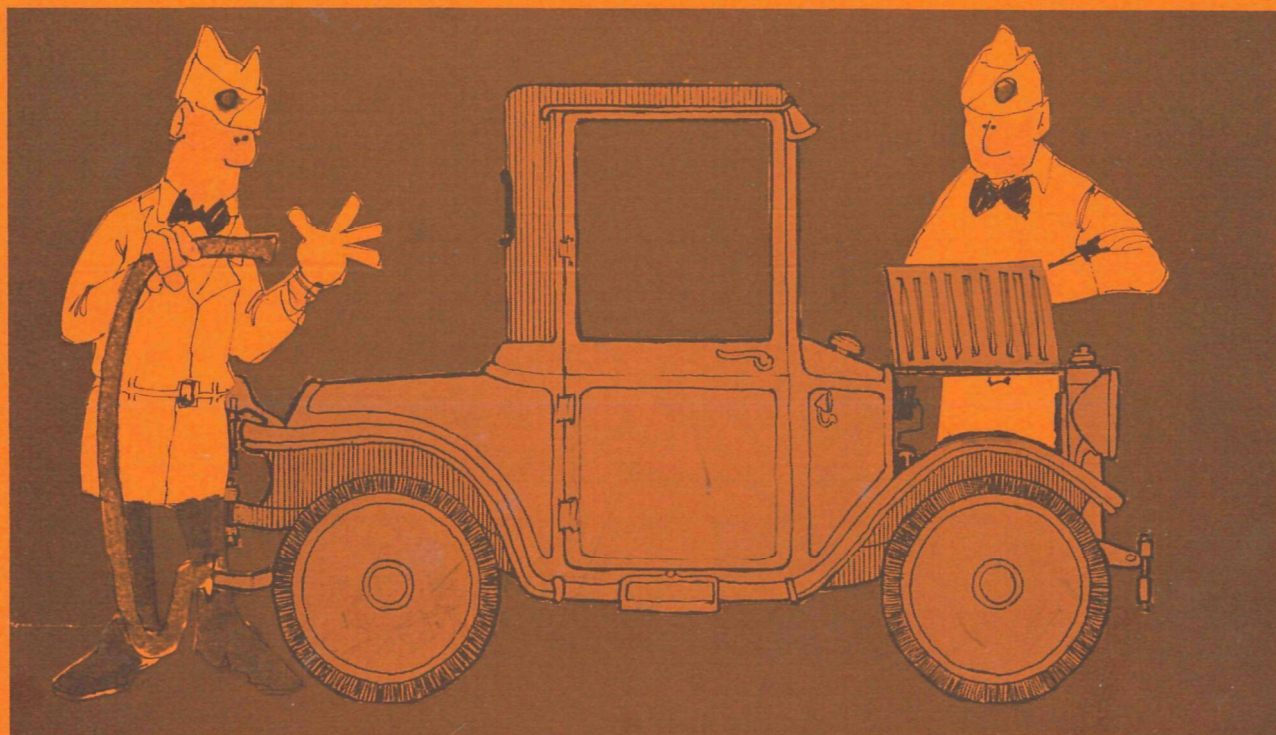


EPA 460/3 - H-004

# A Study of Mandatory Engine Maintenance for Reducing Vehicle Exhaust Emissions

VOLUME VI. A Comparison of Oxides of Nitrogen Measurements Made  
With Chemiluminescent and Non-Dispersive Radiation  
Analyzers



Year End Report  
July 1972

In Support of:

APRAC Project Number CAPE-13-68

for

Coordinating Research Council, Inc.

Thirty Rockefeller Plaza

New York, New York 10020

and

Environmental Protection Agency

Air Pollution Control Office

5600 Fishers Lane

Rockville, Maryland 20852

**TRW**  
SYSTEMS GROUP

ONE SPACE PARK • REDONDO BEACH, CALIFORNIA 90278

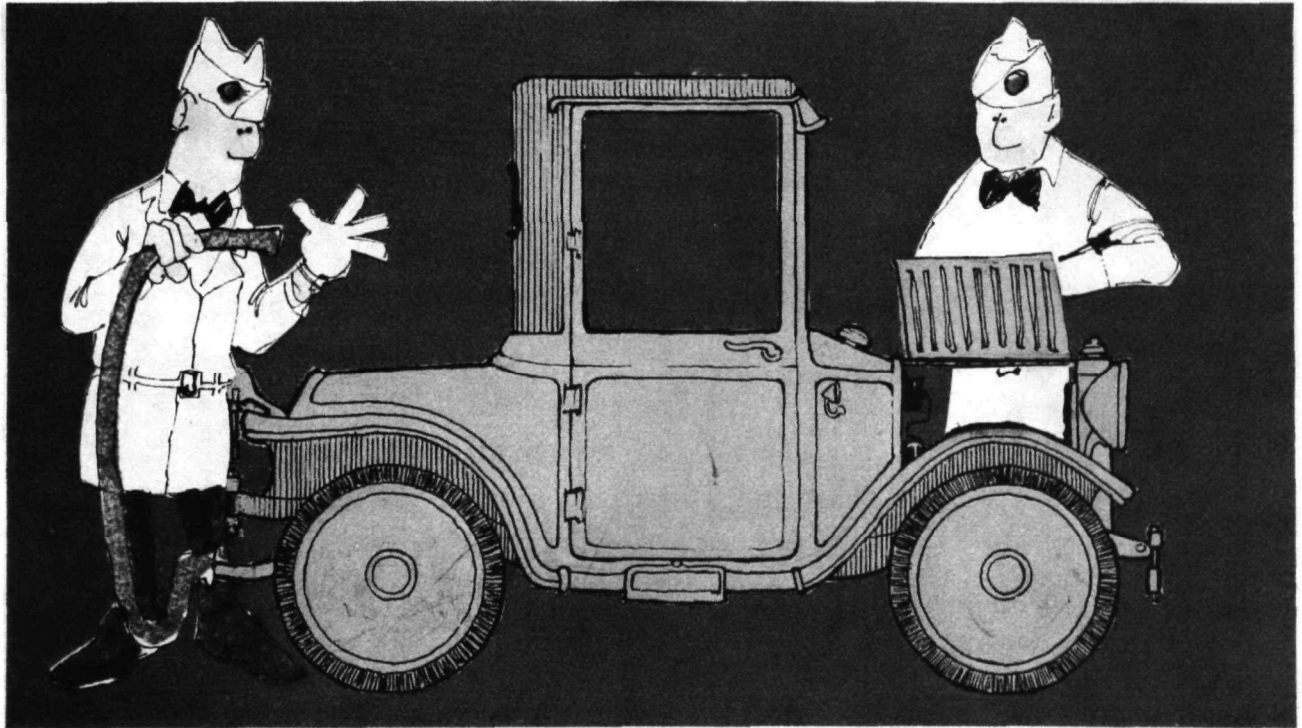


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## PREFACE

This report, "A Study of Mandatory Engine Maintenance for Reducing Vehicle Exhaust Emissions," consists of six volumes. The following are the subtitles given for each volume:

- Executive Summary, Volume I
- Mandatory Inspection/Maintenance Systems Study, Volume II
- A Documentation Handbook for the Economic Effectiveness Model, Volume III
- Experimental Characterization of Vehicle Emissions and Maintenance States, Volume IV
- Experimental Characterization of Service Organization Maintenance Performance, Volume V
- A Comparison of Oxides of Nitrogen Measurements Made With Chemiluminescent and Non-Dispersive Radiation Analyzers, Volume VI

The first volume summarizes the general objectives, approach and results of the study. The second volume presents the results of the mandatory inspection/maintenance system study conducted with a computerized system model which is described in Volume III. The experimental programs conducted to develop input data for the model are described in Volume IV (Interim Report of 1971-72 Test Effort) and V. Volume VI presents comparative measurements of NO and NO<sub>x</sub> using chemiluminescence and NDIR/NDUV instruments and differences in these measurements are examined.

The work presented herein is the product of a joint effort by TRW Systems Group and its subcontractor, Scott Research Laboratories. TRW, as the prime contractor, was responsible for overall program management, experimental design, data management and analysis, and the economic effectiveness study. Scott acquired and tested all of the study vehicles. Scott also provided technical assistance in selecting emission test procedures and in evaluating the test results.

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# A COMPARATIVE STUDY OF THE USE OF CHEMILUMINESCENT AND NON-DISPERSIVE RADIATION ANALYZERS FOR THE MEASUREMENT OF OXIDES OF NITROGEN IN DILUTE SAMPLES OF AUTOMOTIVE EXHAUST

## INTRODUCTION

At present, two distinctly different types of instrumentation are widely used to measure automotive exhaust emissions of the oxides of nitrogen ( $\text{NO}$  and  $\text{NO}_2$ ). Until quite recently, virtually all such measurements were made using non-dispersive infrared (NDIR) analyzers for  $\text{NO}$  and non-dispersive ultraviolet (NDUV) analyzers for  $\text{NO}_2$ . The use of chemiluminescence (CL) analyzers has recently gained wide acceptance for the measurement of both  $\text{NO}$  and  $\text{NO}_2$  ( $\text{NO}_x$ ).

Many investigators, however, have noted that significant differences exist in the data obtained with both of these measurement techniques, although little discussion of these differences is found in the literature. This latter fact is attributable in part to both the wide acceptance of CL techniques and the specification by the Environmental Protection Agency that CL instrumentation be used as the measurement technique for the Federal  $\text{NO}_x$  exhaust emissions standards for 1973 and subsequent model-year light duty vehicles. It is the purpose of this report to describe an experimental study which was undertaken to describe differences between CL and NDIR/NDUV measurements, as applied to dilute samples of automotive exhaust gas.

## TEST VEHICLES AND PROCEDURES

The test vehicles that were employed for this experimental program were part of the experimental fleet of cars being tested on the CAPE 13-68 Engine Parameter Deterioration Program. This fleet originally consisted of 450 privately owned 1960 through 1971 model-year automobiles. The fleet was composed of all domestic makes of vehicles, in addition to some foreign makes. These automobiles were selected at random.

The experimental  $\text{NO}_x$  measurements were conducted concurrently with the regular Engine Parameter Deterioration tests. These tests consisted of measuring the automobile exhaust emissions in accordance with the 1975 Federal Test Procedure and the Federal Short Cycle test procedure, as

well as during selected diagnostic driving modes. The NO<sub>x</sub> experimental investigation was based on the constant volume sampler (CVS) bag emissions: the three samples obtained for the 1975 Federal Test Procedure and the single bag resulting from the Federal Short Cycle test procedure. The "Drierite" brand of dessicant was renewed at the beginning of each vehicle test and was not changed during measurement of the four successive bag samples.

