MEASUREMENT OF N-NITROSAMINE CONCENTRATIONS IN NIOSH DIESEL EXHAUST/COAL DUST STUDY

by

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ABSTRACT

The atmospheres within and prior to the animal exposure chambers in the NIOSH diesel exhaust/coal dust study were monitored for the presence of seven volatile N-nitrosamines. The samples were collected on a monthly and sometimes on a weekly basis. The analytical results showed frequent presence of N-nitrosodimethylamine in low nanogram (0-150) amounts mostly in the chambers containing diesel exhaust and diesel exhaust plus coal dust. Low nonogram concentrations, usually lower than N-nitrosodimethylamine, of N-nitrosodiethyl and N-nitrosodipropyl amines were also found occasionally in these chambers. The presence of nitrosamines in the exposure chambers were largely scattered with relative standard deviations in diesel chambers in excess of 100% and did not show any definite trend of occurrence with time. The samples were analyzed by either gas chromatography-thermal energy analyzer (GC/TEA) or by gas chromatography-Hall electrical conductivity detector (GC/HECD) methods. The analytical limit of quantitation in both methods was 6 ng/m^3.

INTRODUCTION

Nitrosamines are a group of chemicals represented by the structural formula R2=N-N=O, where R may be either an alkyl or aryl group. The chemical bond N-N is weaker than either R2=N or N=O in this chemical structure. These compounds are usually formed by the nitrosation of secondary amines with nitrite ion. They may also be formed in the atmosphere if other precursors such as oxides of nitrogen, other amides or nitrogenous compounds such as ureas, carbamates or guanidines are present (1-5). Because of the fact that N-nitrosamines have been found to be potent chemical carcinogens (6-9) a great deal of interest has been shown in these compounds in recent years. Due to the suspected presence of nitrogen oxides and other nitrosamine precursors in the diesel engine environment (10),the NIOSH Diesel Exhaust/Coal Dust study called for regular monitoring of N-nitrosamines in the animal exposure chamber atmospheres. Recently, N-nitrosamines have been detected in diesel crankcase emissions (11) thus confirming the relevance of this planned study by NIOSH.

The purpose of this report is to present the results of the N-nitrosamine measurements during the NIOSH Diesel Exhaust/Coal Dust study.

EXPERIMENTAL SECTION

Sample Collection: Samples for N-nitrosamines were collected on a monthly basis according to a sampling protocol which called for a sampling train consisting of a 37-mm glass fiber type filter followed by a Thermosorb/N adsorbing tube. The sampling train was designed to trap non-volatile nitrosamine particulates as well as other particulates on the filters and the volatile nitrosamine vapors on the adsorbing tubes. Because of interferences observed with 0.8 micron cellulose membrane (type AA) filters during the analysis of the first month's filter samples, the use of glass fiber filters in the sampling train was used for subsequent sampling. Samples were collected at the rate of 2L/min for approximately 7 hours each.

Some weekly samples were also collected using the same sampling protocol as used for the monthly samples during the later part of the study (February/March 1982) for seven continuous weeks.

Three samples, one for 2 hours, a second for 5 hours and a third for 6 hours, were also collected in the mixing chamber at various time period during this part of the study.

Sample Analysis: The samples were analyzed for the following nitrosamines whose common abbreviations are also given below.

NDMA	Nitrosodimethylamine
NDEA	Nitrosodiethylamine
NDPA	Nitrosodipropylamine
NDBA	Nitrosodibutylamine
NPIP	Nitrosopiperidine
NPYR	Nitrosopyrrolidine
NMOR	Nitrosomorpholine
NDPhA	Nitrosodiphenylamine

The analyses were performed by using the following three methods. A brief description of these methods as well as the procedures are given below.

(1) GC/TEA:

A gas-liquid chromatograph (GC) equipped with a thermal energy analyzer (TEA) detector was used for the N-nitrosamine analysis. In this detector, the N-N bond of $R_2N-N=O$ is catalytically broken, NO is combined with ozone to produce an excited NO_2 molecule which is detected by luminescence produced on its returning to the ground state. The production and detection for the exicted nitroso radical is proportional to the concentration of the parent N-nitrosamine in the analyte.

