling line 90 cm long, 2 mm i.d., connected the probe to a valve at the rear of the chemiluminescent analyzer. The pressure just upstream of this valve was measured to be 330 torr. The sampling line was heated to 65°C to prevent water condensation. Downstream from the valve the pressure dropped to 45 torr. The effect of the high sampling line pressure is discussed in more detail below.

Nitrogen oxides (NO and NO_x) were measured with a laboratory built chemiluminescent gas analyzer (CLA). This analyzer is similar in design to commercially available instruments, but incorporated several features which significantly reduced the corrections associated with viscosity and third body quenching effects. A calibrated rotameter was used to maintain a constant and known flowrate of oxygen plus ozone from the ozone generator. The sample flow rate was measured using a mass flow meter (Tylan Corporation), and the ratio of $\text{O}_2 + \text{O}_3$ to sample was maintained at 0.94. The CLA was operated at a reaction chamber pressure of 3 torr. By adjusting the flow of the sample stream such that 6% of the gas in the

reaction chamber was due to probed sample while 94% was due to the $O_2 + O_3$ stream, the effects of third body quenching can be significantly reduced. For example, using the quenching corrections of Mathews et al.¹, and the calculated equilibrium concentrations⁹ of major species present in a CH_4 /air flame at $\phi = 1.0$ (N_2 , H_2O , CO_2 , H_2 , CO , Ar), the actual NO is found to be 4.2% higher than the indicated NO concentration.

A commercially built NO_x to NO converter (Thermo Electron Corp.) was used to convert NO_2 to NO so that the total oxides of nitrogen (NO_x) could be measured. The converter consisted of No. 316 stainless steel tubing 1.8 m long and 3.22 mm diameter which is resistance heated to $650^\circ C$. The converter was operated at a pressure of 45 torr.

The NO_x converter was conditioned on a daily basis by passing a mixture of NO_2 in air ($0.533 \pm 1\%$, Airco) through the converted heated to $650^\circ C$ for a minimum of 15 minutes. Survival of NO was checked by passing 97 or 511 ppm NO/N_2 calibration gas through the hot converter and comparing the signal obtained with that recorded bypassing the converter. No significant difference was observed: the signal obtained through the converter was 1.8% lower than that observed bypassing the converter.

The converter efficiency in effecting the conversion of NO_2 to NO was checked by passing various concentrations of the 0.533% NO_2 /Air gas diluted in N_2 . On average, the NO concentration detected by the CLA in the NO_x mode (through the converter) was 5% higher than the NO_2 concentration as determined from the rotameter calibrations. This small discrepancy (indicating $>100\%$ conversion efficiency) with the manufacturer's claim of 100% conversion efficiency of NO_2 to NO could not be explained by the presence of NO in the NO_2 /air mixture.

Light emitted by the chemiluminescent reaction of NO with O_3 was

detected by a photomultiplier tube (EMI 9558A) filtered through a CS2-63 Corning filter to block wavelengths below 6000Å. The output of the PMT was measured on a Keithley electrometer and displayed on a strip chart recorder. The response curve of the CLA shown in Figure 4 is linear in NO concentration to at least 2400 ppm NO. These measurements were later extended to NO concentrations greater than 6000 ppm with no observable deviation from linearity.

C. TALM Spectrometer

Probe measurements of thermal NO produced in the CH₄/air flat flame burner were compared with measurements using a non-intrusive spectroscopic technique called tunable atomic line molecular spectroscopy (TALMS). This technique has been pioneered by Hadeishi and his co-workers^{5,6}, and has been utilized to determine low concentrations of NO in a room temperature absorption cell with high selectivity and sensitivity¹⁰. These authors used the accidental near coincidence between the Cd ion line at 214.438 nm and discrete rotational-vibrational lines in the A²Σ⁺ - X²Π,γ bands of NO. By using a single isotope, ¹¹⁴Cd, they reported a detection limit of NO in N₂ of 180 ppb in a 20 cm cell.

The basis for detection of molecules by tunable atomic line molecular spectroscopy is the splitting and polarization of atomic emission lines by an external magnetic field. In a direction parallel to the magnetic field, the Cd line at 214.4 nm is split into σ⁺ and σ⁻ circularly polarized components: the high frequency σ⁺ component is circularly polarized in a counterclockwise direction, while the low frequency σ⁻ component is circularly polarized in the opposite direction. By varying the strength of the magnetic field, one of the Zeeman components of the Cd emission line is tuned into exact coincidence with a discrete rotational-vibrational line in the γ band of NO. The matching Zeeman component indicates the extent of

absorption by NO, while the unmatched σ component indicates background absorption only. A differential measurement of the matched and unmatched Zeeman components of the Cd emission line provides a quantitative measurement of the NO in the optical path.

A schematic diagram of the TALM spectrometer is shown in Figure 1. Except for the light source, the instrument is identical to that described earlier⁸. The lamp¹¹ consists of a sealed-off quartz U-tube containing a small amount of cadmium metal (natural abundance Cd) and an inert buffer gas. Nichrome wire heaters wrapped around the U-tube are used to heat the lamp to a few hundred degrees Celsius and provide a small amount of vaporized Cd (~ 1 torr) which is excited by an electric discharge through the gas. The lamp is housed between the poles of a Varian electromagnet, and the light emitted parallel to the magnetic field is focussed with a quartz lens to a 2 mm diameter spot above the burner surface. The variable phase retardation plate in combination with the linear polarizer allows for the alternate transmission of the matched and unmatched Zeeman components through the monochromator to the detector. The output of the photomultiplier tube is processed electronically and displayed on a strip chart recorder.

To determine the conditions of maximum sensitivity, the differential absorption between σ^+ and σ^- components was measured as a function of magnetic field strength, and is shown in Figure 5. Maximum sensitivity was obtained at 11 kG, and all measurements reported here were taken at this field strength. The dependence of the differential absorption signal due to NO on magnetic field strength shown here is considerably broader than that reported in reference 10. This is because we used natural abundance Cd rather than the single isotope ¹¹⁴Cd, resulting in a broadening of the

emission line by the hyperfine structure of the odd isotopes of naturally occurring cadmium.

The response of the TALM spectrometer to increasing NO concentration is shown in Figure 6. In these experiments the CH₄ and air were mixed in the gas mixing chamber and varying amounts of 4.41% NO/N₂ gas were added. A portion of the gas stream was passed through a 7.5 cm long flow cell placed in the optical path of the spectrometer, while the remainder of the flow was exhausted to a hood. The observed signal was linear in NO concentration to about 1200 ppm NO. At 2000 ppm NO, the percent transmission through the absorption cell was about 28%, and the observed signal is 10% low with respect to the extrapolated linear response. This deviation from a straight line is probably caused by a departure from the Beer-Lambert absorption.

III. RESULTS

A. Probe Measurements of NO

Vertical and horizontal profiles of NO concentration were measured using the uncooled quartz probe and the chemiluminescent gas analyzer, and are shown in Figures 7 and 8. The vertical profile is taken at the center of the burner, and it can be observed that the NO concentration rises slightly from about 13 ppm at 2 mm above the burner surface to 18 ppm at 15 mm above the burner. These concentrations would need to be increased by about 4% to correct for third body quenching in the reaction chamber of the CLA (see above).

The results of adding known amounts of NO to the burner and sampling with the probe are shown in Figure 9. The probe position was kept constant at a height of 5.0 mm above the center of the burner surface. The dashed line represents 100% survival of NO. Clearly a deviation from the line of 100% survival is observed. The survival of NO defined as NO measured/NO added, is approximately 80%.

The discrepancy between NO measured and the total NO (NO added + NO thermal) cannot be attributed to non-linearity of the CLA (see Figure 4) or to losses or anomalies in the gas mixing system (see above). With the CLA operated in the NO_x mode, thermal NO_x was found to be about 30% higher than that measured in the NO mode.