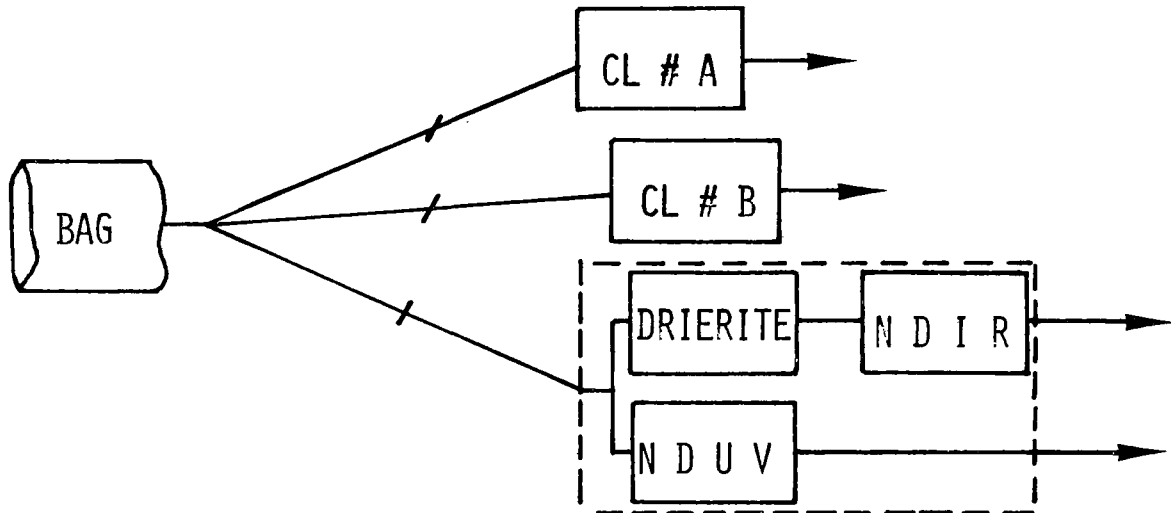
#### EXPERIMENTAL APPARATUS AND TECHNIQUES

The NDIR instrument used for these experiments was a Beckman Model 315A Non-Dispersive Infrared Analyzer and NDUV measurements were made with a Beckman Model 255 Non-Dispersive Ultraviolet Analyzer. Two chemiluminescence instruments were used, both Thermo Electron Model 10A NO-NO<sub>x</sub> Analyzers. All sample handling lines were 1/4 inch O.D. Teflon, wrapped with black (opaque) shielding to prevent any photochemical reactions from occurring in the sample lines. Dilute exhaust samples were collected in Mylar CVS bags, also opaque to ultraviolet and visible radiation. Sample flowrates through each of the NDIR and NDUV instruments were maintained at 10 cubic feet per hour (cfh) with a positive displacement pump placed upstream (a "push" pump) of each instrument. The sample flowrate through each of the CL analyzers was maintained at cfh with a pump downstream ("pull" pump) of each analyzer. It should be noted that a Drierite dessicator was positioned upstream of the NDIR unit to remove water vapor, whereas dessicant is not normally included in any of the sample lines leading to the other instruments. This point will become very important in the analysis of the results, since several effects may be attributed to the presence of Drierite in the sample handling system of the NDIR analyzer.

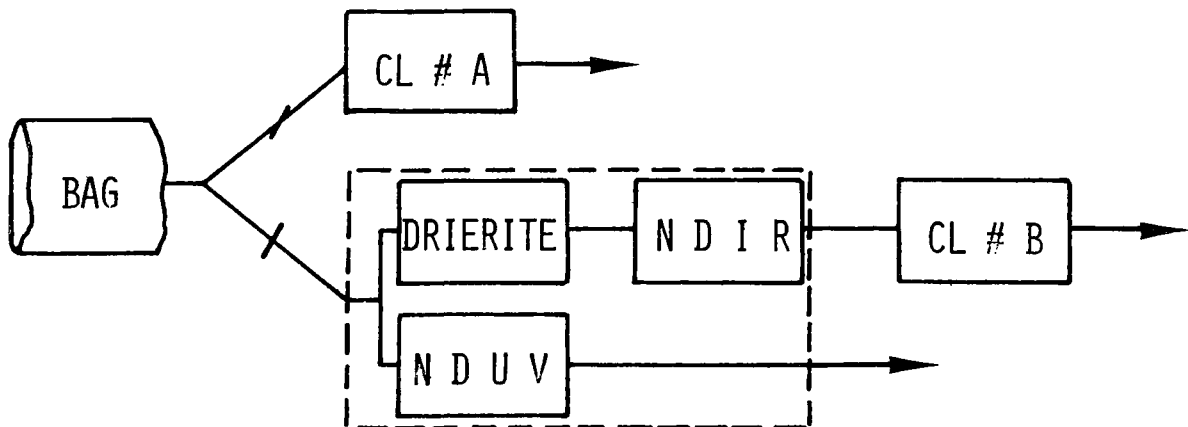
Two instrument configurations were used in this investigation, and they are schematically diagrammed in Figure 1. In the parallel configuration, all four instruments were placed in parallel with one another, and the sample line lengths to the instrument cabinets were equal in order to eliminate any differences which might result from reactions in the sample line. This configuration was used to establish both the degree of agreement between the two CL analyzers and the amount of difference between

FIGURE 1  
SYSTEM SCHEMATICS

PARALLEL CONFIGURATION:



SPLIT CONFIGURATION:





either CL measurement and those of the NDIR/NDUV instruments. These results will be discussed in the following section.

It may also be seen in Figure 1 that the split configuration placed one CL analyzer in parallel with the NDIR/NDUV cabinet (as in the parallel configuration), and the other CL instrument was placed downstream in series with the NDIR analyzer. It again should be noted that the sample is passed through Drierite before entering the NDIR instrument. This configuration was designed to serve four purposes. First, results from both CL #A and the NDIR/NDUV cabinet could be compared with those of the previous experiments (using the parallel configuration) in order to ensure that nothing had changed with time. Second, a comparison of NDIR data with that obtained from CL #B in the NO mode would quantify differences between NDIR and CL measurement techniques, with the Drierite effect removed. Third, a comparison of CL data when both CL instruments were operated in the NO analysis mode would quantify any Drierite effects on NO concentrations. Fourth, a similar comparison of CL data when both were operated in the NO<sub>x</sub> mode would establish any Drierite effects on NO<sub>x</sub> (on both NO, which would now be known, and on NO<sub>2</sub>). The results of this series of experiments will be discussed in a later section.

#### EXPERIMENTAL RESULTS - PARALLEL CONFIGURATION

The experiments with the instrumentation in the parallel configuration consisted of 51 dynamometer runs, each of which yielded 4 bags to be analyzed. Thus 612 independent NO<sub>x</sub> data points resulted from this series of experiments. Measured NO<sub>x</sub> concentrations ranged from approximately 20 to 250 ppm.

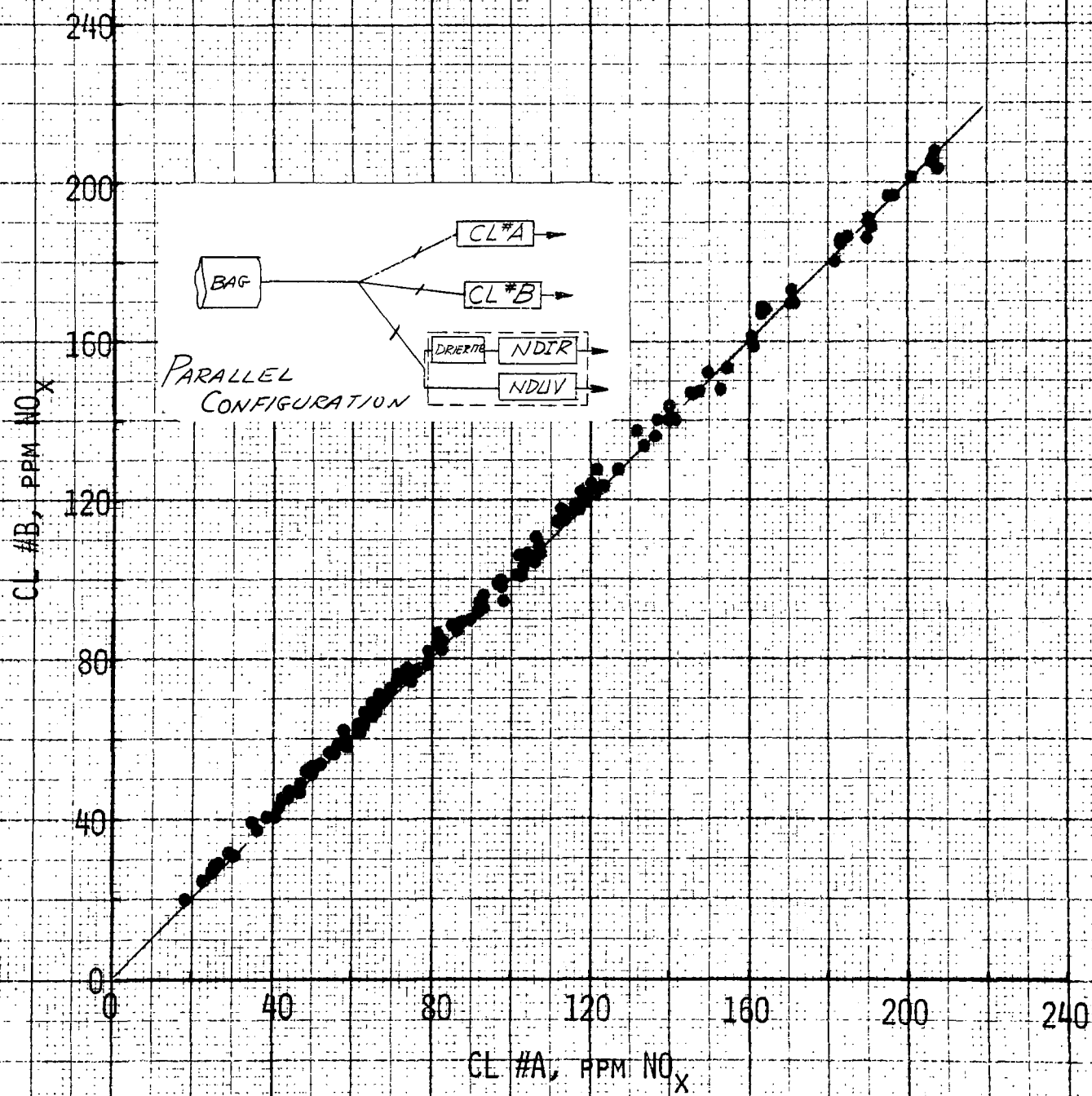
In Figure 2 may be seen a plot of pairs of data from the two CL analyzers. The line appearing in the plot is the 45° datum and it is seen that the data fall very closely about this reference line. A linear regression yielded a line obeying the equation

$$[\text{NO}_x]_{\text{CL}\#B} = 1.0097 [\text{NO}_x]_{\text{CL}\#A} + 1.01867 \text{ ppm} \quad (1)$$

FIGURE 2

PARALLEL CONFIGURATION

CL #B vs. CL #A



This best fit of the data had a correlation coefficient of 0.99943, which means that all but 0.11% of the data is explained by the above relationship. The slope and intercept indicate that the best fit of the data lies very close to a 45° line.