A 6ft. glass Carbowax 20M-2% KOH on Chromosorb W 100/120 mesh chromatographic column was used A desorbing solvent consisting of 75% methylene chloride and 25% methanol was used for Thermosorb tube samples. Filters samples were extracted with methylene chloride. Temperature conditions were: pyrolyzer, 550-600°C; interface,225°C; column, 120°C for 2 min and then progammed to 130°C at the rate of 6°C per minute. An 8-10 uL aliquot of the sample was used for injection.

(2) HPLC/TEA:

A high pressure liquid chromatography (HPLC) was used in conjunction with the TEA detector. This method was particularly suitable to the analysis of non-volatile nitrosamines, such as NDPhA.

An HC Pellosil guard column and a Bondapak NH_2 column or some times, a radial-compression cartridge C_{18} column was used for the HPLC analytical work. The choice of the column depended on the desired degree of specificity and interference. A solvent mixture consisting of 97% isooctane and 3% acetone at a flow rate of 0.5 mL/min was used for all analyses involving HPLC. A 50 uL aliquot of the sample was used for injection into the chromatogaph

(3) GC/HECD:

In this method, gas-liquid chromatography is used in conjunction with the Hall electrolytic conductivity detector, where species separation and detection are accomplished by gas chromatographyand the Hall detector in the nitrosamine mode. The nitrosamines are cleaved to produce NO entities which are reduced by hydrogen gas in a reaction tube to ammonia giving rise to an increase in conductivity. The conductivity measurement is proportional to the concentration of the original analyte. By scrubbing out the acidic interferences selective and sensitive nitrosamine detection is achieved.

The analysis was performed on a Tracor Model 560 GC with the gold reactor tube operating at 650°C and hydrogen reactor gas at 20mL/min. Methylene chloride was used for the desorbing solvent and an aliquot of 1-5 uL of the sample was used for injection into the gas chromatograph.

A similar chromatographic column as ued in the above GC/TEA method was employed.

Three laboratories performed the sample analysis at various times during the investigation period of this project. Two laboratories, Monsanto Research Corporation and Radian Corporation were NIOSH contractors and the third laboratory performing the analyses was the Measurements Research Support Branch (MRSB) of NIOSH.
Monsanto Research Inc. used either GC/TEA or HPLC/TEA methods, for the analyses. The analytical range and the precision for both of these methods were approximately 100 pg/m^3 to 10 ug/m^3 for a 1000 L air sample and approximately 5% RSD(relative standard deviation), respectively. MRSB used the GC/TEA method to analyze the samples. The analytical range and the precision were similar to those obtained by Monsanto Research Corporation. Radian Corporation used the GC/HECD Method and their analytical range sensitivity and precision were comparable to the GC/TEA Method used either by Monsanto Research Corporation or MRSB.

All analyses were challenged by spiked samples and other MRSB quality assurance measures. The response to Q.C. checks was satisfactory for these analyses.

In case of any anticipated delay in the start of the sample analysis the samples were stored in the freezer prior to the analysis. Samples were found stable for several months when stored in this way. Not more than 0-12% sample loss occurred when stored in the freezer for 6 months.

RESULTS AND DISCUSSIONS

All analytical methods used in this study had similar sensitivity and precision. The choice of method depends upon the convenience of the laboratory and the nature of the compounds (volatile nitrosamines vs. non-volatile nitrosamines). Sometimes an alternative method can be used for confirmation purposes and thus, the availability of more than one type of nitrosamine methodology was advantageous. GC/MS was used to confirm the identity of the analytes by all groups performing the analyses.

Although the samples were analyzed for seven volatile and one non-volatile nitrosamines, only three, NDMA, NDEA, and NDPA were detected above the limit of detection (LOD) which was 6.0 ng/m^3. The complete analytical data for the nitrosamines are given in the appendix of this monograph

