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Nitrogen Oxide Abatement by Distributed Fuel Addition
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ABSTRACT

The purpose of this project is to develop techniques for nitrogen oxides abatement by distributed fuel addition. The major nitrogen oxide of interest is Nitric Oxide (NO), a precursor to premature forest damage and to acid rain. Recently interest has also been evoked with respect to an additional oxide of nitrogen, namely Nitrous Oxide (N₂O). Therefore, abatement measures for NO_x are being investigated to determine their influence on N₂O as well.

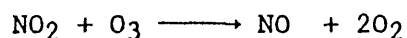
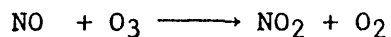
This report briefly describes the significance of N₂O emissions to the environment and the urgent need to develop techniques that can reduce emissions of both NO and N₂O. Reburning through distributed fuel addition may be an effective technique for NO_x (mainly NO) emission control as described in the previous quarterly report. Reburning may also be effective in reducing N₂O levels.

A technique for N₂O measurement by gas chromatography/electron capture detection was developed during this quarter, and is described in this report. This analysis technique will be used in the proposed experimental study to investigate the effectiveness of reburning on N₂O control.

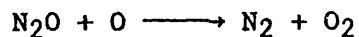
INTRODUCTION

Recently, there has been increasing concern over N_2O emissions into the environment. The atmospheric concentration of N_2O is increasing steadily at a rate of about 0.25% per year with a present concentration of about 304 ppb. There are no known atmospheric sinks for N_2O , which has a lifetime greater than 100 years (1,2).

N_2O is a trace gas which causes ozone depletion and is a contributor to the greenhouse effect. Ozone layer depletion will cause increasing amounts of solar ultraviolet radiation to reach the Earth's surface. This creates potential health problems and has damaging effects on agriculture and fisheries. The greenhouse effect may have an irreversible effect on the global climate. Other NO_x gases, namely NO and NO_2 , have similar destructive effects on the ozone through the reactions:



However, Nitric Oxide and Nitrogen Dioxide gases are reactive with short lifetimes in the atmosphere. Consequently, NO_x gases released by processes such as coal combustion do not reach the stratosphere where O_3 is found. On the other hand, N_2O released with NO_x gases, diffuses into the stratosphere because of its inert nature. In the stratosphere, about 10% of N_2O reacts with excited oxygen atoms:

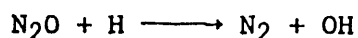


while another 90% undergoes photolysis:



Although only a fraction of N₂O becomes NO, this path is responsible for 70% of O₃ destruction. There is some dispute whether combustion is a major source for the increase of N₂O in the atmosphere. There is no doubt that the rise in N₂O correlates with the rise of fossil fuel combustion activities. Limited data suggests that there may be a relationship between NO and N₂O emissions, although this is sharply disputed.

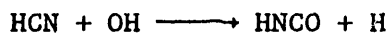
The United States may currently be the largest contributor to atmospheric N₂O, due primarily to emissions from coal combustion and heavy oil fired boilers. Kinetic considerations suggest that in a flame all N₂O formed should be consumed over a short time period through the reaction:



Nevertheless, N₂O emissions have been observed from combustion systems and seem to be related to the late devolatilization of coal nitrogen from char. Like fuel NO_x, N₂O production is related to the amount of chemically bound nitrogen present in the fuel, and is very sensitive to how the fuel is burned.

The following is a presentation of some of the ideas behind N₂O formation in combustion flue gas that were presented in a recent EPA/N₂O Workshop⁽¹⁾.