Figure 3 presents a plot of pairs of data from the NDIR/NDUV cabinet and one of the CL instruments (the previous data indicate that virtually either CL analyzer may have been selected for this comparison). Again the line of unity slope is shown for reference and it is seen that the NDIR/NDUV data are consistently higher than corresponding measurements from CL #A and that this trend becomes more pronounced (diverges from the 45° line) at higher  $\text{NO}_x$  concentrations. The statistical interpretation of these data will be discussed in the next section. Reference to the parallel configuration in the system schematics (Figure 1) will indicate that the data differences appearing in Figure 3 may be possibly attributed to both Drierite effects on the sample and interference gas effects which differ between CL and NDIR/NDUV instrumentation.

#### EXPERIMENTAL RESULTS - SPLIT CONFIGURATION

The experiments with the instrumentation in the split configuration consisted of 38 dynamometer runs, each of which yielded 4 bags to be analyzed. Since both NO and  $\text{NO}_x$  determinations were made, a total of 912 independent data points resulted from this series of experiments. Measured  $\text{NO}_x$  concentrations ranged from approximately 25 to 320 ppm and NO values were observed between approximately 20 and 250 ppm. It should be emphasized at this point that all subsequent discussion will address the split configuration only.

Figure 4 presents a plot of pairs of  $\text{NO}_x$  data from the NDIR/NDUV cabinet and CL #A, which were in parallel to one another. It should be noted that there is a striking degree of similarity between these data and analogous data obtained from the parallel configuration (Figure 3). It may thus be concluded that there had not been a measurable change between the two series of experiments. The equation which best describes the data appearing in Figure 4 is given by

FIGURE 3

PARALLEL CONFIGURATION

NDIR/NDUV vs. CL #A

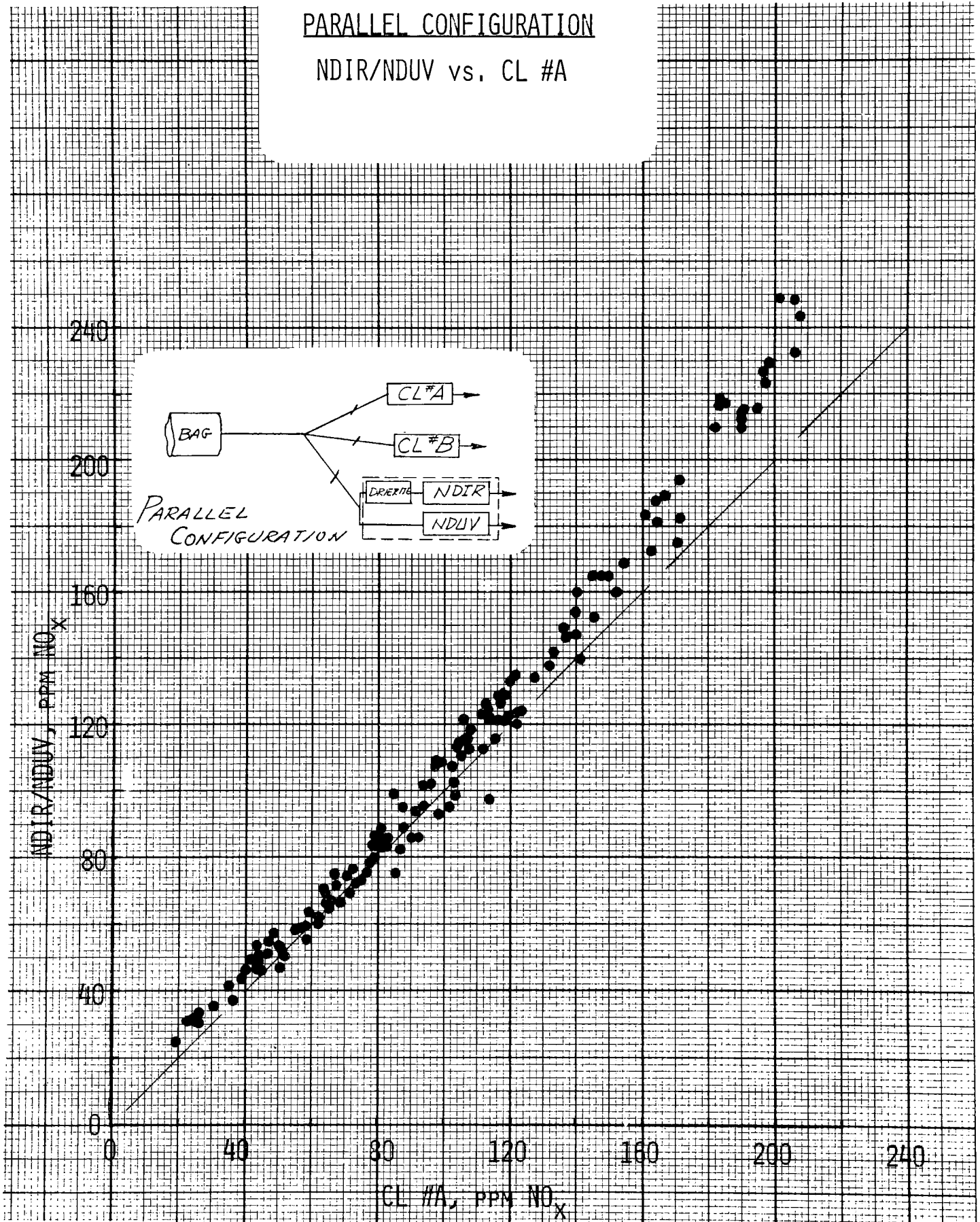
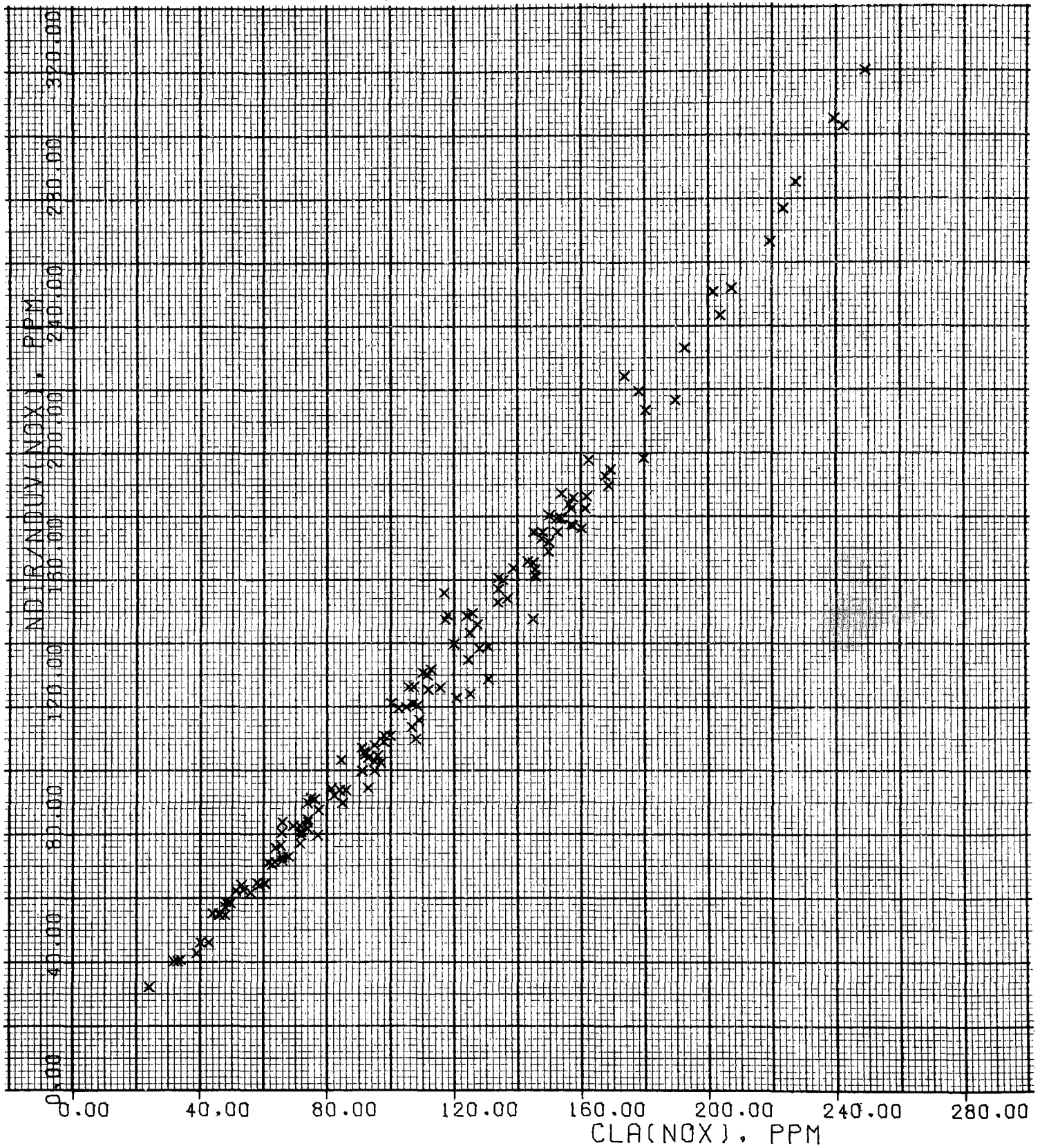


FIGURE 4  
NDIR/NDUV (NOX) VS. CLA (NOX)



$$[\text{NO}_x]_{\text{NDIR/NDUV}} = 1.21890 [\text{NO}_x]_{\text{CL\#A}} - 6.84340 \quad \text{ppm} \quad (2)$$

This best fit of the data yielded a correlation coefficient of 0.99181 (all but 1.63% of the data is explained by the above relationship). It is again noted that the data lie above the 45° line and diverges at higher  $\text{NO}_x$  concentrations.

In order to quantify the effects of Drierite on  $\text{NO}_x$  concentrations, a comparison of CL #A results and those obtained from CL #B, when both were operated in the  $\text{NO}_x$  mode ( $\text{NO}_2$  converter in operation) appears in Figure 5. A linear regression of the data was performed and the resultant best fit was found to obey the equation

$$[\text{NO}_x]_{\text{CL\#B}} = 0.87264 [\text{NO}_x]_{\text{CL\#A}} + 6.59542 \quad \text{ppm} \quad (3)$$

This description of the data yielded a correlation coefficient of 0.98284 (96.60% of the data is explained by the above relationship). There are several important observations which may be made at this point. In Figure 1 it was seen that the two CL analyzers agree very closely to one another on  $\text{NO}_x$  measurements when they are placed in parallel. Figure 5, however, shows little agreement with Figure 1, and this difference may be attributed to the presence of Drierite in the sample handling system which precedes CL #B. Furthermore, it is seen from Figure 5 that the two CL instruments diverge at higher concentrations, with the instrument downstream of the Drierite (CL #B) yielding lower measured  $\text{NO}_x$  values than CL #A. This was not found to be the case with the results from the NDIR/NDUV instruments, (see Figure 3) which yielded increasingly higher  $\text{NO}_x$  readings than CL #A at higher  $\text{NO}_x$  concentrations. Based on the high degree of agreement between the two parallel CL instruments (Figure 1), it may thus be concluded that the presence of Drierite results in lower  $\text{NO}_x$  concentrations, although measured  $\text{NO}$  concentrations obtained by NDIR result in higher measured  $\text{NO}_x$  values for the NDIR/NDUV system.