The analytical results suggest that most frequently those exposure chambers which contained either diesel exhaust ambient or diesel exhaust and coal dust ambient frequently contained measurable amount of either NDMA, NDEA, or NDPA. Low levels (below 10 ng/m^3) of NDMA were also found occasionally in chambers containing coal dust and clean air. On rare occasions,a detectablequantity of NDEA or NDPA was also found in these chambers. Figures 1 and 2 show the plots of the concentration of NDMA, as a function of time for exposure chambers 7 through 12. Chambers 7-9 contained coal dust and diesel exhaust and chambers 10-12 contained diesel exhaust only. Figure 3 illustrates the concentration of NDMA as a fuction of time, based on its occurrence in the group of chambers containing either clean air (CLEAN), coal dust plus diesel (COALD),and diesel exhaust only (DIES). Figures 4 and 5 show the variation of the three nitrosamines concentrations, NDMA, NDEA and NDPA, with time in the coal plus diesel and the diesel exposure chambers, respectively. As is apparent from the results, the values obtained from the monthly samples collected during the earlier part of this study did not show any definite trend of variation with time. It was, therefore, thought that the samples of atmosphers collected at a closer time interval both within and prior to the exposure chambers might prove useful in establishing a trend in the variation of the analytical data with time. Hence, in order to investigate trends in the nitrosamine data, samples were collected on a weekly basis continuously for seven weeks during the months of February and March, 1982. These weekly samples were collected both inside and outside (in the air stream prior to entering the exposure chambers) the exposure chambers. The place for the sampling port for the outside air collection in the air stream duct was chosen to avoid any contamination with the chamber ambient by diffusion.

Statistical analysis of the analytical results are the basis of the following discussion. A question of significant importance is whether the diesel exhaust, does, in fact, raise the nitrosamine level in the exposure chambers. Table 1 presents the per cent of nondetectable nitrosamines by analyte and chamber type. It is noted that for NDEA, for each of the four kinds of chambers, the percent of non detectables always exceeds 90%. Statistically, the four kinds of chambers do not differ in their NDEA levels, i.e., application of a chi-square test with three degrees of freedom does not yield a significant result at the 10% level. For both NDMA and NDPA the chi-square tests yield highly significant results, indicating that the chambers containing diesel and coal+diesel ambient have many more detectable values than the clean air and coal chambers.

Table 2 presents the means and coefficients of variation (CV) for the nitrosamine concentrations in each type of exposure chamber. Means and CV's have been computed two ways- (a) setting nondetectable values equal to 0; (b) setting nondetectable values equal to the detection limit (6 ng/m^3). The frequency distributions of the measurements appear in Table 3a, b, and c.

Tables 3a-c show that there are a few measurements which might be thought to increase the average values and inflate the CV's. Tree measurements (the highest measurements for the clean air, coal, and diesel chambers) were excluded for NDMA, and the means and CV's were recomputed. These new results appear in Table 2 in parentheses. The main observation which can be made from from Table 2 is that when there are a significant number of detectables, as in the diesel and coal-diesel chambers for NDMA and NDPA, the CV's exceed 100% even after some large values are excluded for NDMA. For the clean air and coal chambers, the CV's are usually less than 100%, with the exception of the clean air chamber for NDEA, and the coal chamber for NDMA. Substitution of the detection limit for the nondetectables will produce an underestimate of the CV. It is clear, then, that the nitrosamine data is subject to considerable variability.

One of the objectives of this study is to provide estimates of nitrosamine concentrations in the various groups of chambers. How good these estimates are depends on their precision. As noted above, the precision of the nitrosamine measurements in those chambers where the detectable levels are relatively high, is poor. There are several possible explanations for this. One is that the precision of the sampling and analytical method may be poor. Another explanation is that there may be considerable variability in the generation of nitrosamines from the diesel fuel.

Data on the precision of the analytical method is presented in Table 4. With each batch of field samples, samples with known spikes were analyzed. Analysis of the spiked samples provided the precision estimates as given in Table 4. The CV's for NDMA, NDEA, and NDPA are 20%, 16%, and 25% respectively. These, then, are precision estimates for analytical variability. Assuming a sampling error estimate of 5%, the total sampling and analytical variabilities for the above analytes are computed to be 25%, 21%, and 29% respectively.