B. Optical Measurements of NO

Optical measurements of NO using tunable atomic line molecular spectroscopy were obtained by doping the burner gases with known amounts of NO. The cadmium atomic emission line was focussed to a 2 mm diameter spot 5.0 mm above the burner surface with the optical axis along the centerline of the burner. A typical recorder trace of the differential absorption signal observed by thermal NO and added NO is shown in Figure 10. A range

of NO concentrations from 50 to 1000 ppm was added to the burner, and a plot of the observed signal strength as a function of NO added is shown in Figure 11. Extrapolation to zero doping of NO results in an estimate of the thermal NO measured optically of 60 ppm. This optical measurement is more than three times larger than the thermal NO measured with the chemiluminescent analyzer and the uncooled quartz probe.

A series of calibration experiments was attempted using heated quartz cells. These cells were 14.3 cm long and were filled with 152 torr of 97 ppm NO in N₂ calibration gas. Upon heating in a Lindbergh furnace to 1000°C, the TALMS signal due to NO disappeared, and was not recovered by cooling the cell to room temperature. .pa

IV. DISCUSSION

Much research has been directed toward the development and characterization of analytical techniques for NO measurement in combustion mixtures. Bowman¹² has reviewed probe measurements in flames for a variety of probe types and combustion conditions. He indicates that the major fluid mechanical disturbance to the subsonic flow field by the probe is streamline distortion, which in turn, results in a perturbation of concentration gradients in the vicinity of the probe. This is not a serious problem for measurements in the post flame region where concentration gradients are very small. A potentially more serious problem discussed in the review regards composition changes due to inadequate quenching of homogeneous and/or heterogeneous reactions in the probe. Bowman states that for many species measurements convective quenching probes generally are not suitable for concentration measurements in laminar flames due to the relatively slow cooling rates.

Cernansky¹³ has reviewed sampling and measurement of NO and NO₂ in

combustion systems, and, in particular, has discussed the effects of probe materials, the chemiluminescent analyzer, and combustion conditions which enhance the concentration of NO_2 . The role of uncooled quartz probes in altering measured NO/NO_2 ratios is discussed, as well as the behavior of catalytic converters in effecting NO_2 to NO conversions. Under fuel rich conditions stainless steel converters can reduce NO to N_2 and O_2 concurrently with the reduction of NO_2 to NO , thus yielding an error in total NO_x . The importance of this observation for stoichiometric flames is not clear.

Meinel and colleagues¹⁴⁻¹⁷ report on comparative studies on NO measurement in combustion systems in a series of papers. A new non-dispersive ultraviolet analyzer was described which had a limit of detectability of approximately 0.5 ppm for an absorption cell of 39 cm. Concentrations of NO were measured in an engine using this technique and compared with those from a chemiluminescent analyzer. Samples were extracted from the engine with quartz microprobes for both analyses, and a stainless steel converter was interfaced with each instrument to effect conversion of NO_2 to NO to achieve a total NO_x measurement. Measurements with both instruments agreed to within 10% or less for a range of equivalence ratios between 0.8 and 1.1. Quenching corrections for the CLA, the conditions in the reaction chamber, (the ozonated oxygen to sample ratio, and the pressure), and the flow metering techniques were not specified. A study comparing the measurement of NO in propane/air and hydrogen/air flames using an in situ differential absorption technique and a non-dispersive ultra violet technique of a sample extracted with a cooled quartz microprobe was described in the last paper¹⁷ of the series. Good agreement was obtained for the two types of NO measurements in lean flames, but for stoichiometric and rich flames the in situ measurements were

between 20 and 30 percent lower. The authors speculate that NO may have been produced within the probe.

Falcone¹⁸ measured NO in lean and rich atmospheric methane/air flames. The concentration of NO was adjusted through doping. Three types of NO measurements were compared. Two involved sample extraction with uncooled quartz microprobes and one was an in situ method. In a series of experiments samples were extracted from both lean and rich flames and then passed through an analytical train into a CLA analyzer or into an absorption cell where NO was detected by laser absorption spectroscopy utilizing a tunable diode laser as a light source. After quenching corrections for the CLA were made, agreement between the measurements using the two detectors was very good. In another series of experiments NO concentrations measured in situ with laser absorption and by CLA following sample extraction were compared for both lean and rich flames. Although discrepancies among various data reduction procedures for in situ measurements prevail throughout the experiments, no discrepancy greater than 20% was claimed for the measurements in lean flames. No destruction of NO was detected in the lean flames, within experimental error. Although significant scatter was observed in the in situ measurements, it appeared that a portion of the NO was destroyed in the rich flames. Concentrations of NO measured in the rich flames by laser absorption and probe sampling/CLA agreed to within 20 percent. It is important to note that the lower level of detection of NO for the in situ technique was 200 ppm.

One of the most extensive studies of optical and probe CLA measurements of NO in combustion systems has been described in a series of papers of Zabielski et al^{2,19} and reports by Dodge et al²⁰, Colket et al²¹, and Zabielski et al²². Many of the measurements were performed on NO

seeded, laminar atmospheric $\text{CH}_4\text{-O}_2\text{-N}_2$ flames. Probes were water-cooled quartz or stainless steel, and analyses of probe behavior indicated that quenching of the gas sample was achieved through convection. No aerodynamic quenching was obtained for the water cooled probes in spite of pressure ratios as low as 0.05. They indicate that no particular advantage is gained from back pressures less than 0.5 atmospheres for sampling from atmospheric pressure flames. The in situ measurements of molecular absorption were accomplished using a hollow cathode resonant lamp or a high pressure Xe lamp. Flames of three different equivalence ratios were investigated, $\phi = 0.8, 1.0$ and 1.2 . No major discrepancies ($>25\%$) were found between the in situ and probe/CLA measurements. The ratio of probe to spectroscopic values taken under the same conditions in premixed flames were greater than 1.0.

Although there is disagreement regarding whether optical or probe measurements of NO doped CH_4 /air flat flames are higher, there is general agreement that discrepancies are less than 30%. These results appear to be true for uncooled quartz probes as well. Most of these measurements required relatively high concentrations of added NO due to the lack of sensitivity of the various optical techniques used.

Figure 9 shows the concentration of NO measured in the post flame region with the chemiluminescent analyzer as a function of added NO. Thermal NO (see also Figures 7 and 8) is measured to be 16 ppm. Applying a 4.2% quenching correction (see above, section II B) and accounting for conversion from NO to NO_2 as determined by measurements in the NO_x mode of the analyzer (see above, section III A) increase the thermal NO to about 22 ppm. By contrast, the optical measurement of thermal NO produced in the same flame and measured at the same height above the burner (5.0 mm) is 61 ppm.

It is important to consider in more detail the nature of the differences between these two measurements. The probe measured NO represents the sum of the NO added and NO thermal less the NO lost in the flame or in the probe sampling system. Quenching effects and mixing losses have already been accounted for. Signal intensity obtained with CLA can be related to NO concentration since the instrument is linear and reliable calibration mixtures are available and give consistent results. On the other hand, signal intensity obtained with the TALM spectrometer as a function of NO added to the flame cannot be easily converted into NO concentration in our experimental system. The data shown in Figure 11 are extrapolated to zero doping (i.e., thermal NO) assuming no losses through the flame. For example, referring to Figure 10, it is assumed that the concentration due to thermal NO can be determined quantitatively by assigning the signal increase first observed to a concentration of 256 ppm NO. Any loss of NO in the flame is not accounted for. If a loss mechanism does prevail, however, the thermal NO concentration would exceed 61 ppm.

Table I summarizes the data which are shown graphically in Figures 9 and 11. In both cases the experimental points were fitted by a least squares analysis, and the regression constants obtained were used to calculate the measured NO_{CLA} and NO_{TALMS} for given added NO. The NO_{TALMS} were determined assuming no NO losses in the flame. At NO concentrations comparable to those used by other experimenters¹⁴⁻²², the ratio of NO_{TALMS}/NO_{PROBE} assumes values similar to those reported. It is important to note that the tabulated ratios would be somewhat smaller if a loss mechanism were assumed for the NO_{TALMS} values.