Figure 6 presents a plot of  $\text{NO}$  data which helps to explain the above observed  $\text{NO}_x$  differences. It is seen in this plot of CL #B against CL #A, when both were operated in the  $\text{NO}$  mode (converter bypassed), that the instrument downstream of the Drierite measures consistently higher values



FIGURE 5  
CLB (NOX) VS. CLA (NOX)

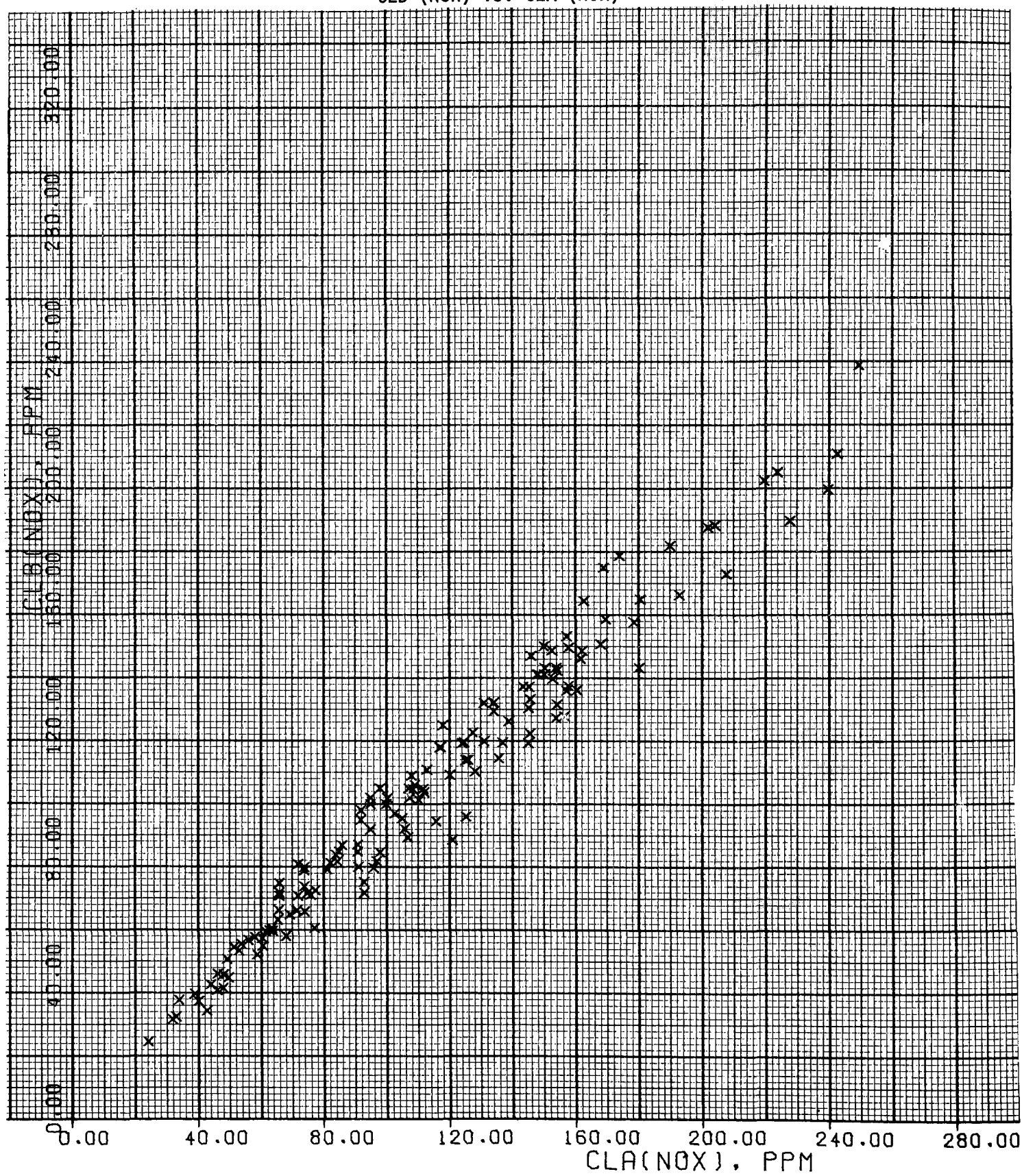
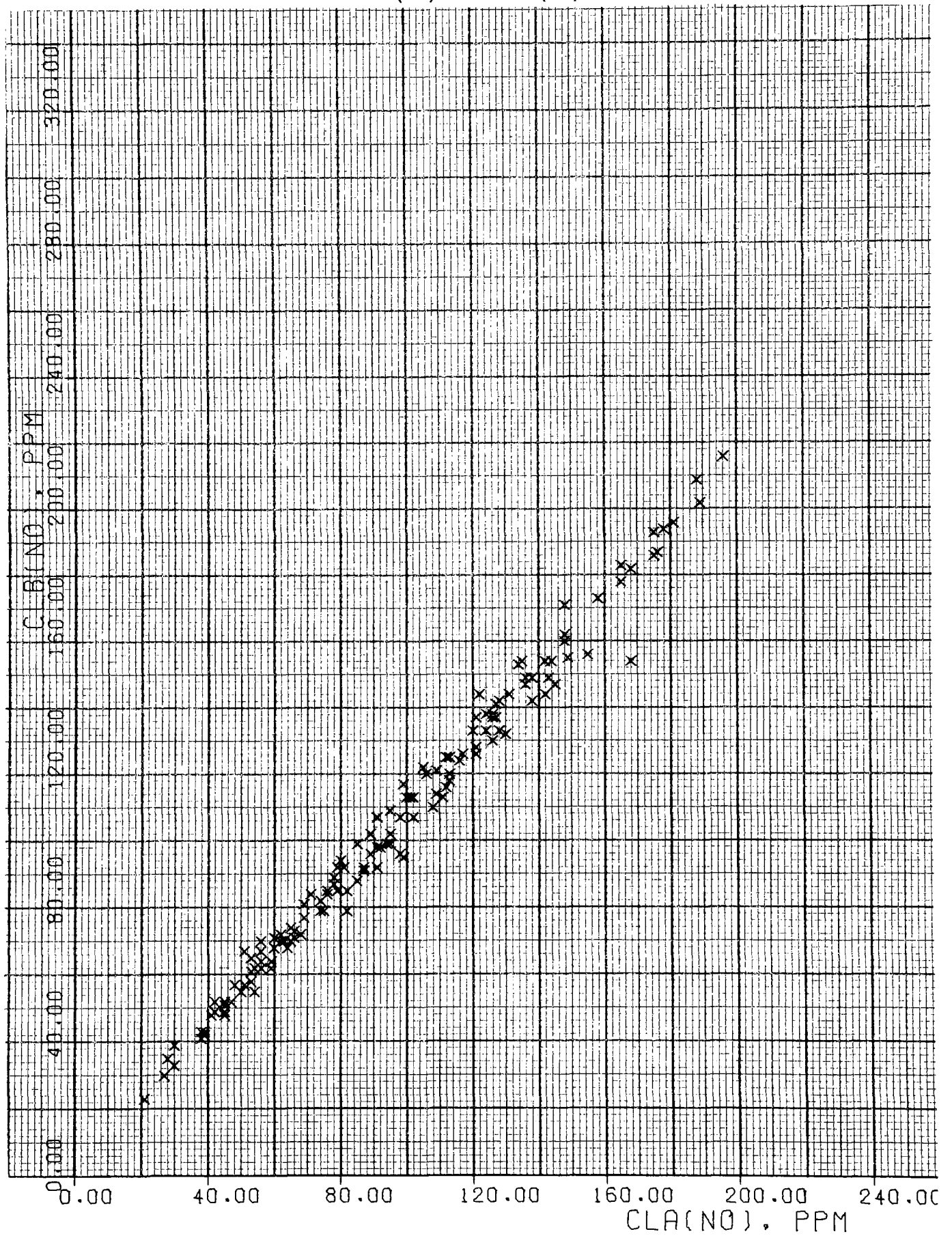


FIGURE 6  
CLB (NO) VS. CLA (NO)

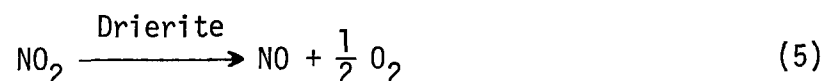


of NO than does the instrument which does not include Drierite in its sample handling system. The best fit of the data was found to obey the equation

$$[\text{NO}]_{\text{CL\#B}} = 1.04808 [\text{NO}]_{\text{CL\#A}} + 3.97905 \text{ ppm} \quad (4)$$

with a correlation coefficient of 0.99315 (all but 1.36% of the data is explained by the above relationship).

A comparison of Figure 5 and 6 allows several important conclusions to be drawn about the chemical effects of Drierite on dilute samples of automotive exhaust gases. Figure 6 indicates that the presence of Drierite in the sample handling system causes NO concentrations to increase. Figure 5 indicates that Drierite causes NO<sub>x</sub> concentrations to decrease. Since NO<sub>x</sub> (NO and NO<sub>2</sub>) decreases while NO has been seen to increase due to the presence of Drierite, the conclusion is that Drierite removes NO<sub>2</sub> from the sample gas and partially converts some NO<sub>2</sub> to NO. This may be explained by the following (conceptual) reaction on Drierite.



That this reaction, or one similar to it, does not go to completion in all cases may be seen by Figure 5. If Drierite converted all NO<sub>2</sub> to NO, or converted all NO<sub>2</sub> that it removed into NO, the NO<sub>x</sub> data would have fallen along the line of unity slope (as was the case of the data in Figure 2).

It is appropriate at this time to reexamine the data in order to quantify the efficiencies of Drierite in removing NO<sub>2</sub> and producing NO in samples of dilute automotive exhaust gas. The efficiency of Drierite in removing NO<sub>2</sub> may be expressed as

$$\begin{aligned} \eta_{\text{NO}_2 \text{ removal}} &= \frac{\text{NO}_2 \text{ removed by passage through Drierite}}{\text{NO}_2 \text{ present before passage through Drierite}} \\ &= \frac{[\text{NO}_x]_{\text{CL\#A}} - [\text{NO}]_{\text{CL\#A}} - [\text{NO}_x]_{\text{CL\#B}} + [\text{NO}]_{\text{CL\#B}}}{[\text{NO}_x]_{\text{CL\#A}} - [\text{NO}]_{\text{CL\#A}}} \quad (6) \\ &= 1 - \frac{[\text{NO}_x]_{\text{CL\#B}} - [\text{NO}]_{\text{CL\#B}}}{[\text{NO}_x]_{\text{CL\#A}} - [\text{NO}]_{\text{CL\#A}}} \end{aligned}$$

Since this psuedo-equilibrium constant could be a function of the  $\text{NO}_2$  concentration in the sample, the data was reexamined to yield a plot of  $\eta\text{NO}_2$  removal as a function of initial  $\text{NO}_2$  concentration, as seen in Figure 7.