Examination of the CV's of the data in Table 1, is not adequate for determination of the generation variability of the nitrosamine data. An analysis of variance approach can be taken to adjust the NDMA data for difference from year to year and month to month. (See Table 5). The analysis is done on the log scale, since sampling data such as this is often thought to be distributed log-normally. Also, the LOD value of 6 ng/m^3 for those values less than the LOD has been used. The pooled precision is now 88.4%, so there does seem to be considerable generation variability in the data. The analysis of variance also allows us to conclude that there is a statistical difference in the data from year to year.The data for nitrosamine covers the period from May, 1980 to November 1982. The average NDMA measurements for 1982 are higher than those for 1981 and 1980, at the 1% probability level. Within each year there is some non-homogeneity. The measurements for May, 1980 are higher (at 1% level) than those for the other 1980 months. For 1981, the measurements for January, February, and March are statistically higher than the measurements for the other months. There is an appearance of a slight cyclical trend in the NDMA data--from June, 1980 to January, 1981, rising; from February, 1981 to November 1981, falling, and after that some variability. For the NDMA data, then, it can be concluded that there is variablity of the measured levels over time. Also, some of the excessive variability in the data (CV's exceeding 100%) is due to this variability in the generated amount of NDMA. It is noted that there is still considerable unexplained variability, some of which may be due to differences from one type of chamber to another.

By fitting an analysis of variance model to the NDMA data, and, in addition to adjustments for year and month, making adjustments for chamber type,the CV of the data is reduced to 67.8%. Diesel and coal-diesel chamber NDMA measurements are clearly different from coal and clean air chamber measurements, at the 1% level, but are not different from each other. The reduced CV data of 67.8% for the values for NDMA alone cannot account for the total variability of the measured analytical values. The estimated sampling and analytical error of 25% still leaves 42.8% of the variability of the data unaccounted for. This variability may be due to unknown variable factors affecting the generation of the nitrosamines. Those factors may include but not be limited to the species of animals present in the exposure chambers, fuel composition, ambient air composition and engine wear.

Nitrosamine values for the clean air and coal dust chambers would be expected to be equivalent across the six chambers (3 each) except for contributions due to animal species and numbers of animals housed. Equivalent nitrosamine concentrations should also occur within the diesel chambers, alone and in combination with coal dust, with the same reservations for animals factors and a possibility of an interaction between coal dust and diesel exhaust components.

Because of the lower number of nondetectables in the case of either NDEA or NDPA, the stastistical approach of analysis of variance cannot be taken. The NDPA data is somewhat different from the NDMA data, in that most of the detectable measurements occur in the 1982 data. For NDPA, in 1980 and 1981 only May, 1980 and June, 1981 have detectable quantities. For the 1982 data every month after April, 1982, has detectable quantities of NDPA. This does suggest that there is a difference between 1983 and the earlier years. (See Table 6 for Tables of numbers of non-detectables over time).

The results of the statistical analysis of the analytical data can be summarized as follows:

a) For NDMA, the diesel chambers have statistically higher quantities of the nitrosamines than the non-diesel chambers. However, there is a statistically significant variation over time. This is one of the reasons that the CV's are high.

b) For NDEA there does not appear to be much difference between the measured nitrosamine data in the diesel and non-diesel exposure chambers. All have percent nondetectables in excess of 90%. Thus, there appears to be almost no NDEA present in those chambers.

c) For NDPA, the diesel chambers have statistically higher quantities of the nitrosamines chemical than the non-diesel chambers. Almost all detectable amounts occur in the 1982 data.

The summary statistics for the three nitrosamines are presented in Table 7, where average figures for NDEA over the three-year period, and separate averages for each year for NDMA and NDPA are given.

The weekly data in this study provided the same difference by chamber group as the monthly data. On three different occasions during the study i.e., on March 3, 31, and September 29, 1982 the samples were collected in the mixing chamber for 2,6 and 5 hours each respectively. The diesel exhaust in the mixing chamber was susequently diluted to one-ninth of its original composition prior to its entry into the exposure chambers. As such,the samples collected in the mixing chamber should contain much higher concentrations of nitrosamines if they are produced in the effluent from the diesel engine exhaust. The results of mixing chamber sample analysis are shown in Table 3.

As is obvious from the low levels of nitrosamines in Table 8, the hypothesis that nitrosamines were produced largely in the diesel engine exhaust does not appear applicable in this case.