The TALMS technique employed here offers greater sensitivity than previous in situ optical measurements of NO. At these lower NO

concentrations, the discrepancy between in situ and probe measurements is significantly greater. The thermal NO measured with the chemiluminescent analyzer is approximately a factor of three lower than the optical in situ measurement.

It is important to question the validity of our probe data considering the high back pressure in the probe. The higher pressure increases the residence time of the sample in the probe, increasing the significance of homogeneous and heterogeneous reactions in the uncooled quartz probe. Colket et al.²¹ have investigated probe effects in detail and have suggested ways of reducing sampling probe effects. Lucas²³ has examined the effect of the probe back pressure in experiments using our experimental apparatus comparing measured NO for different values of probe back pressure. For pressures between 330 and 65 torr, measured NO levels differ by less than 10%.

V. CONCLUSIONS

A comparative study of nitric oxide measured in the post combustion environment of an atmospheric premixed CH_4/air stoichiometric flat flame has been conducted. An uncooled quartz microprobe was used for sample extraction, and analysis was accomplished by a chemiluminescent gas analyzer modified to reduce quenching and viscosity corrections. The in situ optical technique employed is called tunable atomic line molecular spectroscopy, and is based on the splitting and polarization of atomic emission lines induced by an external magnetic field.

Concentrations of NO were determined by doping the burner with known amounts of NO. At NO doping levels near 1500 ppm, the ratio $\text{NO}_{\text{optical}}/\text{NO}_{\text{probe}} = 1.3$ was in agreement with that reported by others. The high sensitivity of the TALMS technique permitted measurement in the thermal NO range ($\text{NO} < 100$ ppm). We found optical measurements of thermal NO to be approximately three times larger than the corresponding probe measurements.

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TABLE I

NO_{added} (ppm)	NO_{CLA} (ppm)	NO_{TALMS} (ppm)	$\frac{NO_{\text{OPTICAL}}}{NO_{\text{PROBE}}}$
50	61	110	1.80
75	81	136	1.68
100	100	160	1.60
150	139	210	1.51
200	178	260	1.46
250	217	310	1.43
500	411	560	1.36
750	605	810	1.34
1000	799	1060	1.33
1250	993	1310	1.32
1500	1187	1560	1.31

FIGURE CAPTIONS

- FIGURE 1 Schematic diagram of the experimental apparatus: EM electromagnet; S atomic light source; L quartz lens; B porous plug burner; T x-y-z translation stage; Q uncooled quartz probe; CLA chemiluminescent gas analyzer; VPRP variable phase retardation plate; M monochromator; D photomultiplier tube; C mixing chamber; R rotameters.
- FIGURE 2 Vertical temperature profile of the CH₄/air flat flame measured at the center of the burner. Temperatures are not corrected for radiative losses. $\phi = 1.00$; $Q_T = 30,000$ sccm.
- FIGURE 3 Horizontal temperature profile of the CH₄/air flat flame measured at a height of 5.0 mm above the burner surface. Temperatures are not corrected for radiative losses. $\phi = 1.00$, $Q_T = 30,000$ sccm.
- FIGURE 4 Response curve for the chemiluminescent gas analyzer. This signal strength is seen to be linear in NO concentration to at least 2500 ppm NO.
- FIGURE 5 Differential absorption signal due to NO as a function of magnetic field strength. Maximum sensitivity was observed at 11 kilogauss. The Cd light source contained natural abundance cadmium.
- FIGURE 6 TALMS signal as a function of increasing concentration of NO. The solid line represents the linear response. At 1000 ppm NO, the measured signal is 2.8% below the extrapolated linear response. This deviation from linearity increases to 5.1% at 1500 ppm NO and 10.4% at 2000 ppm NO.
- FIGURE 7 Probe measurement of NO concentrations as a function of height above the burner surface. These values are taken at the center of the burner, and are not corrected for third body quenching effects.
- FIGURE 8 Radial profile of NO concentrations measured with an uncooled quartz sampling probe. The NO concentrations are not corrected for third body quenching effects.
(a) 15.0 mm above the burner surface
(b) 5.0 mm above the burner surface
- FIGURE 9 NO measured versus NO added determined with an uncooled quartz probe and the chemiluminescent gas analyzer. The probe is fixed 5.0 mm above the center of the burner. Significant deviation from the dashed line representing 100% NO survival is observed. The thermal NO concentration is 16 ppm.

FIGURE 10

Strip chart recorder trace showing the differential absorption signal obtained by TALMS. The chart drive of the recorder was stopped at the point when NO was added, and re-started once the signal stabilized. (~1 minute later). The maximum differential absorption signal corresponds to 256 ppm added NO plus thermal NO. The decay of this signal corresponds to halting the added NO; turning the burner off results in the loss of thermal NO.

FIGURE 11

Signal strength measured by TALMS versus NO added, for a stoichiometric CH₄/air flame ($\phi = 1.00$). A least squares fit of the data points results in the equation

$$S = 3.07 \times 10^{-4} [\text{NO}]_{\text{added}} + 1.87 \times 10^{-2},$$

where S is the signal strength in arbitrary units and the coefficient of correlation is 0.987.

