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SINGLE CYLINDER SPARK IGNITION ENGINE STUDY OF NO AND NO<sub>2</sub>  
EMISSIONS FOR METHANOL, ISO-OCTANE AND NITROGEN DOPED  
METHANOL WITH EMPHASIS ON MEASUREMENT TECHNIQUE\*

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ABSTRACT

NO and NO<sub>2</sub> emissions from a single cylinder CFR engine were measured as a function of fuel air equivalence ratio for the spark ignited combustion of methanol, iso-octane and nitrogen doped methanol. In all cases, no NO<sub>2</sub> was detected for fuel-rich or stoichiometric combustion, while significant amounts of NO<sub>2</sub> were found for fuel-lean combustion.

The exhaust system and exhaust sampling system were thoroughly tested for NO to NO<sub>2</sub> conversions, NO<sub>2</sub> to NO conversions and NO<sub>x</sub> losses. These tests showed that all conversions or losses were of relatively minor importance, and therefore that the NO and NO<sub>2</sub> concentrations reported were not artifacts of either the exhaust system or the exhaust sampling system.

Several devices for desicating the exhaust sample were tested to determine their effects on the NO<sub>x</sub> concentration of the sample. A Perma Pure dryer was found to be suitable for this purpose, while other devices examined removed up to 100% of the NO<sub>2</sub>.

For the fuel-nitrogen case, significant increases in the NO<sub>x</sub> emissions were measured at fuel-lean equivalence ratios. No increases in the NO<sub>x</sub> emissions were detected at rich conditions.

## INTRODUCTION

During the last few years there has been a growing interest in the use of methyl alcohol as an alternative to petroleum derived liquid fuels (1-6).<sup>\*</sup> This trend is nowhere more apparent than in the literature dealing with the potential use of methanol as an automotive fuel (7-25). The aim in many of the recent reports (12-25) on this subject has been to provide data with which the performance and emissions characteristics of engines and vehicles operating on methanol could be compared to those operating on gasoline.<sup>\*\*</sup> The comparative levels of  $\text{NO}_x$  emissions, in particular, have received considerable attention, probably due to the serious problems associated with  $\text{NO}_x$  control and reduction.

For a variety of test conditions, the generally reported  $\text{NO}_x$  emissions for methanol are found to be 30-50% lower than those for gasoline at fuel-lean conditions and 0-30% lower for stoichiometric and fuel-rich operation. However, these conclusions can not be accepted without question since there are at least two reports (16,18) of considerably smaller differences between the  $\text{NO}_x$  emissions for methanol and gasoline on the lean side; and there are further reports (13,14,18) that  $\text{NO}_x$  emissions are even higher for methanol than for gasoline under fuel-rich conditions.

A more subtle detail related to  $\text{NO}_x$  emissions is the question of the chemical state of the nitrogen oxides, i.e., the mix of  $\text{NO}$  and  $\text{NO}_2$ . Indeed, it has been reported in one study (12) that up to 50% of the  $\text{NO}_x$  emissions from methanol fueled vehicles is in the form of  $\text{NO}_2$ . However, no systematic investigation of  $\text{NO}$  and  $\text{NO}_2$  emissions from methanol fueled engines appears to

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\* Numbers in parentheses designate References at end of paper.

\*\* The term "gasoline" is used loosely here to include iso-octane.

have been performed in spite of the numerous performance and emissions studies on engines and vehicles operating on methanol. This lack of information concerning NO<sub>2</sub> emissions has been due, in part, to the use of instruments which are unable to detect NO<sub>2</sub> and to sampling techniques that might result in substantial losses of the highly water soluble NO<sub>2</sub> (13-16,18,19).

In this paper an effort has been made to address certain aspects of the questions raised above, i.e.,

1. What are the absolute levels of NO<sub>x</sub> emitted from a methanol fueled engine and how do these levels compare to those from a reference fuel?
2. What is the relative mix of NO and NO<sub>2</sub> emitted from a methanol fueled engine?
3. To what extent must the exhaust sampling system be tested to ensure against artifacts in the NO<sub>x</sub> measurements?

In addition, the effect of "fuel-nitrogen" was studied due to interest in the possible contribution to NO<sub>x</sub> emissions from chemically bound -N that might be found in methanol produced from coal.