The occasional presence of small amounts of nitrosamine in the mixing chamber and the observed scatter in the overall analytical values of nitrosamines present in the exposure chambers prompted the use of samplers containing nitrosatable analytes during the investigation. These samplers consisted of Thermosorb tubes impregnated with a high concentration (1-5 mg) of an amine of relatively high molecular weight compound such as thiomorpholine or morpholine. The amine in the tubes is converted to the corresponding nitrosamine in an atmosphere containing nitrosating precursors such as oxides of nitrogen or other nitrogenous compounds which may be needed for nitrosamine formation. These nitrosating amine samplers were used on three occasions during this study, i.e., in the months of June, July and December, 1982. Air inside as well as outside the chambers was collected for analysis of nitrosated amines. Chambers with animals as well as the empty chambers were sampled. Substantial amounts of the nitrosamines were formed on these nitrosatable tubes in the ambient of inside as well as outside the exposure chambers, more being formed inside the chambers than outside. Air in clean air and coal dust chambers produced less N-nitrosamines than the environment of diesel and coal dust plus diesel. Because of the nature of nitrosating samplers no quantitation of nitrosation data was possible. These analytical results indicated that precursors to nitrosamine formation are present in and prior to each exposure chamber as evidenced by the nitrosatable amine in samplers being converted into the corresponding nitrosamine. The results, however, suggest that amines, probably from the diesel engine, and the nitrogen oxide inherent in the exposure environment may be combining leading to the production of the observed nitrosamines. The mixing chamber environment may not have adequate precursors of nitrosamines (NOx) present most of the time, or sufficient reaction residence time, thus producing only minimal amount of nitrosamines. The precursors of the nitrosation reaction may also arise from the amine contamination in the cleaning agents, precursors originating from animal feed or excreta in the chambers or other nitrogeneous compounds used in the exposure chamber environment. Thus the observed nitrosamines appear to occur subsequence to the emission of diesel exhaust from the engine. Scattering of analytical data may possibly be the result of an unpredicted amount of the residual precursors present in the sampling sites. Because of the lack of a sound explanation for the presence of NOx precursors in the chamber environment the formation and occurrence of N-nitrosamines in the exposure chambers are not clearly understood.

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TABLE 1. NUMBER (N) AND PERCENT NONDETECTABLES

BY ANALYTES AND CHAMBER TYPES

Chamber Type	NDMA		NDEA		NDPA	
	N	%	N	%	N	%
CLEAN	91(96)	95	88(90)	98	89(93)	95
COAL	77(92)	84	84(86)	97	87(89)	96
DIES	35(92)	38	81(86)	94	70(89)	79
COALD	36(92)	39	78(86)	91	70(89)	79

NOTE: Total number of samples are indicated in parentheses.

TABLE 2. MEANS AND COEFFICIENTS OF VARIATION OF ACTUAL NITROSAMINES DATA BY CHAMBER TYPE

	NDMA					NDEA					NDPA				
Chamber Type	No. of Obs. (N)	Mean (LOD) (ng/m^3)	CV (%)	Mean (0) (ng/m^3)	CV (%)	No. of Obs. (N)	Mean (LOD) (ng/m^3)	CV (%)	Mean (LOD) (ng/m^3)	CV (%)	No. of Obs. (N)	Mean (LOD) (ng/m^3)	CV %	MEAN (0) (ng/m^3)	CV %
CLEAN	96	7.3	150	1.6	720	90	6.9	110	1.1	790	93	6.3	27	0.56	500
	*(95	6.2	21	0.45	520)*										
COAL	92	10	190	5.3	390	86	6.6	68	0.73	720	89	6.6	66	0.89	590
	*(91	8.6	120	3.5	330)*										
DIES	92	35	140	33	160	86	9.4	170	4.0	440	89	9.5	110	4.8	260
	*(91	31	110	28	120)*										
COALD	86	6.8	59	1.1	450	92	34	130	32	140	89	10	150	5.4	310

Note: Mean (0) replaces nondetectables by zero ng/m^3 for computing means and CVs.
Mean (LOD) replaces nondetectables by LOD of 6 ng/m^3 for computing means and CVs.