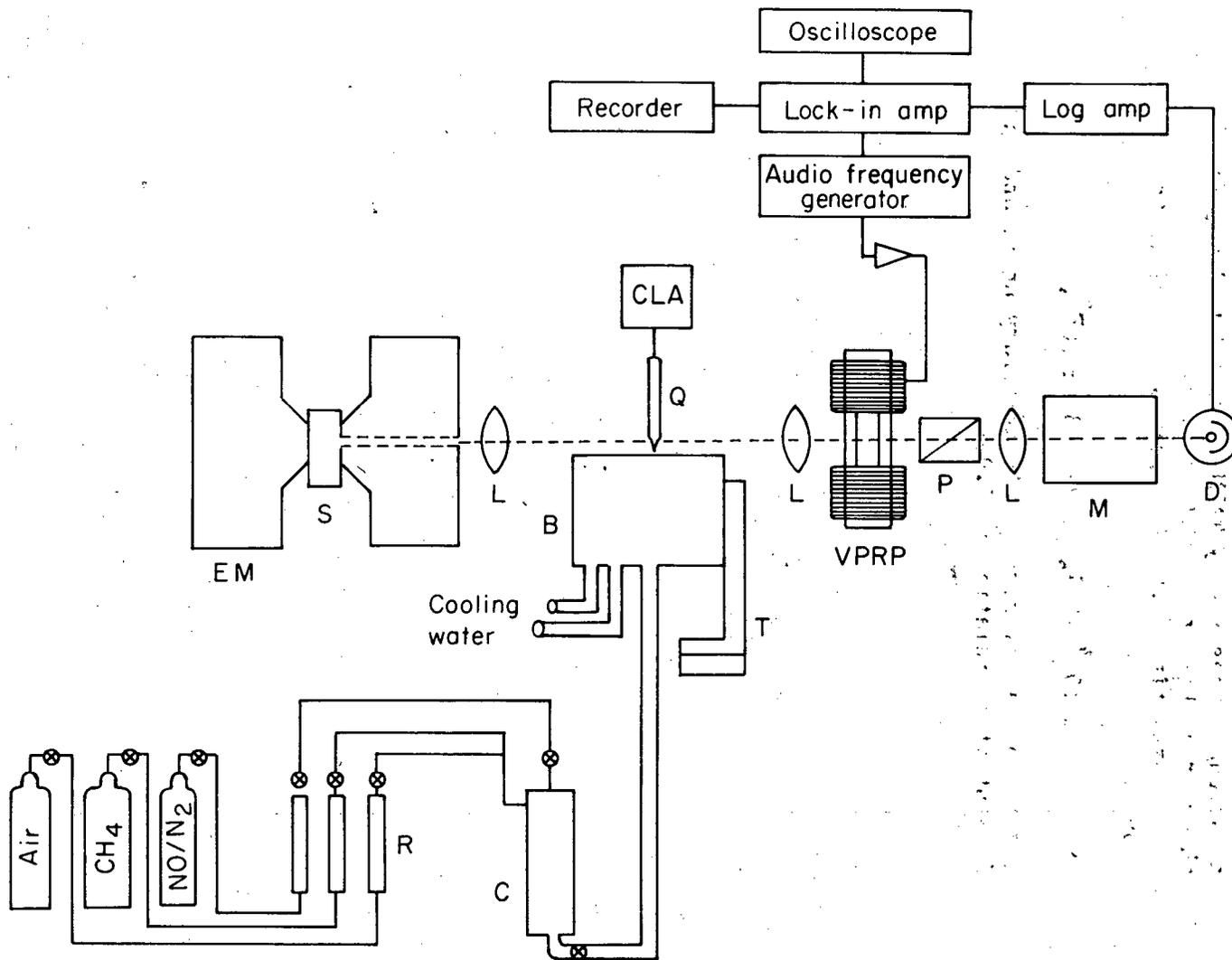
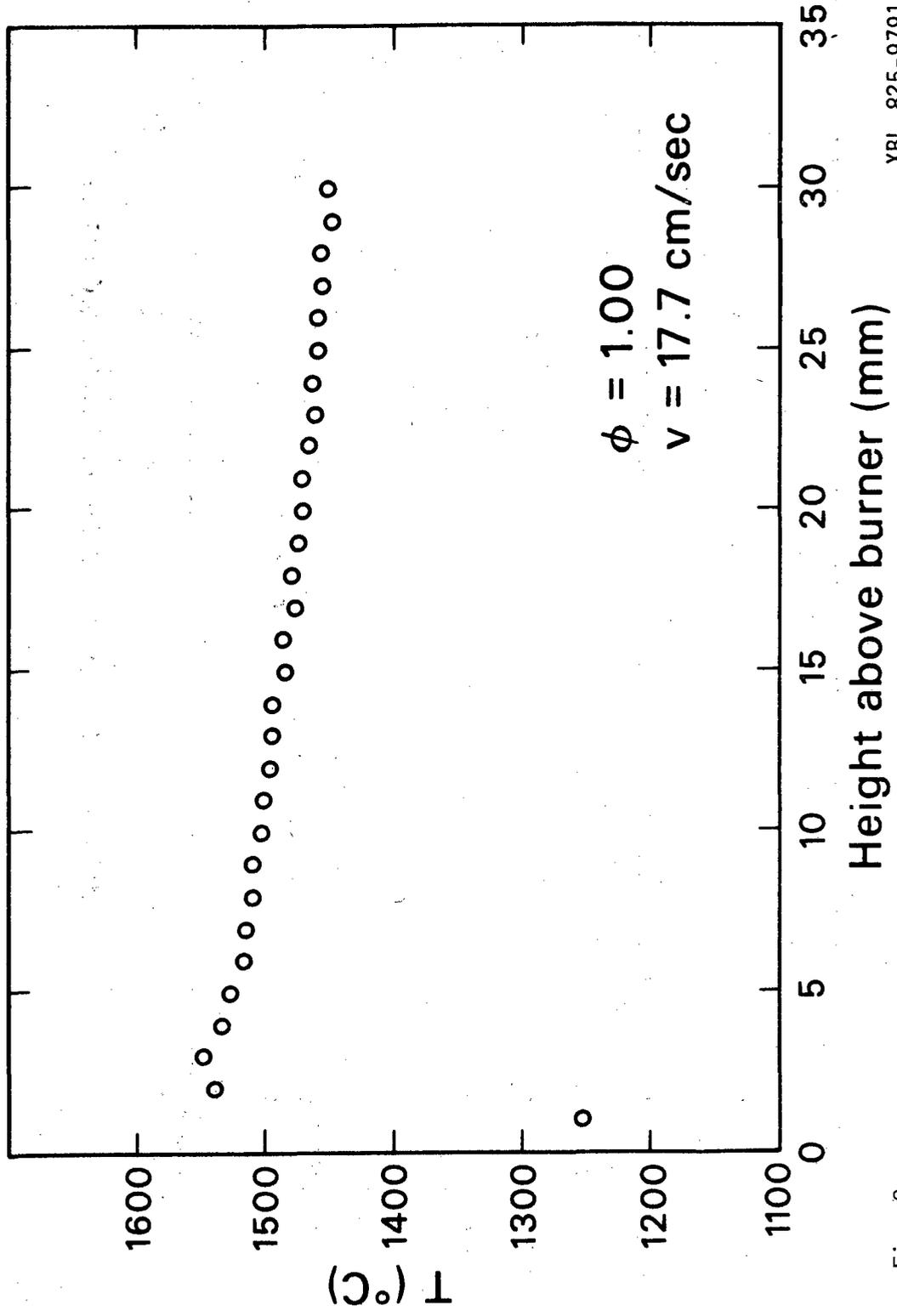