The solid curve drawn through the data in Figure 7 was found to best describe the relationship between the observed  $\text{NO}_2$  removal efficiency by Drierite and the amount of  $\text{NO}_2$  present before passage through Drierite and obeys the equation

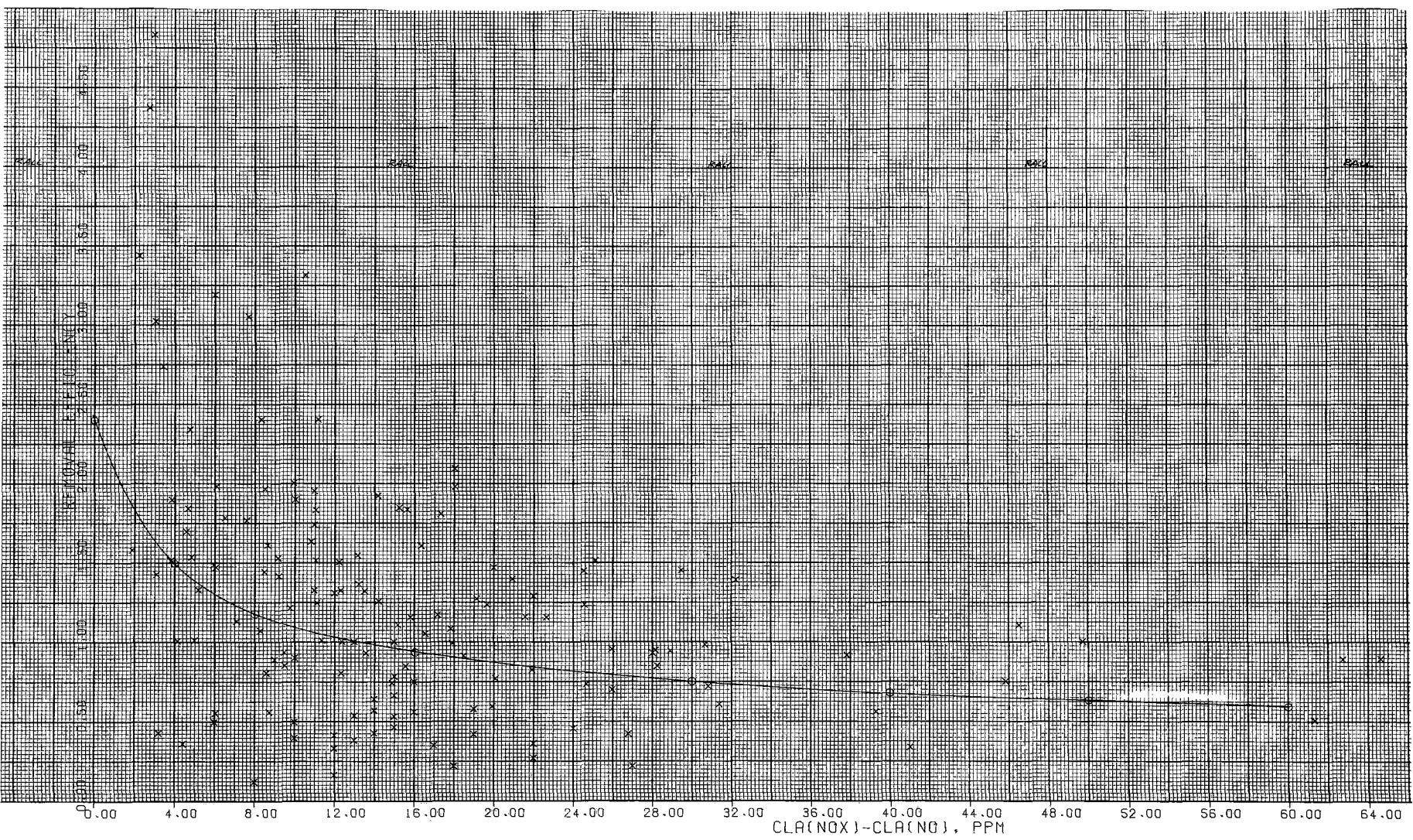
$$\eta\text{NO}_2 \text{ removal} = 2.3994 [\text{NO}_2]_{\text{available}}^{-0.3420} \quad (7)$$

This decrease in removal efficiency with increasing concentrations of incoming  $\text{NO}_2$  may be qualitatively interpreted as a saturation effect and suggests the presence of active sites for reaction on the solid surface of the Drierite material. Furthermore, close scrutiny of the analogous curves for each successive bag sample analysis (three for the 1975 cycle and one for an EPA short cycle) indicate that the  $\text{NO}_2$  removal efficiency of Drierite deteriorates with time; i.e., with the amount of exhaust sample which has been passed through it. This might well be a direct function of the amount of water vapor which has been absorbed. The fact that observed Drierite  $\text{NO}_2$  removal efficiencies often have values which are greater than unity at the lower available  $\text{NO}_2$  concentrations is at this time unexplained. It is believed, however, that this results from instrument errors which, although small in absolute value, are large compared to  $\text{NO}_2$  differences of only a few ppm.

In a similar manner, the efficiency of Drierite in converting  $\text{NO}_2$  to NO may be expressed as

$$\begin{aligned} \eta\text{NO production} &= \frac{\text{NO produced by Drierite}}{\text{NO}_2 \text{ removed by Drierite}} \\ &= \frac{[\text{NO}]_{\text{CL\#B}} - [\text{NO}]_{\text{CL\#A}}}{[\text{NO}_x]_{\text{CL\#A}} - [\text{NO}]_{\text{CL\#A}} - [\text{NO}_x]_{\text{CL\#B}} + [\text{NO}]_{\text{CL\#B}}} \\ &= \frac{[\text{NO}]_{\text{CL\#B}} - [\text{NO}]_{\text{CL\#A}}}{\eta\text{NO}_2 \text{ removed } ([\text{NO}_x]_{\text{CL\#A}} - [\text{NO}]_{\text{CL\#A}})} \end{aligned} \quad (8)$$

FIGURE 7  
REMOVAL EFFICIENCY



Since this efficiency could be dependent on the amount of  $\text{NO}_2$  removed by Drierite (the amount of  $\text{NO}_2$  available for conversion to  $\text{NO}$ ), the above efficiency was plotted against the amount of  $\text{NO}_2$  which was removed, as seen in Figure 8.

These data are seen to have considerably less scatter than those of Figure 7 and the solid curve was found to best describe these data according to the equation

$$\eta_{\text{NO}} \text{ production} = 3.7888 [\text{NO}_2]_{\text{removed by Drierite}}^{-0.7295} \quad (9)$$

Again a possible Drierite saturation effect is observed, and this hypothesis is also supported upon examining the data from each of the four sample bags. Again efficiencies are seen to exceed unity at lower values of the x-axis and this phenomena is believed to be a function of instrument variability, but is otherwise unexplained. The important factor in these efficiency analyses, however, is that both values are clearly not zero, and that the hypothesized reaction scheme is effective in explaining the observed effects on  $\text{NO}$  and  $\text{NO}_2$  concentrations.

Now that the effect of Drierite on the chemical composition of dilute automotive exhaust gas samples has been described, it is appropriate to investigate the different response characteristics of NDIR, NDUV and CL instrumentation. It has been well established that NDIR/NDUV instruments respond strongly to water vapor and that the subsequent inclusion of Drierite (and other dessicants) in the sample handling system has effectively eliminated this problem. Also, it has been long known that NDIR/NDUV systems respond positively to several interference gases that are also found in automotive exhaust, such as propane, carbon dioxide and carbon monoxide.

In order to investigate the magnitude of these interference gas responses, data from the split configuration were again scrutinized. Figure 9 is a  $\text{NO}$  plot of pairs of data from the NDIR and CL#A when it was operated in the  $\text{NO}$  mode. As was the case for the analogous  $\text{NO}_x$  curve (Figure 4), it is seen that the NDIR instrument yields higher measured values than the CL instrument in parallel with it and that this tendency