* Largest measurement is deleted here

TABLE 3A. FREQUENCY DISTRIBUTION OF MEASURED NITROSAMINE DATA FOR NDMA BY CHAMBER TYPE

CLEAN		COAL		DIES		COALD	
Reading (ng/m^3)	Frequency	Reading (ng/m^3)	Frequency	Reading (ng/m^3)	Frequency	Reading (ng/m^3)	Frequency
LOD	91	< LOD	77	< LOD	35	< LOD	36
8.0	2	7.0	3	7-10	4	9-10	2
8.9	1	10	3	11-20	10	11-20	13
18	1	11	1	21-30	14	21-30	7
110	1	12	1	31-40	7	31-40	5
		20	1	41-50	5	41-50	8
		22	1	51-60	1	51-60	3
		30	1	61-70	1	61-70	6
		46	1	71-80	2	71-80	3
		47	1	81-90	2	81-90	3
		84	1	91-100	1	91-100	2
		170	1	101-110	3	100	1
				111-120	3	140	1
				131-140	2	150	1
				160	1	410	1
				260	1		

TABLE 3B. FREQUENCY DISTRIBUTION OF MEASURED NITROSAMINE DATA FOR NDEA BY CHAMBER TYPE

CLEAN		COAL		DIES		COALD	
Reading (ng/m^3)	Frequency	Reading (ng/m^3)	Frequency	Reading (ng/m^3)	Frequency	Reading (ng/m^3)	Frequency
< LOD	88	< LOD	84	< LOD	81	< LOD	78
17	1	17	1	8.0	1	15	1
78	1	46	1	10	1	16	3
				22	1	20	1
				30	2	46	1
						86	1
						130	1

TABLE 3C. FREQUENCY DISTRIBUTION OF MEASURED NITROSAMINE DATA FOR NDPA BY CHAMBER TYPE

CLEAN		COAL		DIESEL		COAL AND DIESEL	
Reading (ng/m^3)	Frequency	Reading (ng/m^3)	Frequency	Reading (ng/m^3)	Frequency	Reading (ng/m^3)	Frequency
<LOD	89	<LOD	86	<LOD	70	<LOD	70
8.3	1	13	1	7-10	7	9-10	2
10	1	15	1	13-20	4	11-20	12
15	1	46	1	21-30	5	21-30	1
19	1			41	1	31-40	1
				97	1	44	1
				100	1	65	1
						73	1

TABLE 4: ANALYTICAL PRECISION ESTIMATES FOR NITROSAMINES BASED ON SPIKED SAMPLES

ANALYTE	NO. OF SPIKES	MEAN RECOVERY	STANDARD DEVIATION	CV
NDMA	25	0.75	0.15	20%
NDEA	24	0.89	0.15	16%
NDPA	21	1.0	0.25	25%

TABLE 6. NUMBER OF NON-DETECTABLE NITROSAMINES BY TIME (YEAR)

	NDMA				NDEA				NDPA		
	1980	1981	1982		1980	1981	1982		1980	1981	1982
< LOD	68	104	67	< LOD	80	109	142	< LOD	81	129	104
> LOD	15	52	63	> LOD	4	11	2	> LOD	3	3	40

NDMA Chi - square = 20.93, 2 degrees of freedome; probability level $< .001$

NDEA Chi-square = 8.53, 2 degrees freedom; probability Level ~ 0.014

NDPA Chi-square = 48.53, 2 degrees of freedom; probability level $< .001$

TABLE 7. STATISTICAL SUMMARY OF NITROSAMINE VALUES BY ANALYSES CHAMBER TYPE AND TIME (YEAR). (MEANS (0) AND MEANS (LOD) REPLACE NON-DETECTABLE NITROSAMINES BY ZERO NG/M^3 AND 6 NG/M^3 FOR COMPUTATION PURPOSE RESPECTIVELY)

Analyte (Chamber) Type	Year	No. of Obs.	Mean (0) (ng/m^3)	CV (0) (%)	Mean (LOD) (ng/m^3)	CV (LOD) (%)
NDMA (CLEAN AND COAL	1980	44	2.9	570	8.6	180
	1981	78	3.0	390	8.3	120
	1982	66	4.2	500	9.3	220
NDMA (DIES AND COALD)	1980	40	22	170	26	130
	1981	78	27	130	29	110
	1982	66	45	142	45	140
NDEA (OVERALL)	----	348	1.7	600	7.4	130
NDPA (CLEAN AND COAL)	1980	44	0	0	6.0	0
	1981	66	0.98	620	6.8	75
	1982	72	0.93	350	6.4	27
NDPA (DIES AND COALD)	1980	40	6.6	360	12	180
	1981	66	0.18	810	6.1	12
	1982	72	8.8	150	12	93