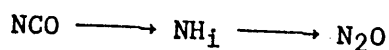
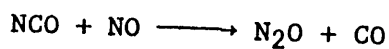
Kramlich (Energy and Environmental Research Corp.), theorized that N₂O from combustion systems could be formed from homogeneous conversions of HCN with N₂O yields greatly dependent on temperature. The reaction



would be favored at low temperatures, whereas, the reaction



would be favored at high temperatures. NCO is a precursor for N₂O formation through the following reaction:



If the temperature is too high, N₂O is destroyed. Consequently, HCN can be converted to N₂O within a narrow temperature range (1200-1650K). Wendt (University of Arizona), presented data in agreement with Kramlich hypothesis. Togan (MIT), suggested that imperfect mixing may cause fuel rich pockets containing N₂O precursors to move into cool fuel lean regions where these pockets mix and react to form N₂O. These precursors may be either HCN or nitrogenous char. N₂O from char may be formed by heterogeneous oxidation or by forming HCN which subsequently oxidizes to N₂O. Results by Houser (Western Michigan University), showed that slowing of HCN destruction did not limit N₂O formation but caused a shift in the destruction path from N₂O precursors. Thus, combustion systems in which fuel is burned at temperatures substantially less than flame temperatures may have higher N₂O emissions. Only a small fraction of the N₂O formed (3-10 ppm) may be due to its formation in the flame, escaping the region of peak combustion temperature into a cooler region where N₂O could survive.

Combustion systems can produce substantial amounts of NO by thermal fixation of nitrogen (thermal NO_x). On the other hand, direct thermal production of N₂O appears to be a minor process.

It is not clear whether N₂O emissions can be correlated with NO_x emissions and there are conflicting data in this respect. Some data suggest a N₂O/NO_x molar ratio of 25%. Nevertheless, the scatter in the data is too great to

indicate any direct correlation between N₂O and NO emissions. Consequently, the speculation that NO_x reduction measures would also reduce N₂O emissions may not always be true. For example, reduction of thermal NO_x does not produce significant reductions in N₂O emissions. On the other hand, reburning studies at Electric Power Research Institute showed a constant N₂O/NO_x emission ratio as NO_x level was reduced by combustion modification.

In summary, it is possible that reburning technology, which is effective in NO_x control, may also be effective in N₂O control.

N₂O MEASUREMENTS

An analytical procedure for on-line N₂O sampling and analysis has been developed and will be used in subsequent testing to determine N₂O concentrations in combustion flue gas. The analysis is performed by gas chromatographic separation and electron capture detection. The cost of the set-up was kept below \$7,000. It consists of a Shimadzu GC/ECD, a Valco 6-port sampling valve with 1 ml loop, a carrier gas purifier for O₂/H₂O removal and an indicating tube for O₂/H₂O detection. Figure 1 shows a typical chromatogram with a list of the instrumental parameters. The approach is a modification of that reported by Sykes (4). Various approaches to N₂O measurement appear in the literature (1,2,3,4). It is clear that Ar/CH₄ mixture is the carrier gas of choice. N₂ is unsuitable for ECD because the sensitivity of the detector depends on trace impurities, especially in carrier gas. Consequently, N₂ may cause long term variation of detector sensitivity. Also, N₂ carrier gas may cause CO₂/N₂O interference because the presence of CO₂ in gas samples increases the sensitivity of the detector. CO₂ interference does not appear to be a problem with GC determination of N₂O when Ar/CH₄ mixture is used as carrier gas (1).

Calibration was performed using a calibration gas containing 95 ppmv N₂O. The same calibration gas was used, diluted to the desired N₂O concentration.

The gas sample valve is placed in the load position and the gas mixture of known N₂O concentration is purged through the loop. The sample intake pressure is maintained at 3 psig. The sample valve is then moved to the inject position. Table 1 shows the calibration data and Figures 2 and 3 show the calibration curves obtained.

N₂O response appears to be linear in range 20-100 ppm and non linear at lower concentrations. A stable baseline was obtained using Ar/CH₄ as carrier gas and N₂O measurements as low as 100 ppb were possible, as seen in Figure 1.

Consecutive tests are reproducible with a maximum difference of about 3% as seen in Figure 2. Similar tests performed after the set-up was shut off for five days and then restarted showed a difference of about 3.5% in the measurements obtained.

Another set of measurements was performed to investigate the effect of the presence of a number of gases, such as CO₂, H₂, CO, and CH₄ on N₂O response. The calibration gas was diluted while keeping CO₂ concentrations constant at 15%. Little difference (less than 3%) was observed compared to the other two sets of calibration data where CO₂ was varied proportionately to N₂O concentration and only N₂O, CO₂ and O₂ gases were present. Thus, CO₂ and other combustion gases (H₂, CO and CH₄), seem to have little or no interference with N₂O response as seen in Figures 3 and 4.