#### EXPERIMENTAL APPARATUS

A Waukesha single cylinder CFR-ASTM engine was used throughout this study. Details of the engine configuration and operating conditions are presented in Tables 1 and 2. The fuels used for this investigation included ASTM grade iso-octane; reagent grade methanol and a 3.0% by volume mixture of pyridine in methanol. This pyridine mixture is equivalent to 0.64% by weight of nitrogen in the fuel. Both the pyridine and the methanol were reagent grade.

Fuel-air equivalence ratios ( $\Phi$ ) were determined both from the measured fuel and air flow rates and from the measured concentration of  $\text{CO}_2$  in the completely oxidized exhaust using the method of Gerrish (26). These two values were generally within  $\pm 2.0\%$  of the mean for lean equivalence ratios and  $\pm 3.6\%$  for rich equivalence ratios. Mean values of the equivalence ratio thus determined are used throughout this paper.

The engine exhaust system and exhaust sampling system are shown schematically in Figure 1. The sample probes were stainless steel; and the sample lines were either stainless steel or polyethylene. Heated lines ( $180^\circ\text{F}$ ) were used where necessary to prevent condensation. During normal operation, the exhaust sample was drawn from the exhaust tank through sample probe number (2) in Figure 1. The exhaust system was maintained at slightly elevated pressures (0.05 psig) to remove the possibility of air leaks into the system.

An ambient temperature and pressure chemiluminescent  $\text{NO} - \text{NO}_x$  analyzer (Thermo Electron Model 44) was used to determine the  $\text{NO}$  and  $\text{NO}_2$  concentrations. Dilution of the exhaust sample with nitrogen or direct drying of the sample were used to lower the dew point of the exhaust sample. The sample dilution technique required a factor of eight to ten dilution of the exhaust sample to prevent condensation at ambient temperatures. However, it appeared that small errors in the diluent gas flow could lead to unacceptably large errors in the measured  $\text{NO}_x$  concentrations, and this method was not used beyond a preliminary phase of the work.

Several devices for drying the exhaust sample were tested under controlled conditions to determine their effects on the  $\text{NO}_x$  concentration of the sample. These tests were conducted using samples with  $\text{NO}_x$  concentrations and dew points typical of the combustion products. The dryers investigated

included: stainless steel and Pyrex condensing coils in ice-water baths; various chemical dryers (e.g., Drierite); combinations of condensing coils and chemical drying agents; and a Perma Pure permeation distillation dryer. Detailed descriptions of these devices are given in the Appendix, and a schematic of the Perma Pure Dryer is shown in Figure 2. The dryer testing system is shown schematically in Figure 3. The results of this investigation, which are presented in Figure 4, showed that approximately 20-30% of the  $\text{NO}_2$  was lost in the condensing coils at typical  $\text{NO}_2$  and water concentration, while for similar conditions 70-100% of the  $\text{NO}_2$  was lost on passage through certain chemical drying agents. This latter result was found either when the drying agents were used alone or when they were used in combination with a condensing coil. In addition, this remarkable loss of  $\text{NO}_2$  was accompanied by a gain of NO that roughly equaled 1/3 of the  $\text{NO}_2$  lost in the drying agents. Similar behavior has been noted by Turner in a previous but less thorough study (27). Some of the losses noted in the present work were further verified with actual exhaust samples taken from the CFR engine; these results are also presented in Figure 4.

The Perma Pure dryer caused no significant changes in the NO or  $\text{NO}_2$  concentrations, and did not remove  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{O}_2$  or  $\text{N}_2$ . It was therefore used for all subsequent sampling work.

The exhaust sampling system was tested by injecting known mixtures of both NO in  $\text{N}_2$  and  $\text{NO}_2$  in  $\text{N}_2$  directly into the sample line, and subsequently measuring the NO and  $\text{NO}_2$  concentrations. These tests showed that a maximum of 2.0% of the NO or  $\text{NO}_2$  was lost or converted in the heated sampling system. More extensive testing of the system was performed as part of the emissions tests, and these are described in detail in the next section.

6 - Perma Pure Permeation Distillation Dryer: (continued) ..

water vapor in the sample and purge flows, respectively. The water is (apparently) removed as a vapor. Purge flow of about 8 scfh room air at approximately 1 psia was used.