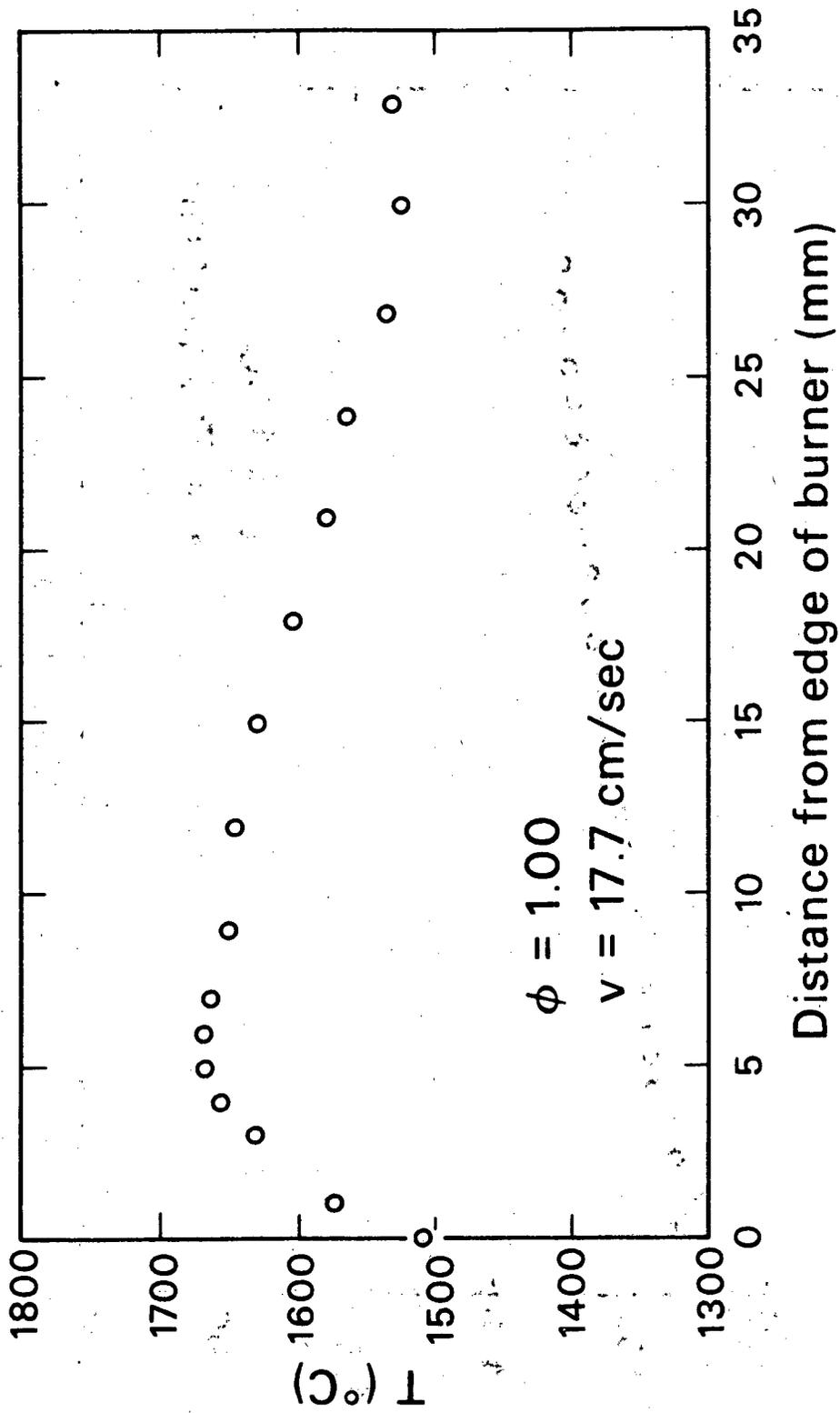
Fig. 1

XBL 822-4489



XBL 825-9791

Fig. 2



XBL 825-9792

Fig. 3

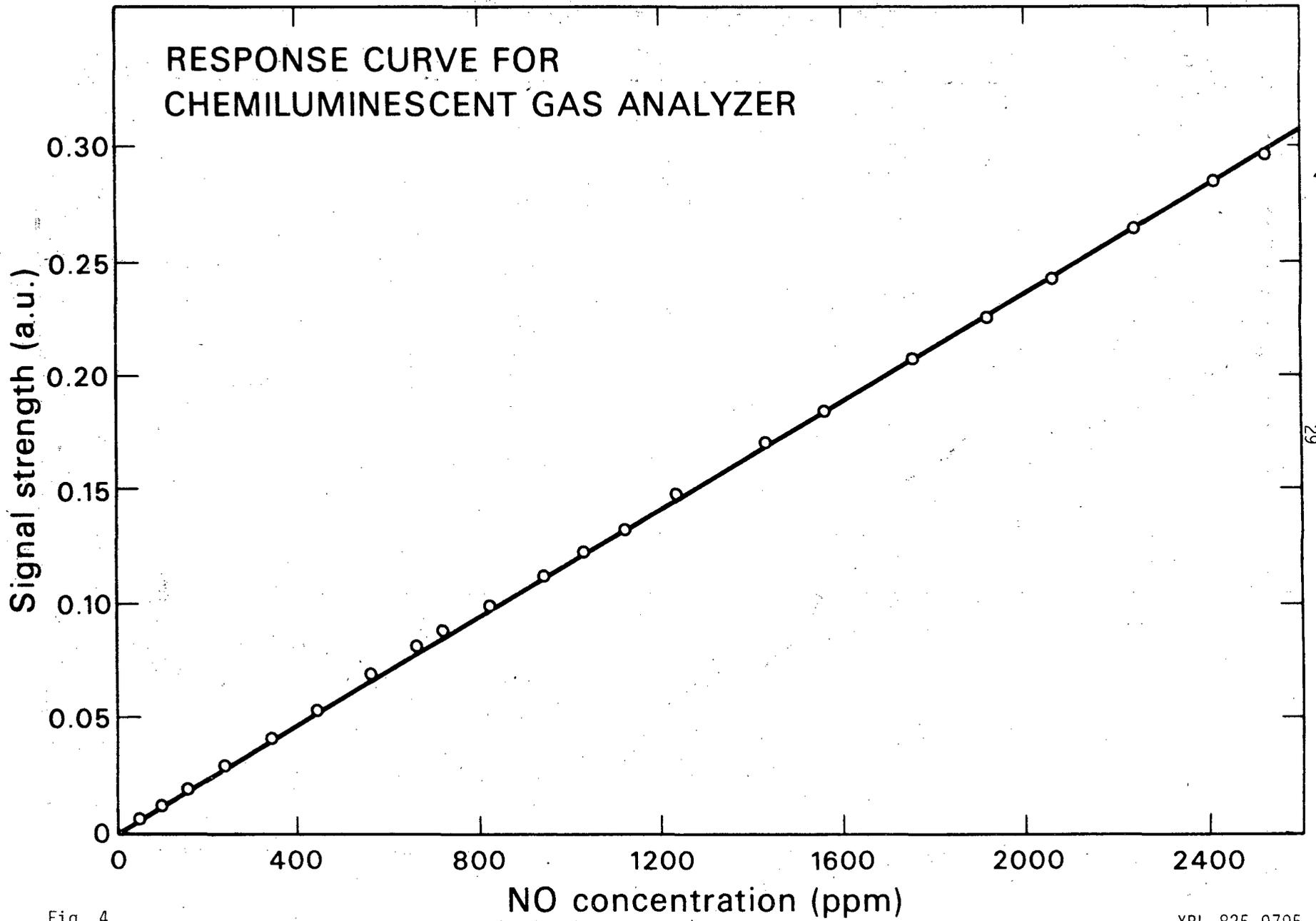
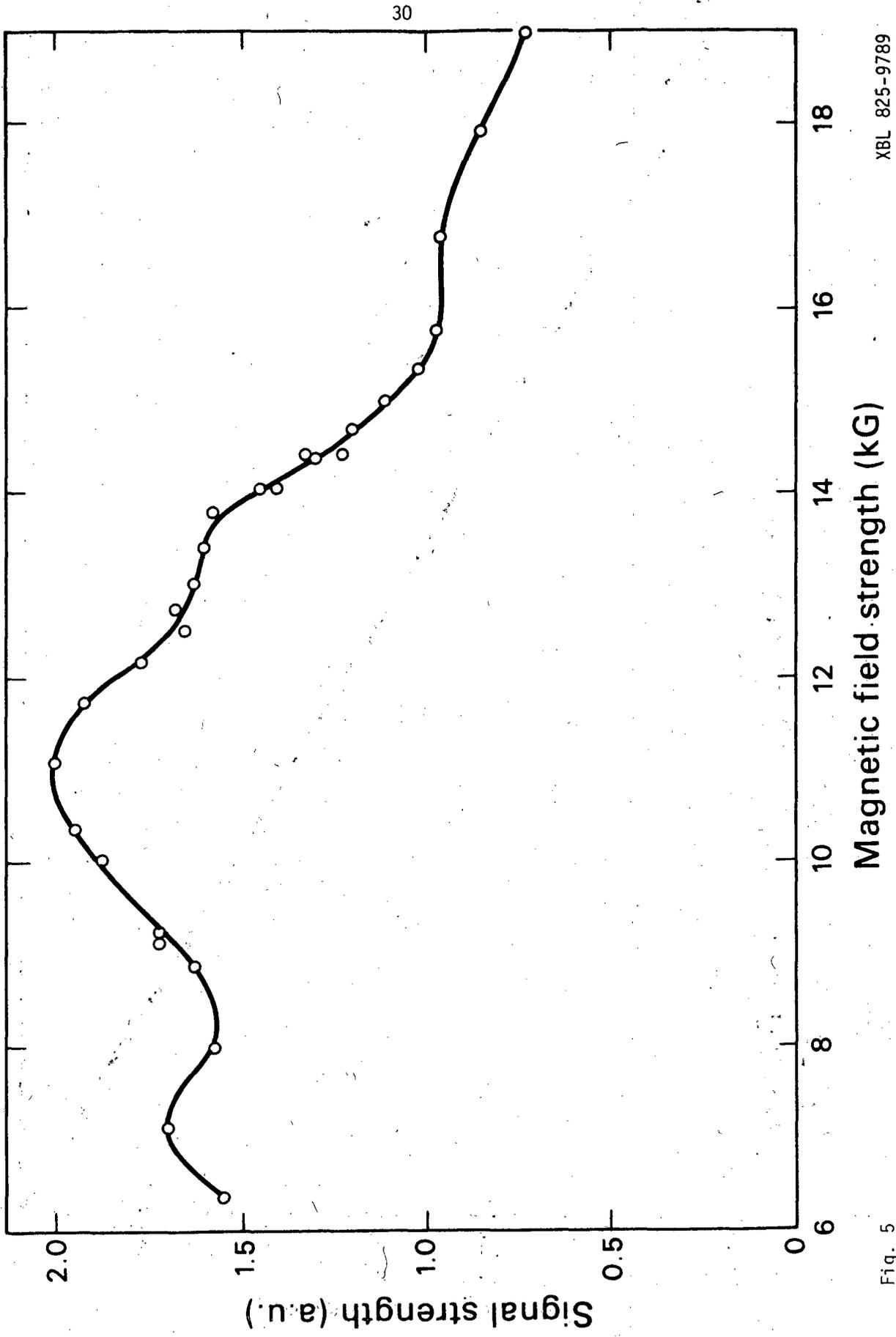