N₂O response seemed to be sensitive to the number of previous injections which is more significant at higher concentrations of N₂O (Figure 5). This can introduce a difference in N₂O responses for the same sample as high as 15%. Several measures were necessary to reduce this difference to less than 3%. These measures will be adopted as part of a recommended operating procedure in N₂O calibration for this particular set-up and analysis.

1. After the initial set-up, introduce 5-6 calibration gas samples. This is necessary to condition the column and the responses should not be considered in the calibration.

2. The calibration must be performed after the initial set-up and following the last analysis on a certain day with each sample injected a minimum of three times.
3. The column must be conditioned and new calibration performed after about 40 tests and/or every day. The column is conditioned by raising the column temperature to 220°C with 20 ml/min carrier gas going through the column for at least 15 hours.

Finally, to minimize ECD contamination by air diffusing from the atmosphere, the flow of carrier gas through the detector will be maintained at all times.

TABLE I

Calibration Gas: 15.14% CO₂, 1% O₂, 95 ppmv N₂O, Balance N₂
 Same calibration gas was used, diluted to
 desired concentration

Gas A: 15.04% CO₂, 5.02% CO, 7% H₂, 2% CH₄,
 Balance N₂

R is ECD response peak height in mm; the
 equivalent of N₂O response at range 10 and
 Att 32

N₂O concentration is in ppmv

SET I		SET II		SET III	
DAY 1, DILUTION WITH N ₂		DAY 2, DILUTION WITH N ₂		DAY 2, DILUTION WITH A	
N ₂ O	R	N ₂ O	R	N ₂ O	R
0.8	9, 10	1.1	12.8, 13.1	1.2	13.2, 13.3, 13.6
1.4	13, 13, 13.2	33.2	192, 194	33.6	192, 192
2.3	20, 20	56.7	292, 296, 298	56.7	300, 302
4.1	35, 35, 35	69.9	342, 344, 346, 348	68.4	354, 356
11.9	78.5, 79.5, 82.5	95	476, 480	76.6	388, 388
20.4	123.5, 123, 127 126, 125			95	476, 480
30.7	182, 182, 183				
45.5	247, 249, 256				
50.8	282, 282.5, 285				
61.3	330, 326, 327				
65.3	355, 351, 351				
75.5	386.5, 390, 390				
95	491, 494				

Sets I and II: CO₂: N₂O ratio is constant = 15.14% : 95ppmv
 $\%CO_2 = 0.16 * N_2O$

Set III: CO₂ concentration is constant at 15%

Linear regression in 20-100 ppm N₂O range:

SET I : N₂O--7.35+0.209*R

SET II : N₂O--7.67+0.217*R

SET III: N₂O--7.93+0.216*R

CONCLUSIONS

A reliable and reproducible analytical procedure was developed for on-line N_2O analysis. This procedure will be used in the proposed experimental study to determine the effects of reburning on all oxides of nitrogen.

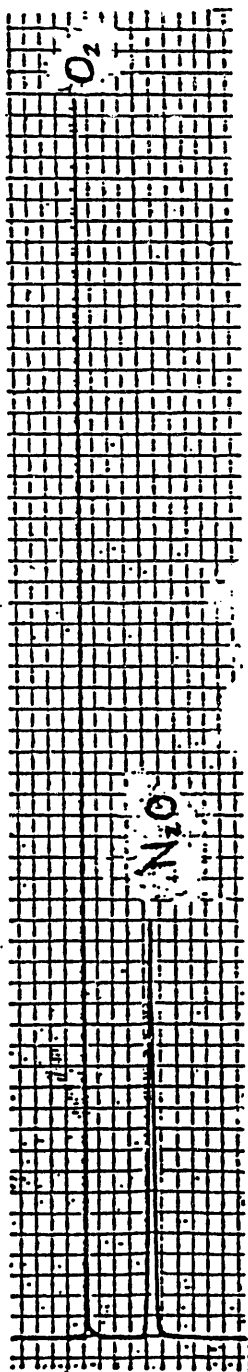
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2. Lanier, W.S. and S.B. Robinson, "EPA Workshop on N2O Emission from Combustion", U.S. EPA Report EPA-600/8-86-035, September 1986.
3. Kramlich, J.C., Grogan, T.C. and J.M. McCarthy, "Non Continuous Sampling and Analysis of Nitrous Oxide from Combustion Sources", Energy and Environmental Research Corporation procedure.
4. Sykes, A.L., "Standard Operating Procedure for Determining Nitrous Oxide Concentrations in Combustion Flue Gas", draft document prepared for EPA, August, 1984.
5. Wendt, J.O.L. and J. Meraab, "Nitrogen Oxides Abatement by Distributed Fuel Addition", U.S. DOE Quarterly Report DE-AC22-87PC79850, November 1987.