LIST OF FIGURE CAPTIONS

- Figure 1 Exhaust Sampling System
- Figure 2 Perma Pure Dryer
- Figure 3 Dryer Testing System
- Figure 4 Loss of  $\text{NO}_2$  Due to Drying Exhaust Sample
- Figure 5 Comparison of  $\text{NO}$  and  $\text{NO}_2$  Emissions of Methanol and Iso-Octane
- Figure 6 Comparison of  $\text{NO}$  and  $\text{NO}_2$  Emissions of Methanol and Nitrogen  
Doped Methanol
- Figure 7 Effect of  $\text{NO}$  to  $\text{NO}_2$  Conversion in the Exhaust System on  
Reported  $\text{NO}$  and  $\text{NO}_2$  Emissions of Methanol





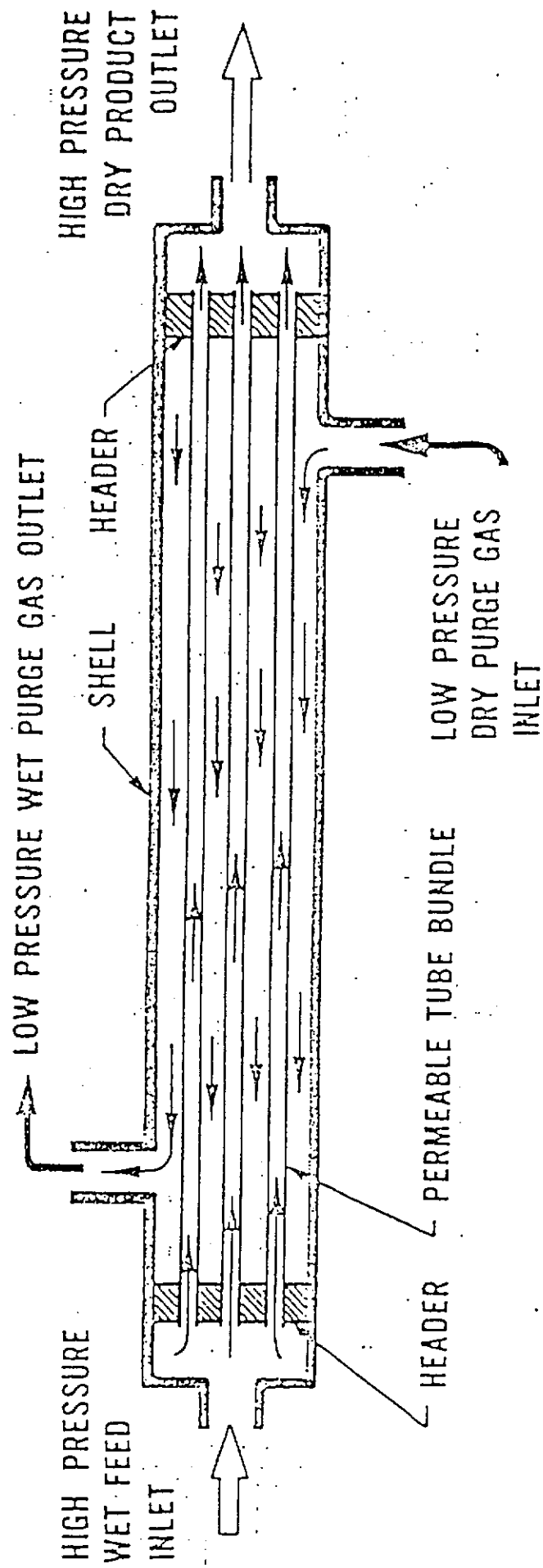


Figure 2

Perma Pure Dryer

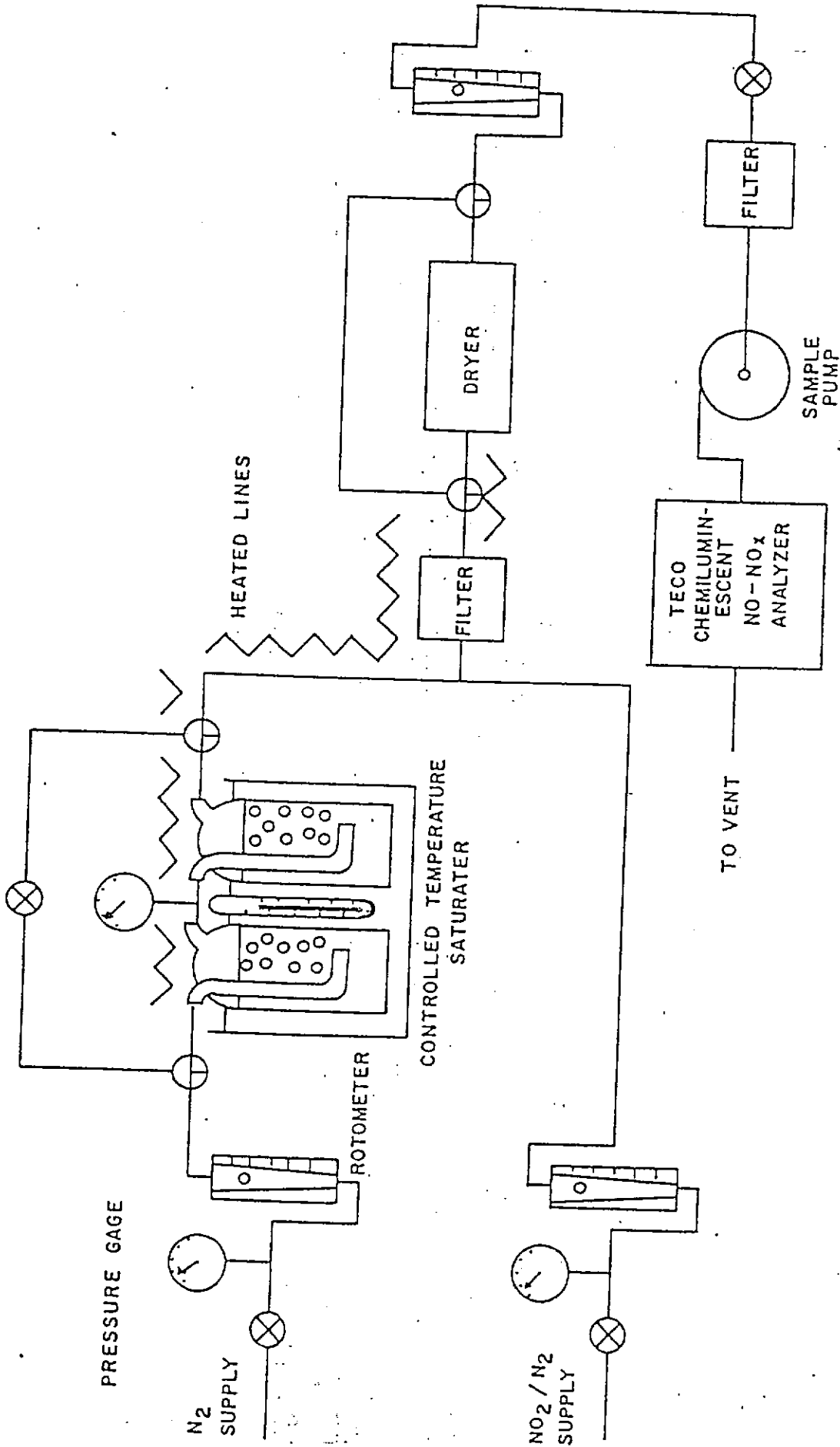


Figure 3

Dryer Testing System

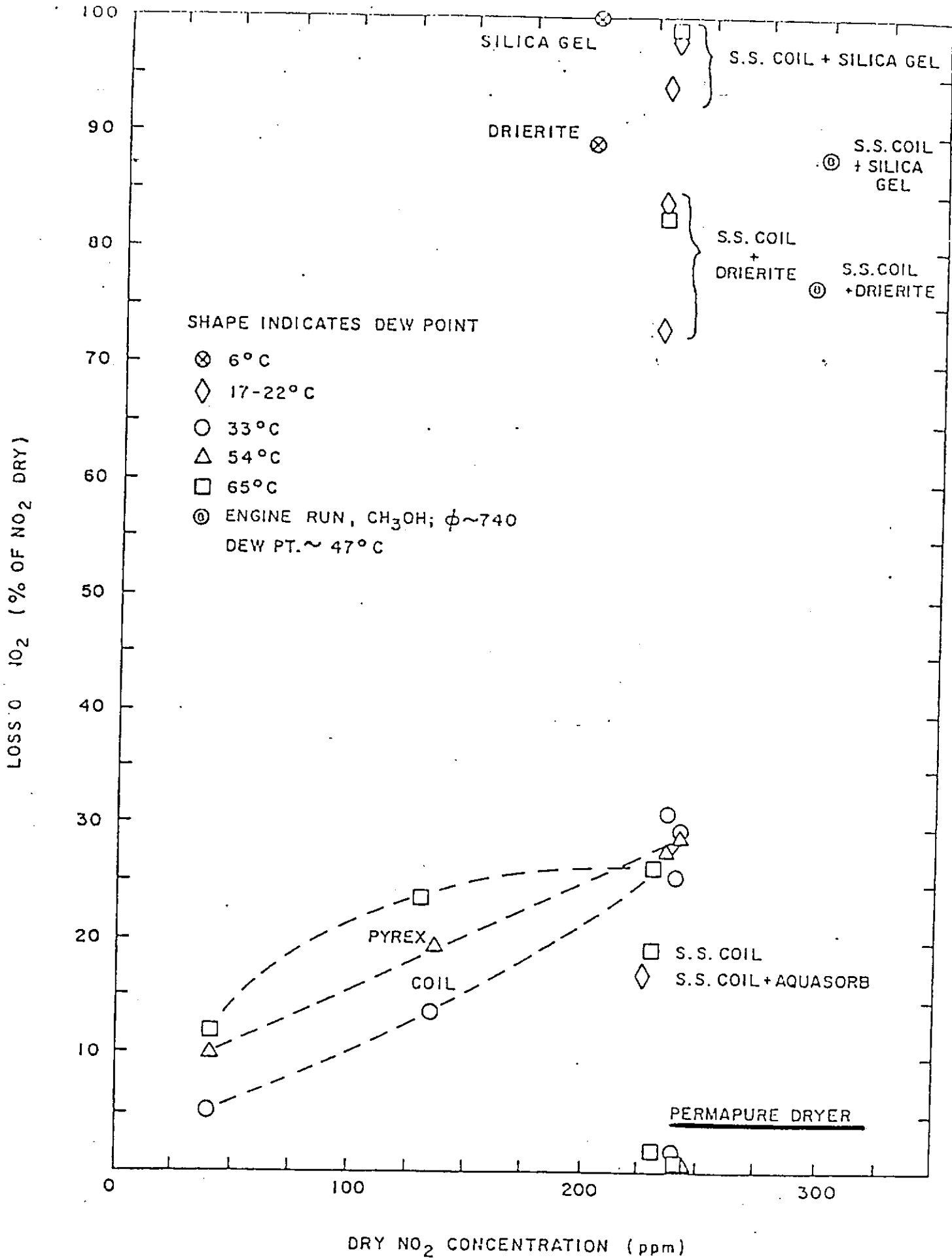


Figure 4