Fig. 4



XBL 825-9789

Fig. 5

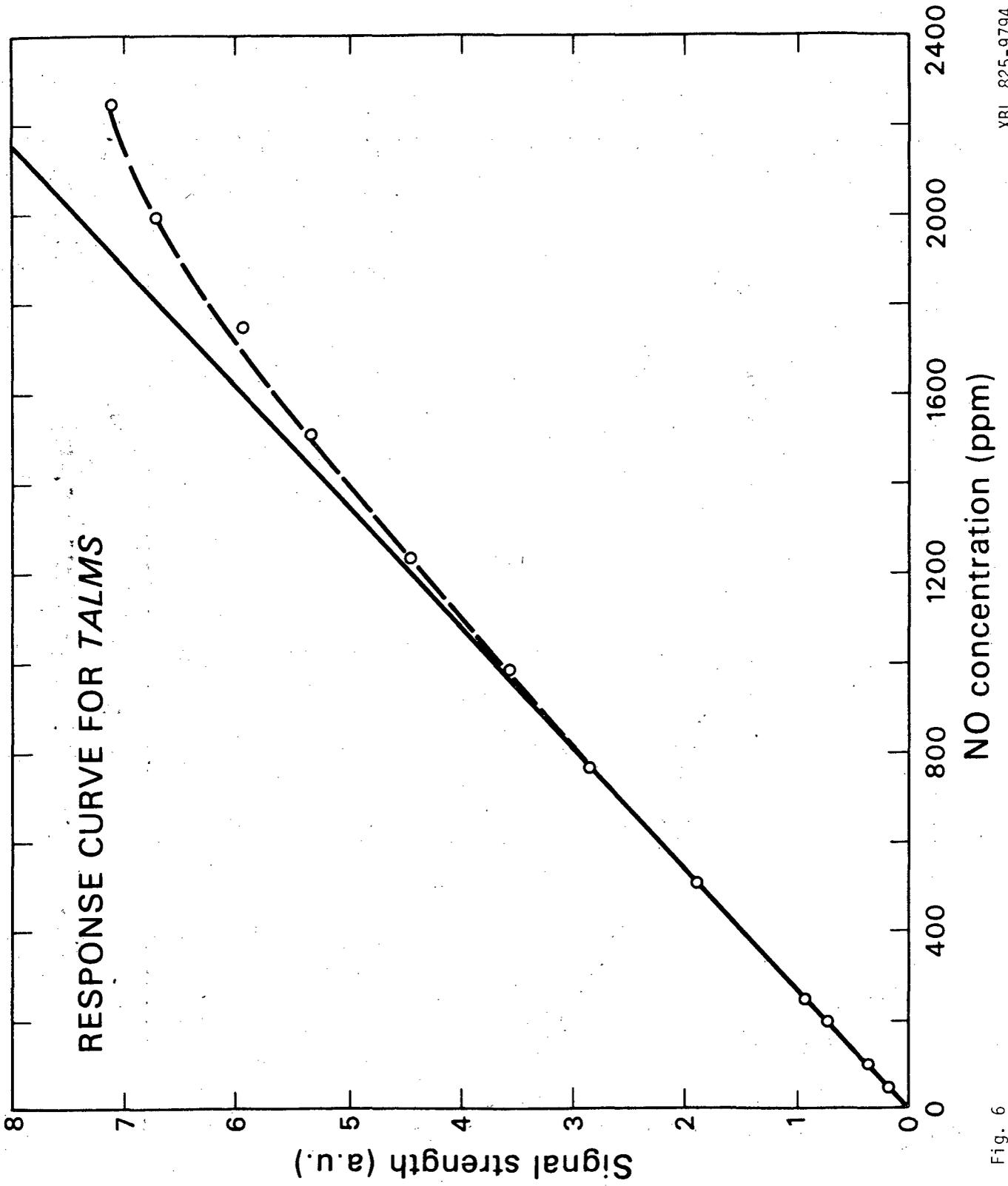
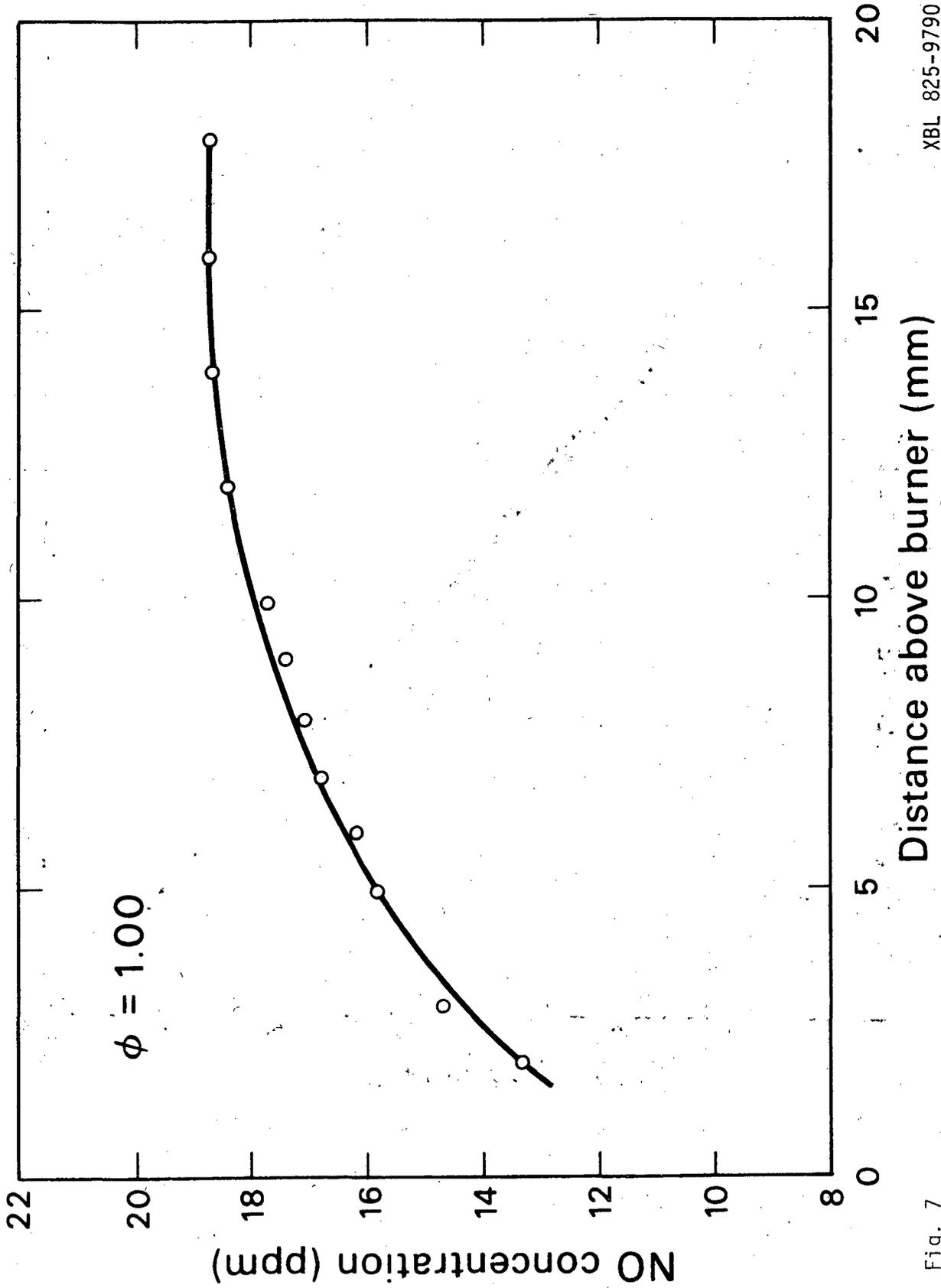
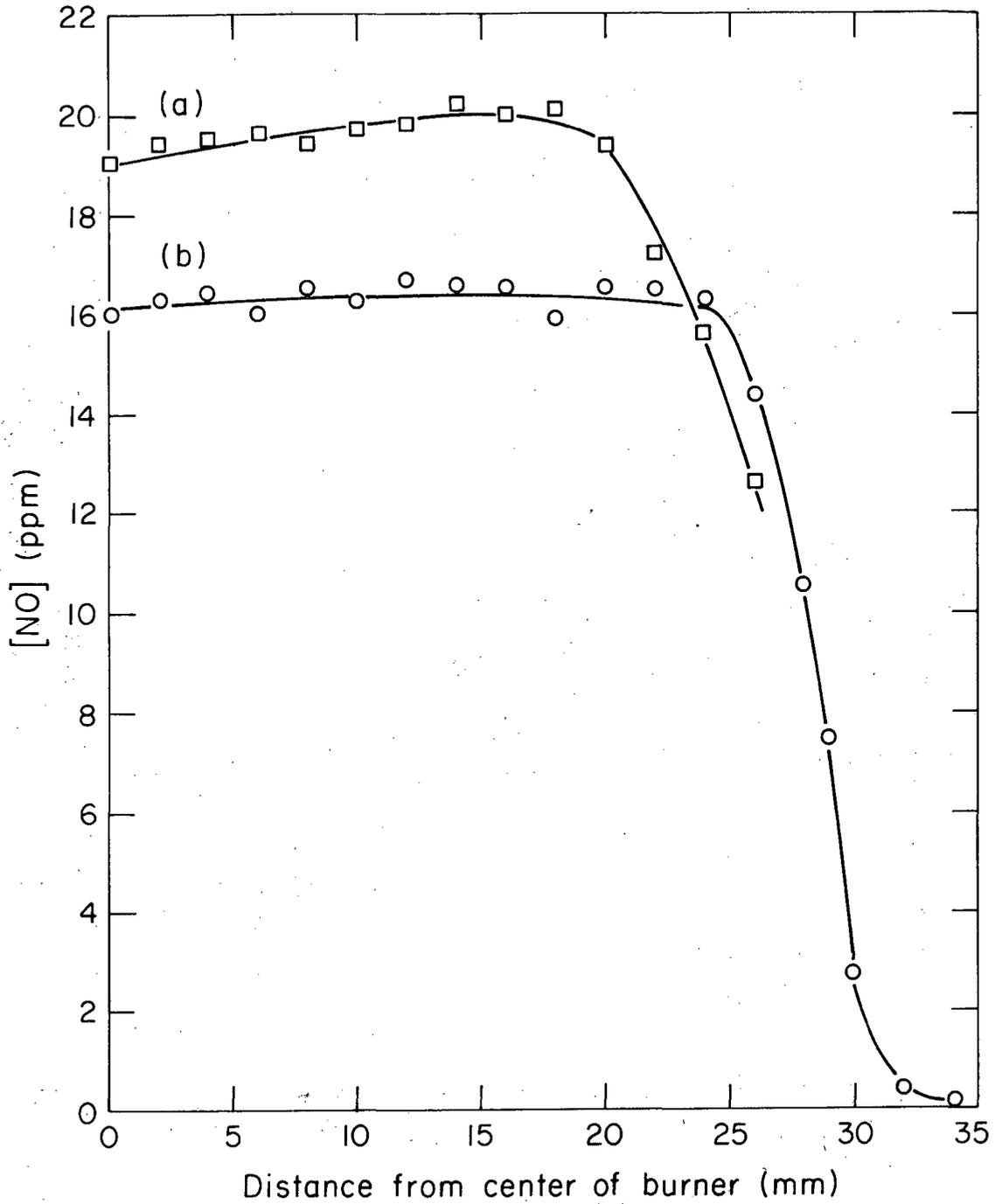