FIGURE 8  
PRODUCTION EFFICIENCY

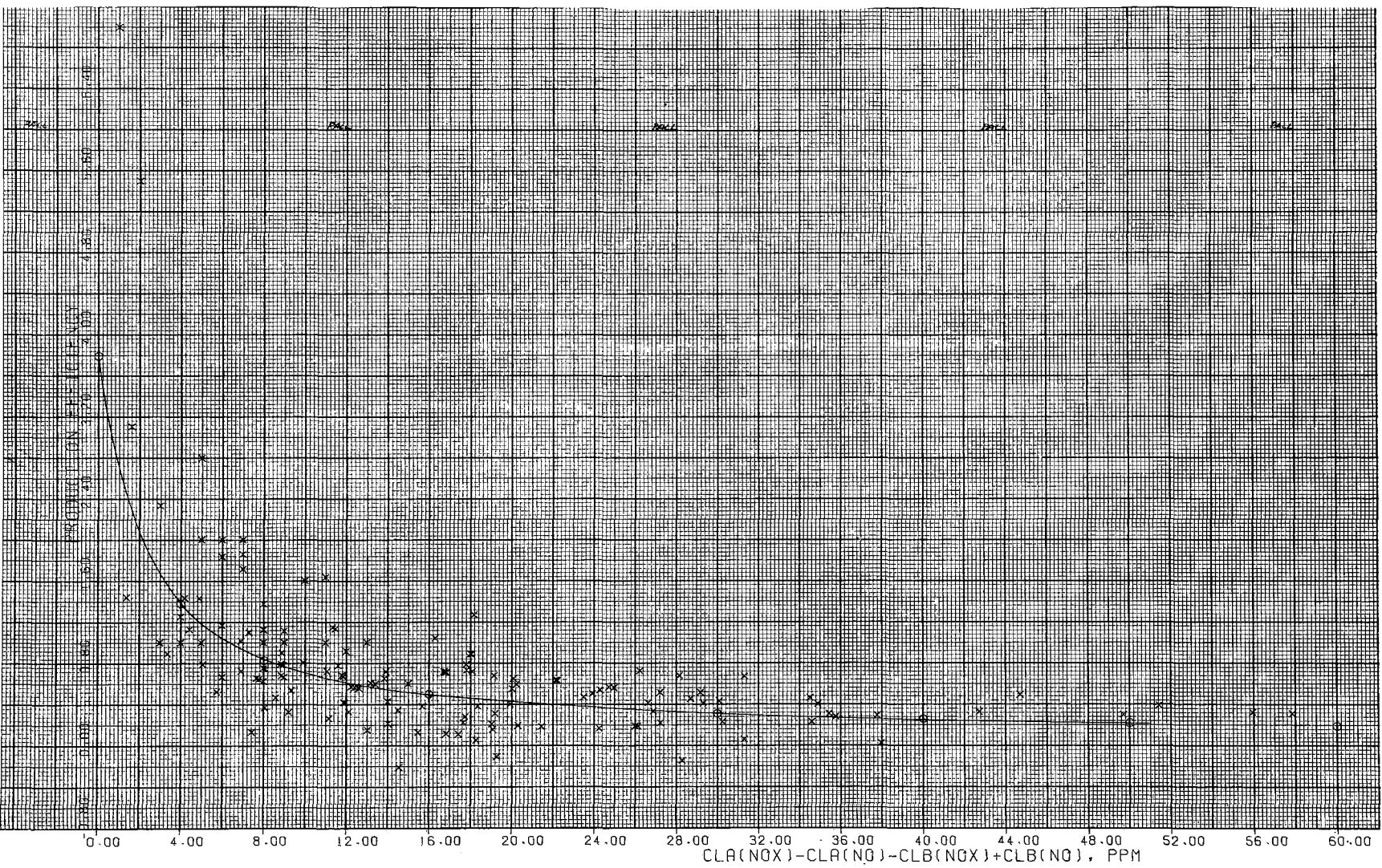
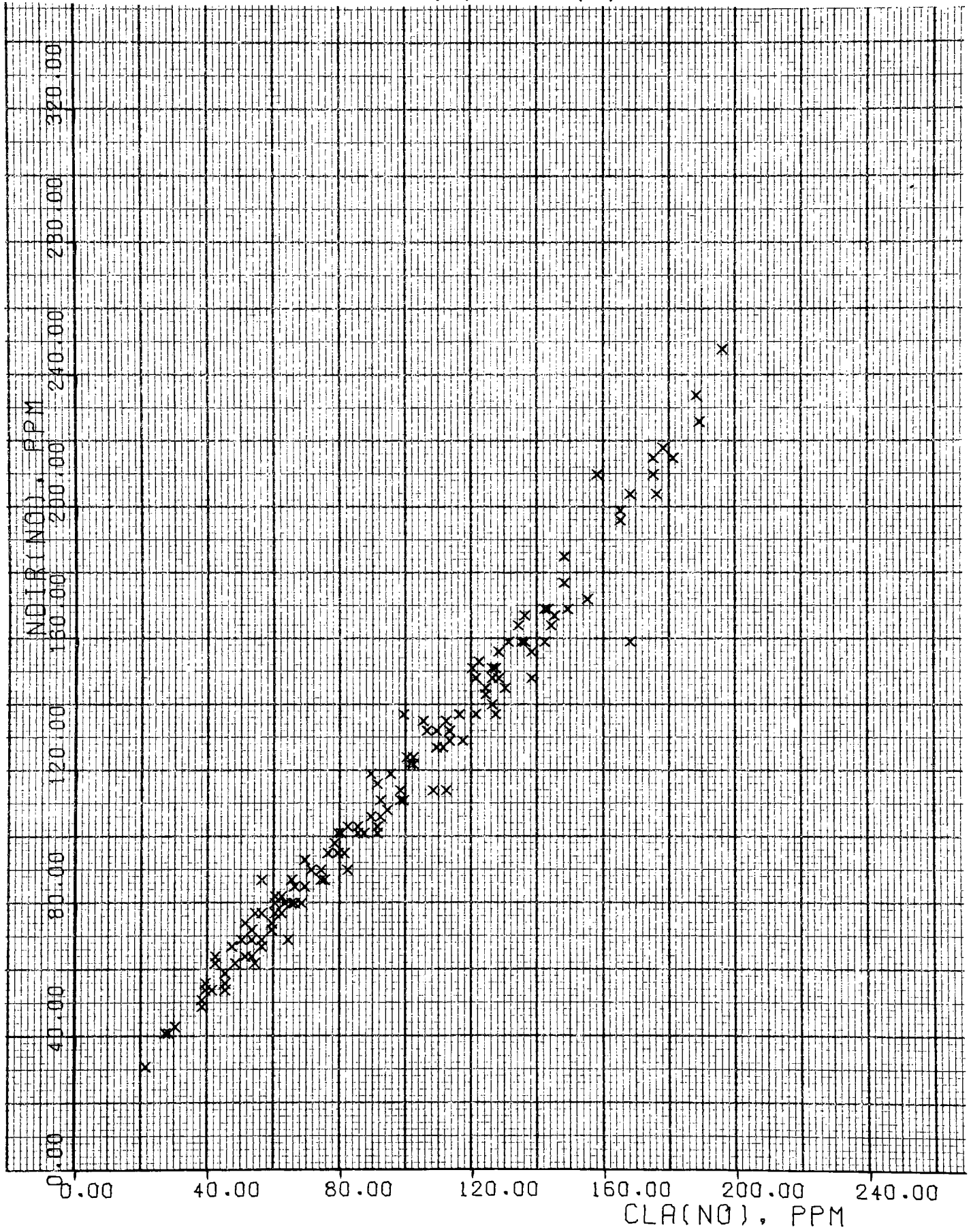


FIGURE 9  
NDIR (NO) VS. CLA (NO)



becomes more pronounced at higher NO concentrations. A linear regression of these data yielded a best-fit equation given by

$$[\text{NO}]_{\text{NDIR}} = 1.12184 [\text{NO}]_{\text{CL\#A}} + 8.36667 \quad \text{ppm} \quad (10)$$

with a correlation coefficient of 0.98788 (all but 2.41% of the data is explained by the above relationship). The difference between the two instruments exhibited by this plot is interpreted to result from both the effects of interference gases and Drierite since there was no dessicant upstream of CL#A.

In order to remove all effects of Drierite, a similar plot of pairs of NO readings from the NDIR and CL#B is seen in Figure 10. Since both instruments were downstream of the Drierite, the differences may be attributed to interference gas effects. A linear regression resulted in a best fit of the data given by

$$[\text{NO}]_{\text{NDIR}} = 1.06970 [\text{NO}]_{\text{CL\#B}} + 4.17953 \quad \text{ppm} \quad (11)$$

with a regression coefficient of 0.99405 (explaining all but 1.19% of the data). It is seen that these data lie below those of Figure 9, given by Equation (10), which is to be expected since it has been shown that Drierite increases NO concentrations. This is summarized by Figure 11.

Since Drierite effects are additive to any interference gas effects, the difference between the regressions of Figure 9 and 10, when referenced again to the line of unity slope, would yield the expression for Drierite effects only (here it is assumed that the two CL instruments respond identically, as was illustrated by Figure 2). Thus, for Drierite effects only, Equations (10) and (11) yield

$$[\text{NO}]_{\text{NDIR}} = 1.05214 [\text{NO}]_{\text{CL}} + 4.18715 \quad \text{ppm} \quad (12)$$

This expression is seen to be extremely similar when compared to Equation (4), which resulted from pairs of CL#A and CL#B NO data (see Figure 6):

FIGURE 10  
NDIR (NO) VS. CLB (NO)

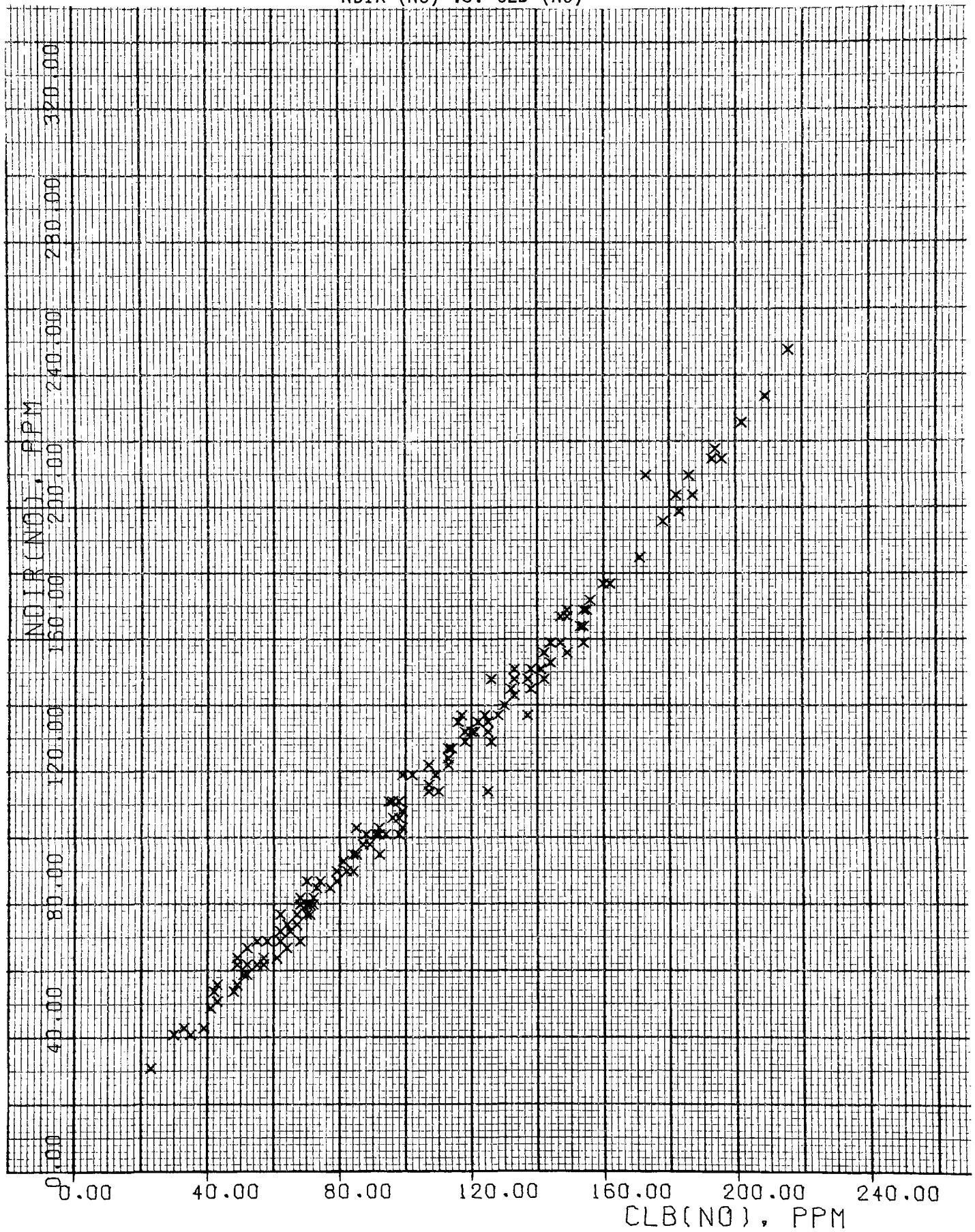
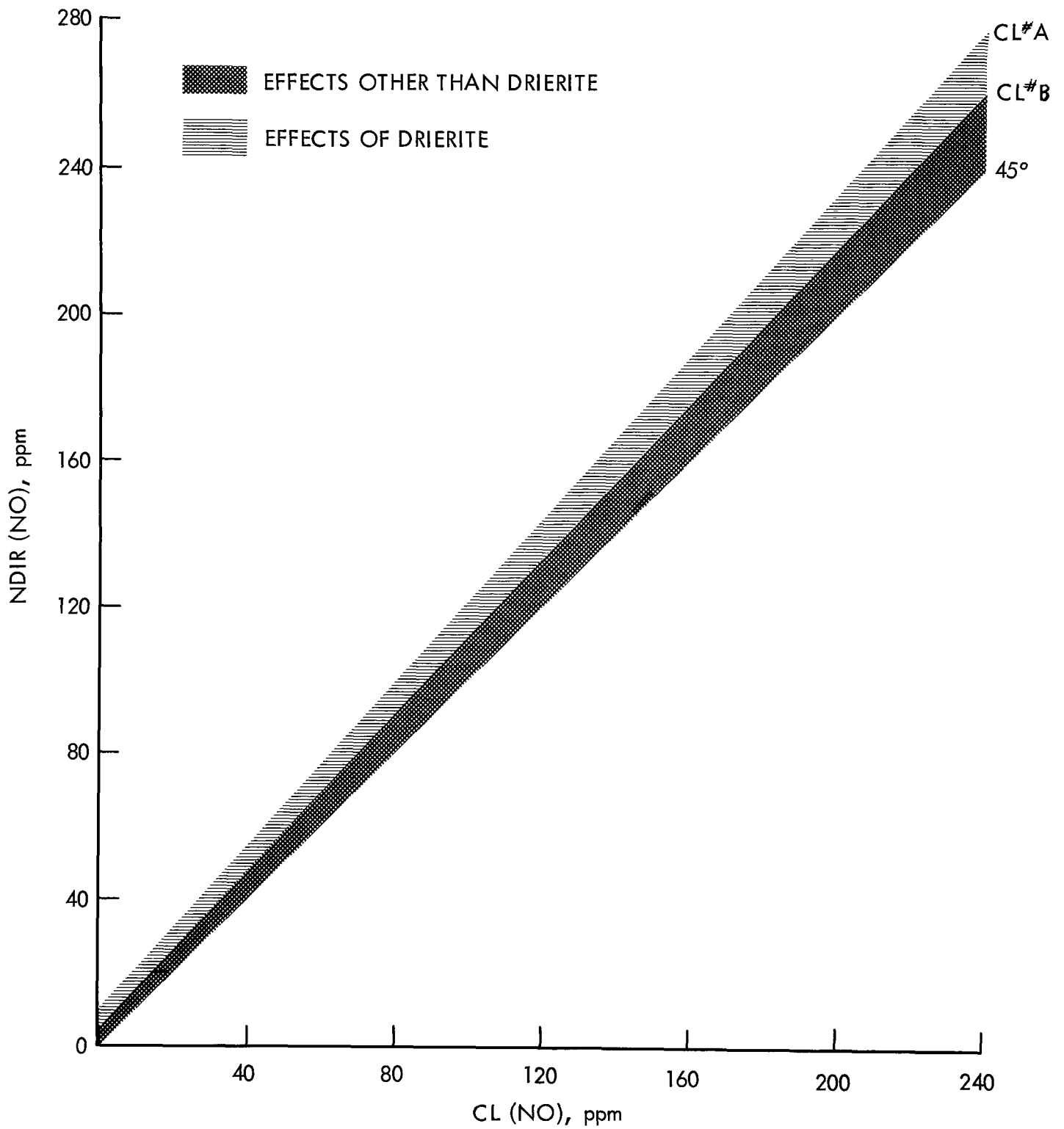