TABLE 5. ANALYSIS OF VARIANCE FOR NDMA

Source	DF	Sum of Squares	F Value	Prob. > F
Year	2	7.53	4.81	0.009
Month in Year	28	80.5	3.68	0.001
Error	341	267		

$R^2 = 0.248$

CV--on original scale which is approximately equal to the standard deviation on the log scale

$$= \sqrt{\frac{267}{341}} = \sqrt{0.782} = 0.884$$

DF-Degree of Freedom

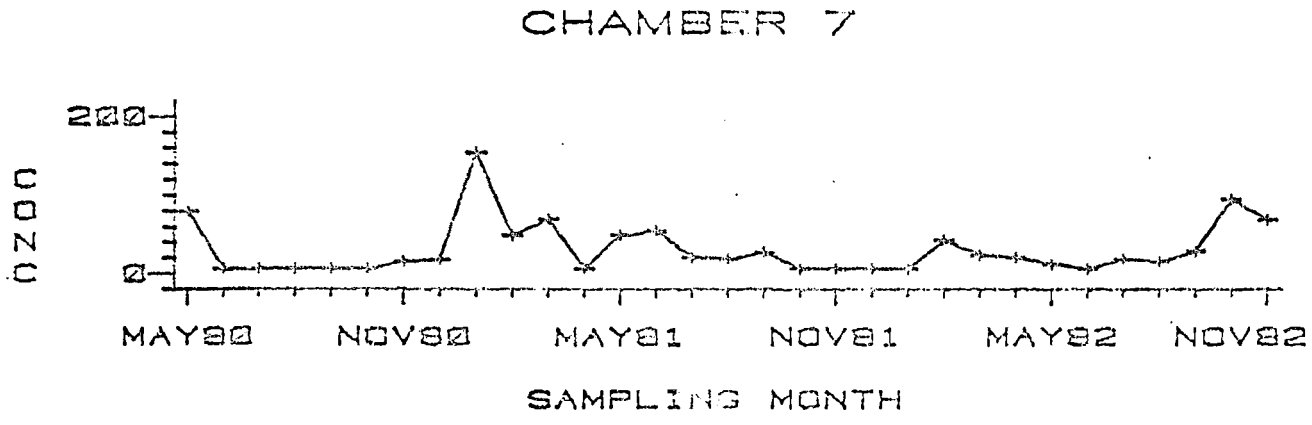
TABLE 8: NITROSAMINES FOUND IN DIESEL EXHAUST BEFORE DILUTION

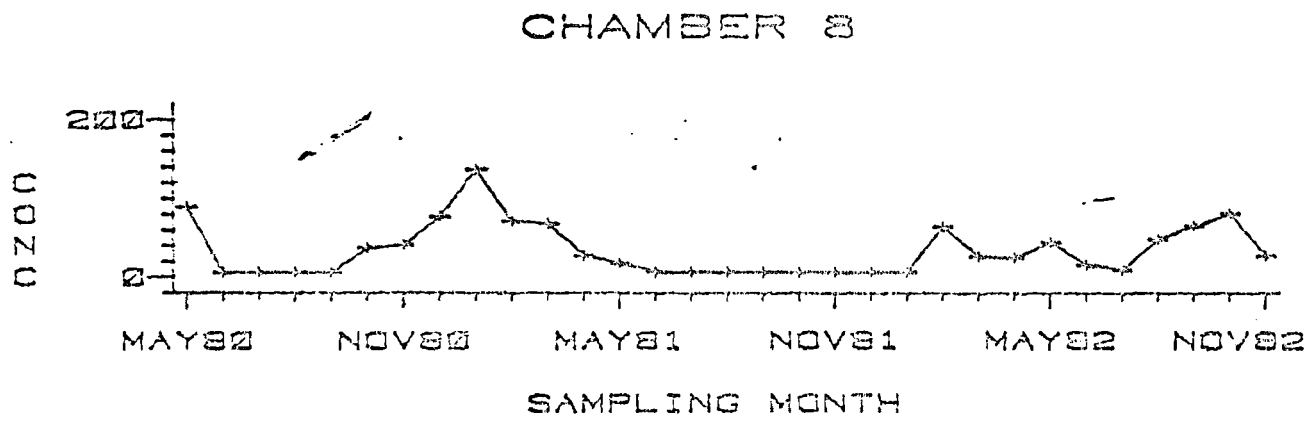
SAMPLING DATE	SAMPLE VOL. (M^3)	NDMA (NG)	NDEA (NG)	NDPA (NG)
3/3/82	0.12	< 5.0	< 5.0	< 5.0
3/31/82	0.72	6.5	< 5.0	15.1
9/21/82	0.61	< 5.0	< 5.0	< 5.0