Fig. 6



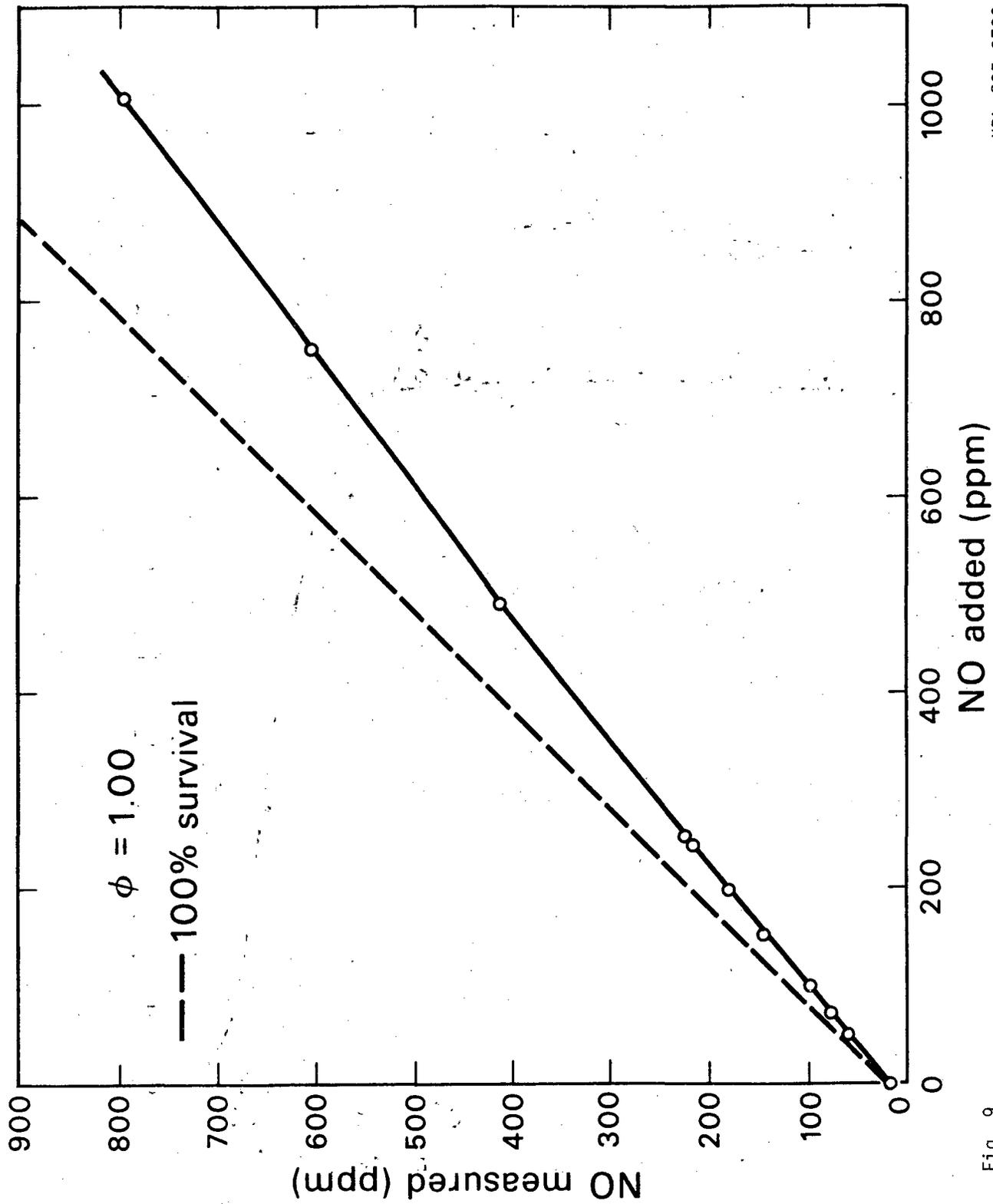
XBL 825-9790

Fig. 7



XBL 822-4490

Fig. 8



XBL 825-9793

Fig. 9

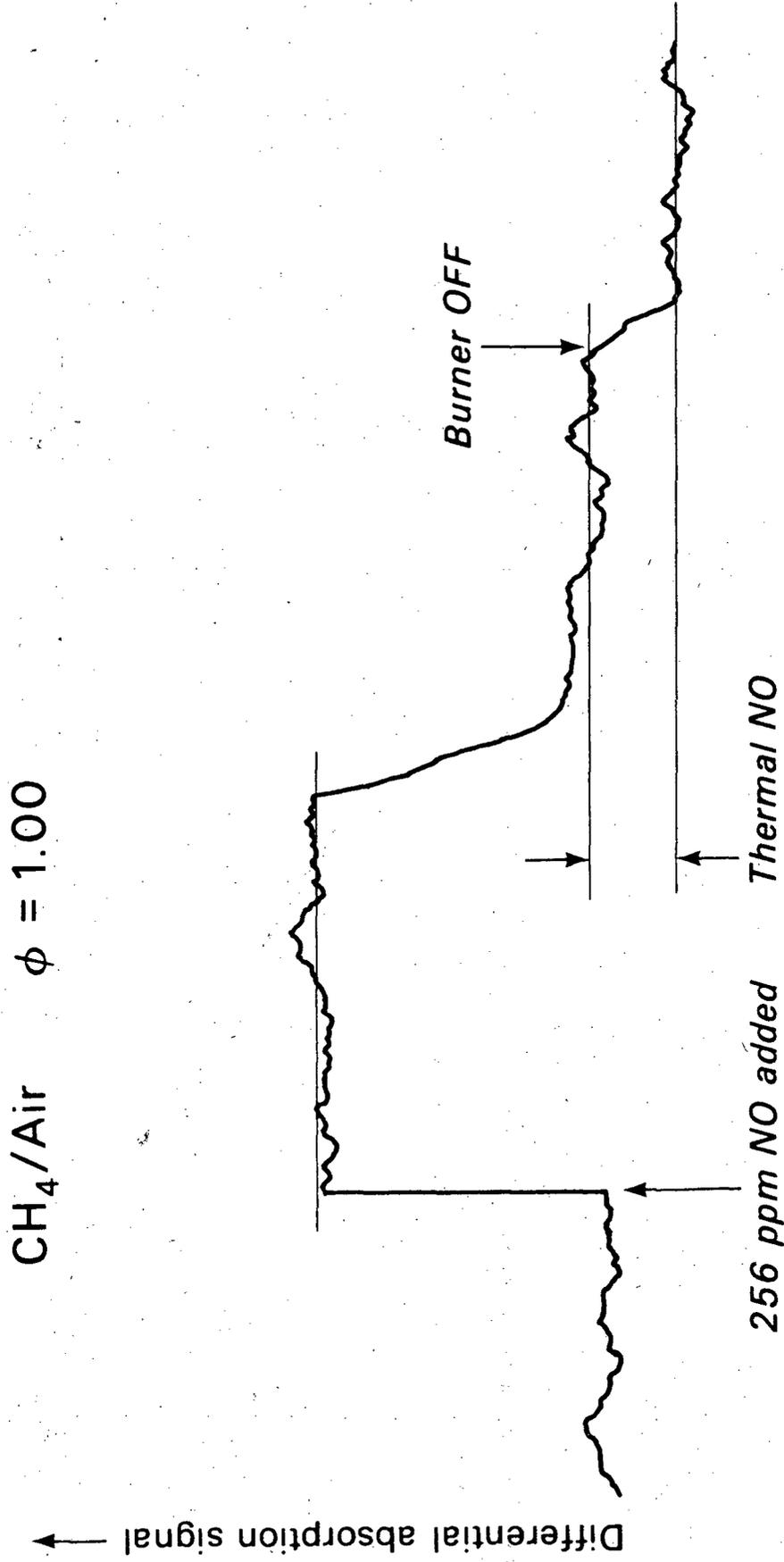