FIGURE 11  
NDIR (NO) VS. CL#A (NO) AND CL#B (NO)



$$[\text{NO}]_{\text{CL\#B}} = 1.04808 [\text{NO}]_{\text{CL\#A}} + 3.97905 \text{ ppm} \quad (4)$$

For convenience of further comparison, these two best-fit equations are replotted in Figure 12. It is seen that the two regression lines lie extremely close to one another. It is thus concluded that the effects of Drierite on NO are accurately measurable by either NDIR or CL techniques, once the effects of interference gases on the NDIR have been eliminated.

In order to investigate whether similar conclusions can be drawn for  $\text{NO}_x$  response, let us reexamine Figures 4 and 5. Figure 4 presented  $\text{NO}_x$  data for NDIR/NDUV plotted against corresponding data from CL#A which was in parallel. Since no Drierite was upstream of CL#A, Figure 4 represents differences which result from all effects (both those of interference gas responses and those due to the presence of Drierite). Figure 5 presented  $\text{NO}_x$  data for CL#B (downstream of Drierite) plotted against corresponding data from CL#A. Thus, this figure represents the effects of Drierite on  $\text{NO}_x$  concentrations. It is noted that the presence of Drierite results in lower  $\text{NO}_x$  values, i.e., negative effect on measured  $\text{NO}_x$  concentrations. Taking the difference between the regression lines of Figures 4 and 5, given by Equations (2) and (3), the resultant equation, when referenced to the original 45° line, is given by

$$[\text{NO}_x]_{\text{NDIR/NDUV}} = 1.34626 [\text{NO}_x]_{\text{CL}} - 13.43882 \text{ ppm} \quad (13)$$

This equation should represent only the effects of interference gas and the Drierite depletion of  $\text{NO}_2$  ("counting  $\text{NO}_2$  twice") on NDIR/NDUV measurement of  $\text{NO}_x$ , with the effect of Drierite increasing NO concentrations effectively cancelled out.

This result may be compared directly with Figure 13, which presents a plot of corresponding pairs of  $\text{NO}_x$  data from the NDIR/NDUV and CL#B. Since CL#B was downstream in series with the NDIR (and therefore the Drierite), Figure 13 directly represents all effects other than those of Drierite on the NDIR measurement. Due to the nonlinear nature of the data, the best-fit was found to be given by



FIGURE 12  
INDEPENDENT EVALUATIONS OF THE EFFECT OF DRIERITE ON NO MEASUREMENTS

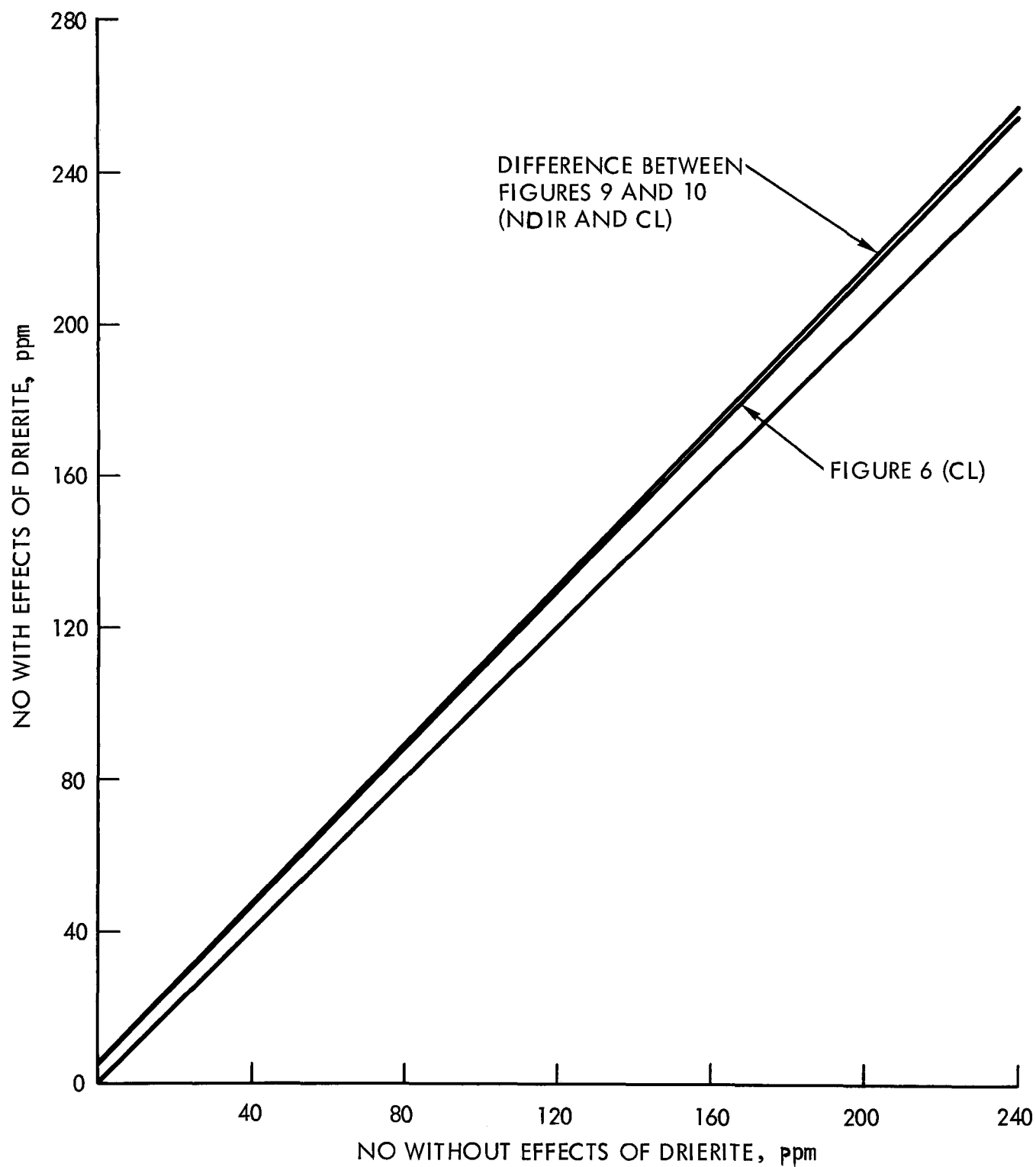
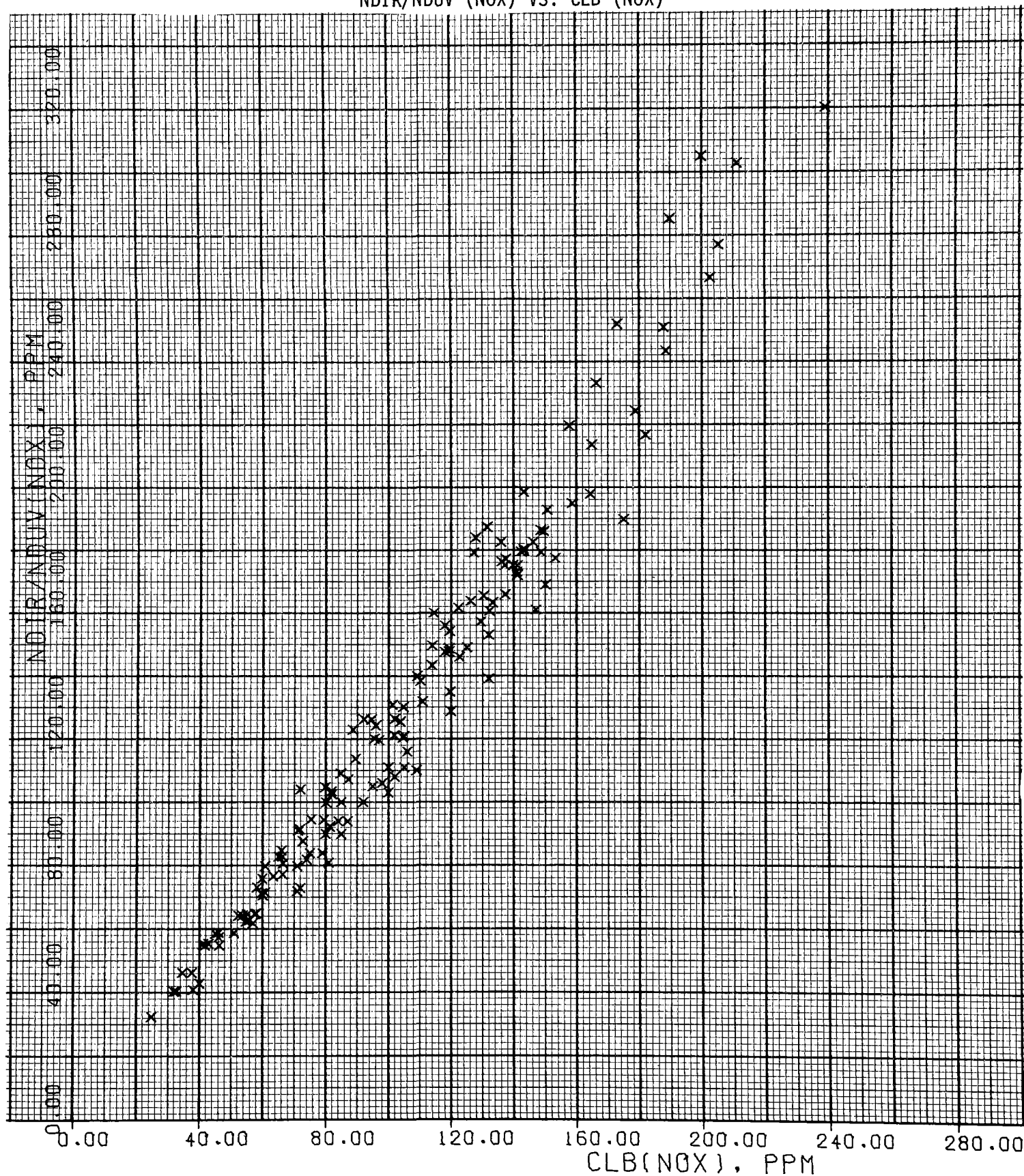