INSTRUMENTAL PARAMETERS

Instrument: Shimadzu GC-8A
Column: Porapak Q, 12 ft x 1/8 in stainless steel conditioned at 220°C
Oven Temperature: 35°C
Detector: Electron Capture, Ni 63 at 350°C
Carrier Gas: Ar/5.22% CH₄ at 20 ml/min
Sample: 1 ml loop at 3 psig intake pressure
Calibration Gas: 15.14% CO₂; 1% O₂, 95 ppmv N₂O, balance N₂ carrier gas passes through a carrier gas purifier for O₂/H₂O removal and an indicating tube for O₂/H₂O detection before entering the GC
Recorder Input Voltage: 1 mV

ALT 1024
Range 1
95 ppm N₂O



ALT 1
Range 1
~ 100 ppb N₂O

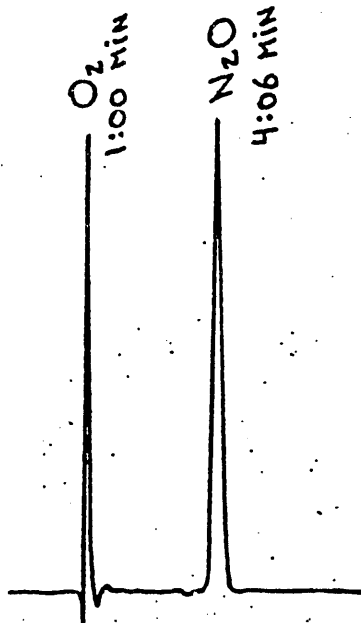


Figure 1. ECD Response

CALIBRATION CURVE FOR N2O GAS IN ppmv

SHIMADZU / ECD RESPONSE - N2O

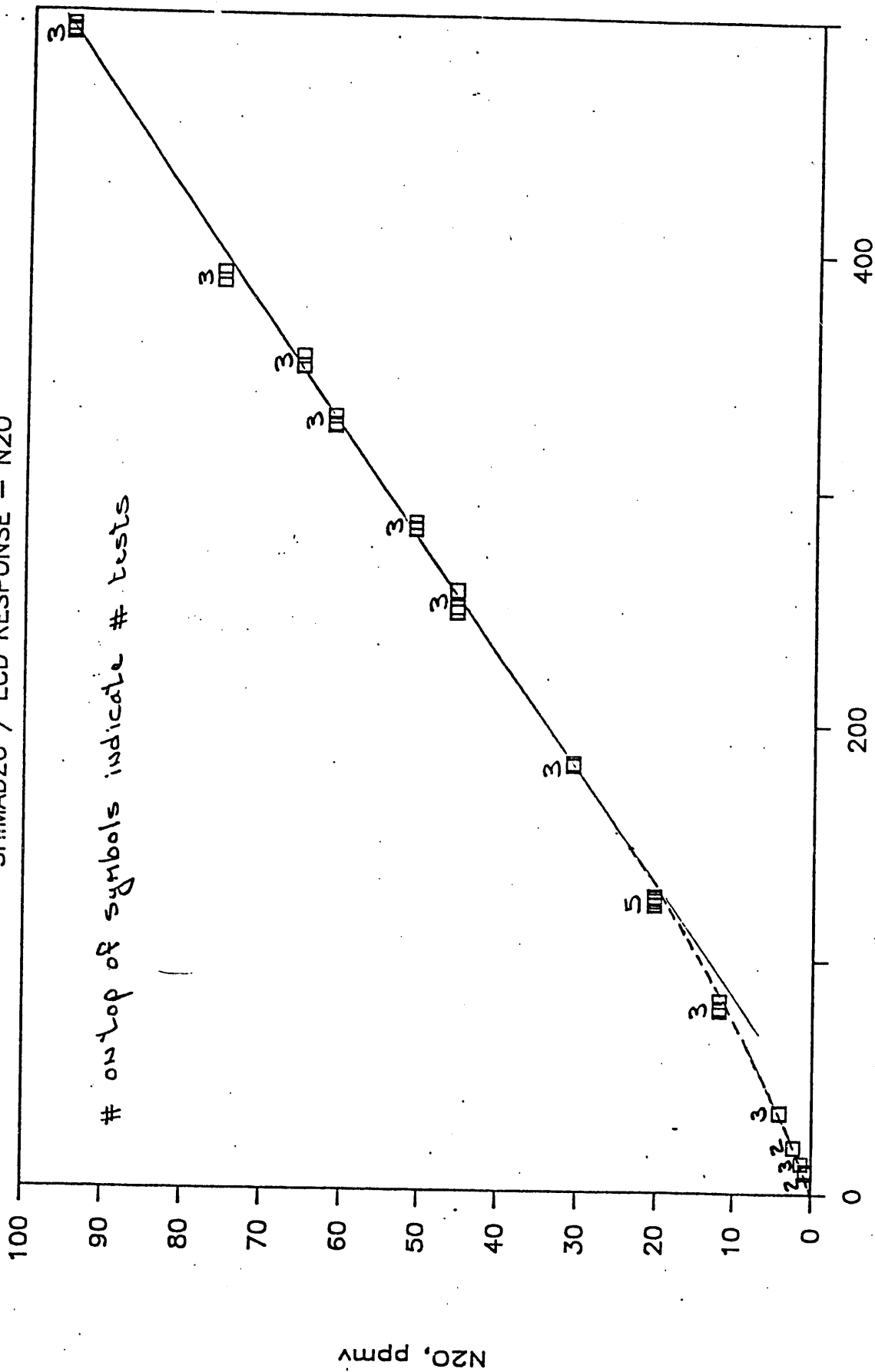
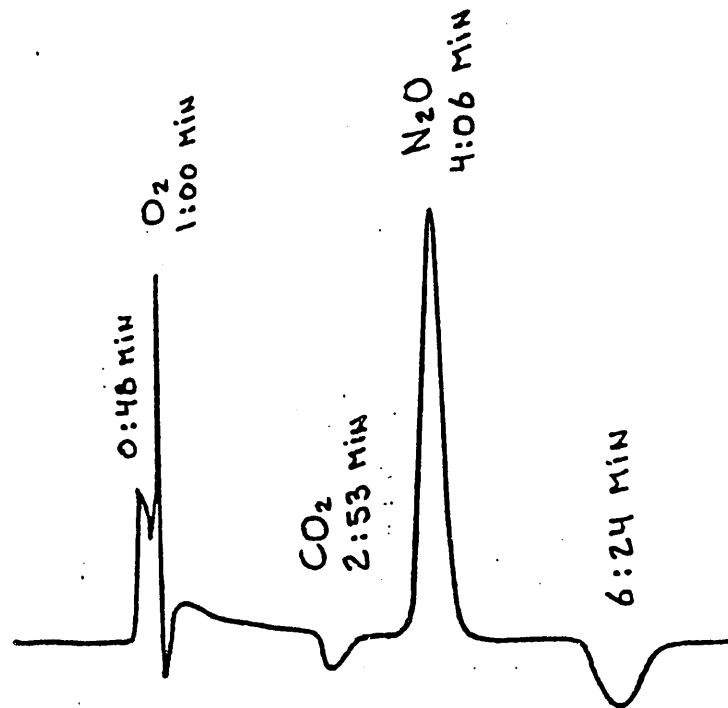


Figure 2. N2O Calibration

ALT 8
Range 10



Gas Mixture :