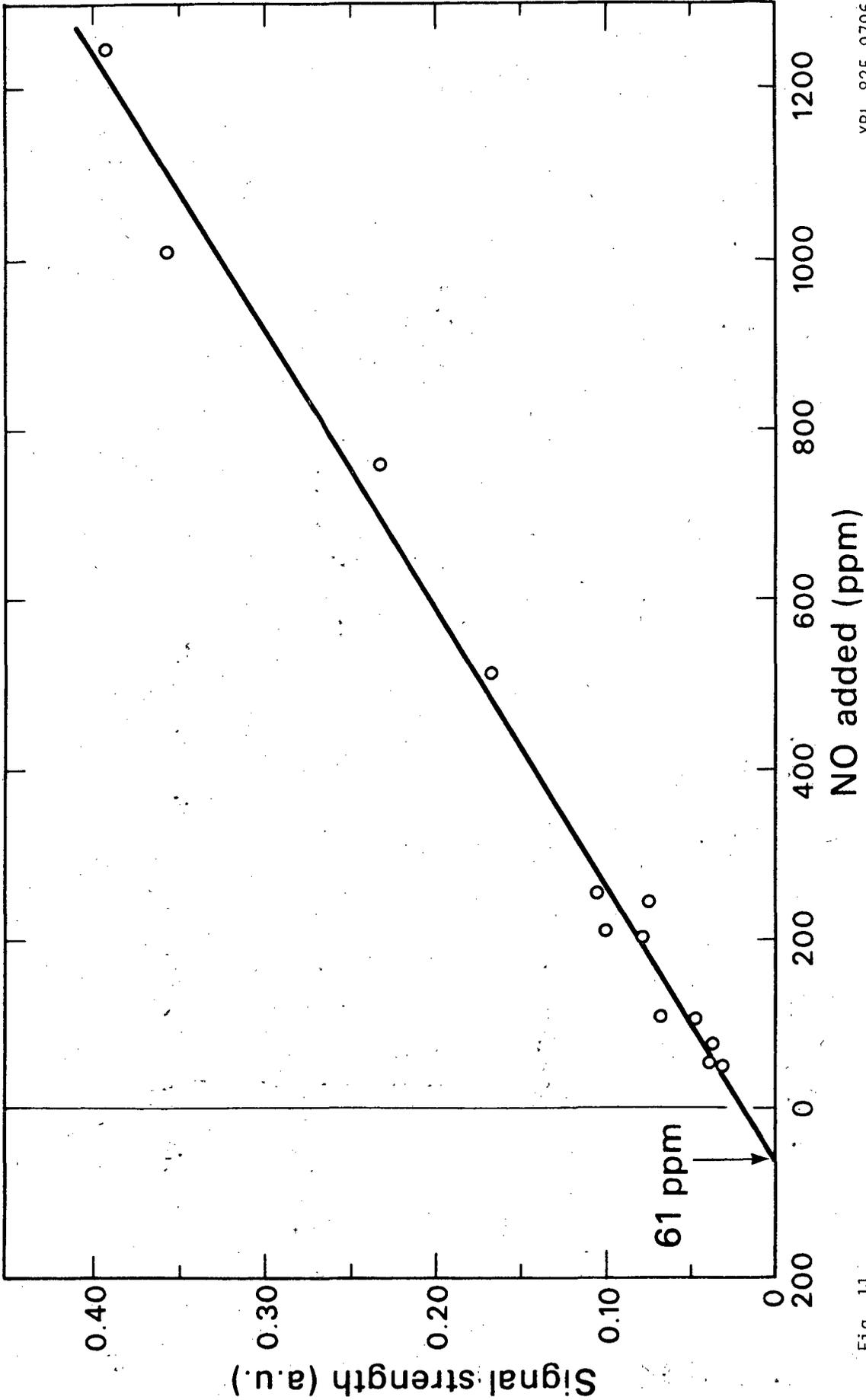


Fig. 10

XBL 825-9797



XBL 825-9796

Fig. 11

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