FIGURE 13  
NDIR/NDUV (NOX) VS. CLB (NOX)



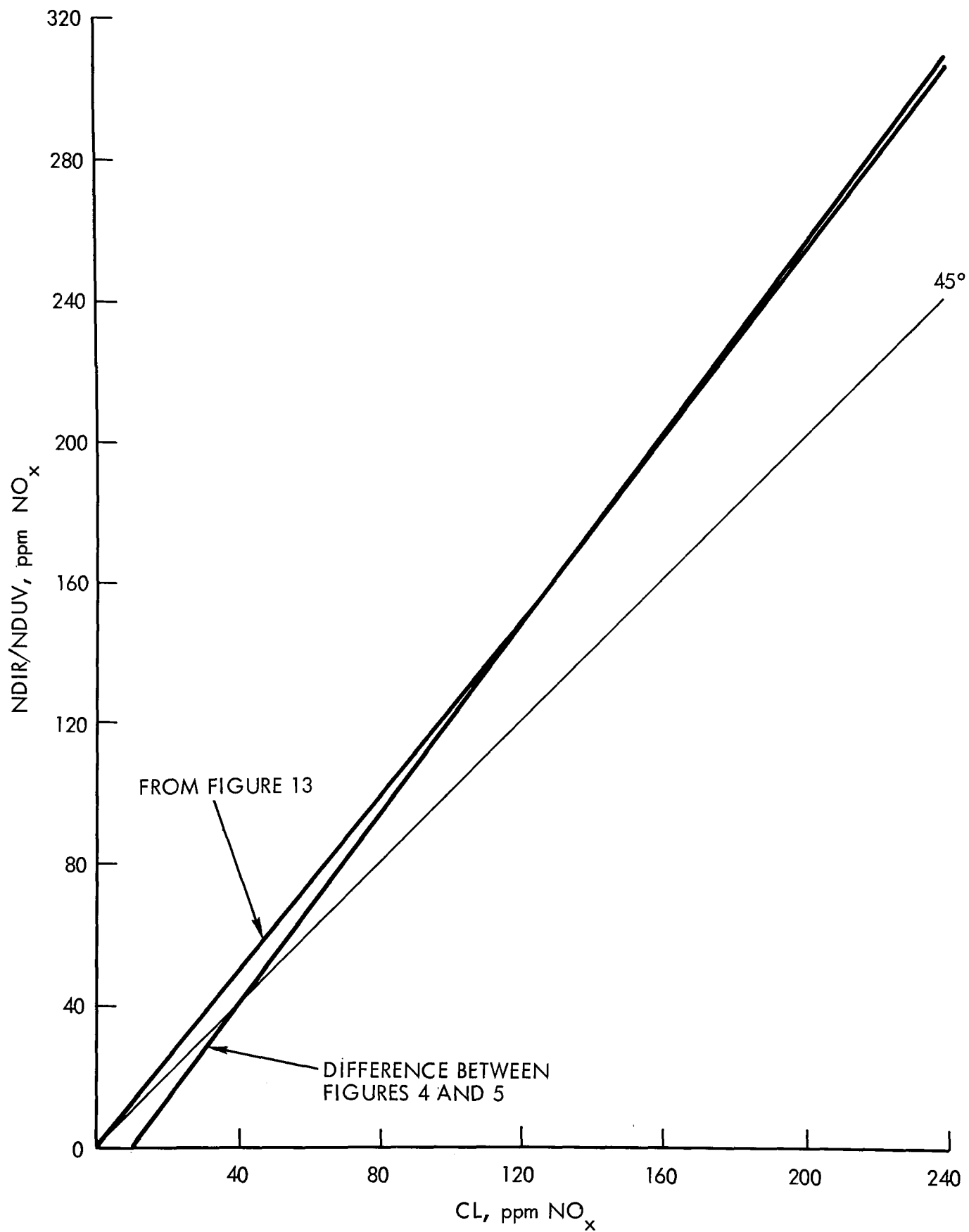
$$[\text{NO}_x]_{\text{NDIR/NDUV}} = 1.00298 [\text{NO}_x]_{\text{CL\#B}}^{1.04328} \text{ ppm} \quad (14)$$

with a correlation coefficient of 0.99465 (explaining all but 1.07% of the data). In order to facilitate comparison of Equations (13) and (14), Figure 14 presents a plot of both equations. It is seen that the agreement between the two approaches is quite strong, especially at higher  $\text{NO}_x$  concentration, and it is thus concluded that interference gas effects on  $\text{NO}_x$  response by NDIR/NDUV instrumentation, as well as the effects of Drierite, can be quite accurately measured by either NDIR/NDUV or CL techniques. A more detailed discussion of this result will be found in the final section of this report.

As the last step of this experimental investigation, an attempt was made to qualitatively explain the observed effects of interference gases on NO measurements by NDIR. It is well known that NDIR instrumentation responds positively to several interference gases, such as carbon dioxide, carbon monoxide and propane (all of which are found in automotive exhaust samples). With flame ionization detectors, as normally used in CVS testing, it is impossible to conveniently determine the concentration of any one species of hydrocarbons, since many are found in typical exhaust samples and are analyzed as a group on the basis of carbon concentrations. A gas chromatograph was not available during these experiments and no quantitative attempt was made to investigate the NDIR response to typical (but unknown) concentrations of propane in dilute samples of automotive exhaust gases.

It was possible, however, to qualitatively examine the effects of typical (measured) concentrations of carbon dioxide and carbon monoxide on the NO NDIR response characteristics. A series of experiments was first conducted to quantify the NDIR response to  $\text{CO}_2$  concentrations ranging from 1.25 to 2.50% in nitrogen. It was found that the NDIR responded to these gases by recording as if 3 to 6 ppm NO had been introduced. Similarly, it was qualitatively determined that the response by the NDIR to CO was about 40% as strong as that for  $\text{CO}_2$ . These data cannot be quantified (and are therefore not reported), since the signal to noise ratio observed during these experiments was too low to reliably examine in detail. It is

FIGURE 14  
INDEPENDENT EVALUATIONS OF THE EFFECTS OF DRIERITE AND  
INTERFERENCE GASES ON NO<sub>x</sub> MEASUREMENTS



evident, however, that the NDIR responds positively to several gases which are present in samples of automotive exhaust. Throughout this interference gas response investigation, no CL response was observed. This observed property of the NDIR to respond to interference gases helps in large part to explain differences, between its measured values and those of the CL analyzer, which are not directly attributable to the effects of Drierite.

## CONCLUSIONS

Based upon the results of this investigation, several conclusions can be drawn. First, using two independent CL instruments placed in parallel with one another, it has been shown that  $\text{NO}_x$  measurements are with high precision using identical CL instruments. Also, the results indicate that  $\text{NO}_x$  values measured by NDIR/NDUV techniques (with Drierite placed in the sample handling system of the NDIR) are significantly larger than those of corresponding CL determinations. This effect becomes more pronounced at higher  $\text{NO}_x$  concentrations.

It has been shown that higher NDIR/NDUV readings for  $\text{NO}_x$ , relative to measured CL values, result from both the effect of Drierite in the NDIR sample handling system and the response of the NDIR to interference gases found in dilute samples of automotive exhaust gas. The action of Drierite on the sample gas is such that  $\text{NO}_2$  concentrations are decreased, and NO concentrations are increased. This conversion of  $\text{NO}_2$  to NO is only a partial one, and thus a net decrease in  $\text{NO}_x$  concentration results. Since, in the NDIR/NDUV cabinet, Drierite is present upstream of the NDIR only, higher NO readings result than would be the case if no Drierite was present. In effect, then,  $\text{NO}_2$  is measured independently by NDUV analysis, and most  $\text{NO}_2$  is then removed and partially converted to NO before a measurement of NO by NDIR analysis is made. This is the primary reason that NDIR/NDUV instrumentation consistently yields higher measured  $\text{NO}_x$  values than those of CL instruments.

The remaining difference between NDIR/NDUV and CL determinations of  $\text{NO}_x$  are explained in large part by the positive response characteristics of the NDIR to interference gases which are present in automotive exhaust. NDIR instruments are known to respond positively to carbon dioxide, carbon

monoxide, and propane, and during this investigation it was found that the response to CO<sub>2</sub> alone explains virtually all differences between NDIR/NDUV and CL measurements of NO<sub>x</sub> which are not directly attributable to the presence of Drierite.