Loss of NO<sub>2</sub> Due to Drying Exhaust Sample

APPENDIX: DESCRIPTION OF DRYING DEVICES

1 - Pyrex Condensing Coil:

0.25-in. OD Pyrex tubing formed into a helical coil for a total length of approximately 31 ft. Coil maintained at approximately 32°F by immersion in an ice-water bath. Always used in conjunction with a 250 ml Pyrex condensate trap which was also kept at about 32°F by immersion in an ice-water bath.

2 - Stainless Steel Condensing Coil:

0.25-in. OD stainless steel tubing formed into a helical coil for a total length of approximately 5.5 ft. Coil maintained at approximately 32°F by immersion in an ice-water bath. Always used in conjunction with a 250 ml Pyrex condensate trap which was also kept at about 32°F by immersion in an ice-water bath.

3 - Drierite ( $\text{CaSO}_4$ ):

8 mesh indicating Drierite used in a 145 ml Pyrex drying column.

4 - Silica Gel ( $\text{SiO}_2 \cdot \text{xH}_2\text{O}$ ):

6 - 16 mesh non-indicating Silica Gel used in a 145 ml Pyrex drying column.

5 - Unknown mesh size indicating Aquasorb used in a prepacked 35 ml polyethylene tube.

6 - Perma Pure Permeation Distillation Dryer:

Model PD-625-24S Perma Pure dryer. 50 tube model, 2 ft long, 0.625-in. OD. Stainless steel shell, DuPont Nafion perfluoro sulfonic acid polymer semi-permeable tube bundle. Dryer operates by passing water vapor from a wet sample through semi-permeable membrane tubes into a dry purge flow. The driving force is the difference between the partial pressures of