15% CO_2 , 7% H_2 , 5% CO , 2% CH_4

0.01 % O_2 , 1 ppm N_2O , Balance N_2

Figure 4. Responses of Various Gases

Calibration Gas : 95 ppm N₂O
Att 128 , Range 10

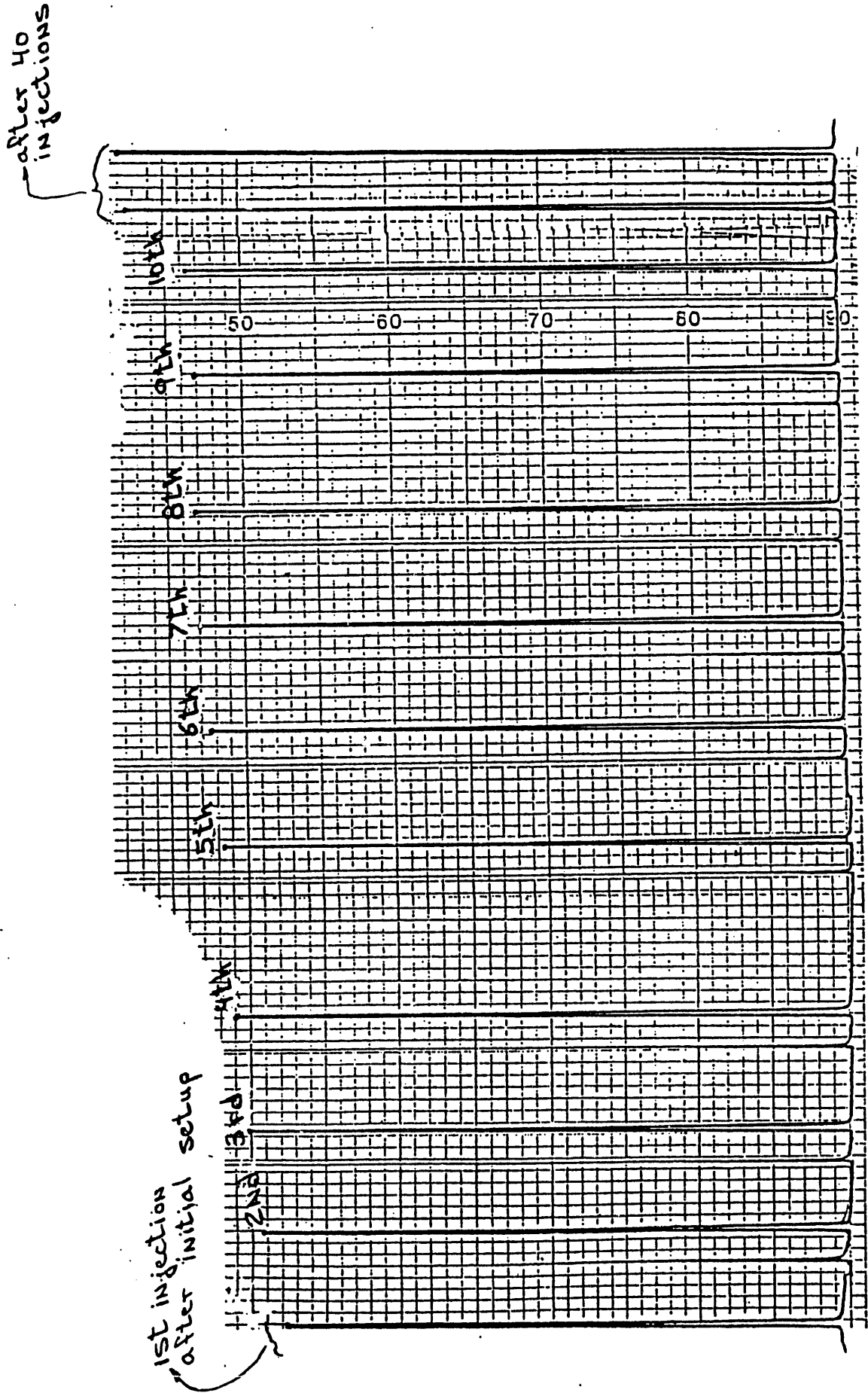


Figure 5. Sensitivity of N₂O Response to No. of Injections

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