LOQ (LIMIT OF QUANTITATION) = 5.0 NG

FIG. 1 NDMA CONCENTRATION IN COAL/DIESEL CHAMBERS

UNITS ARE NG/CUBIC METER





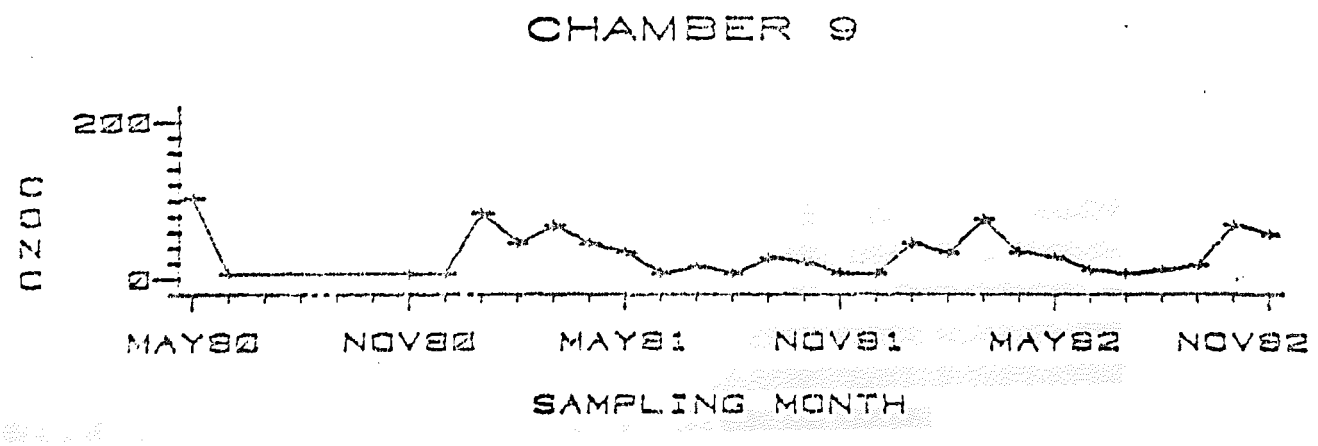
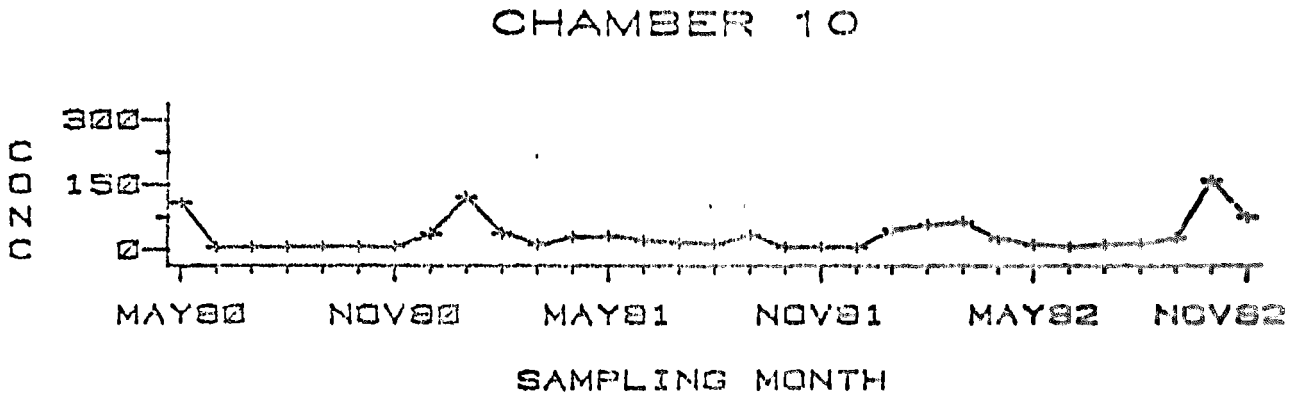
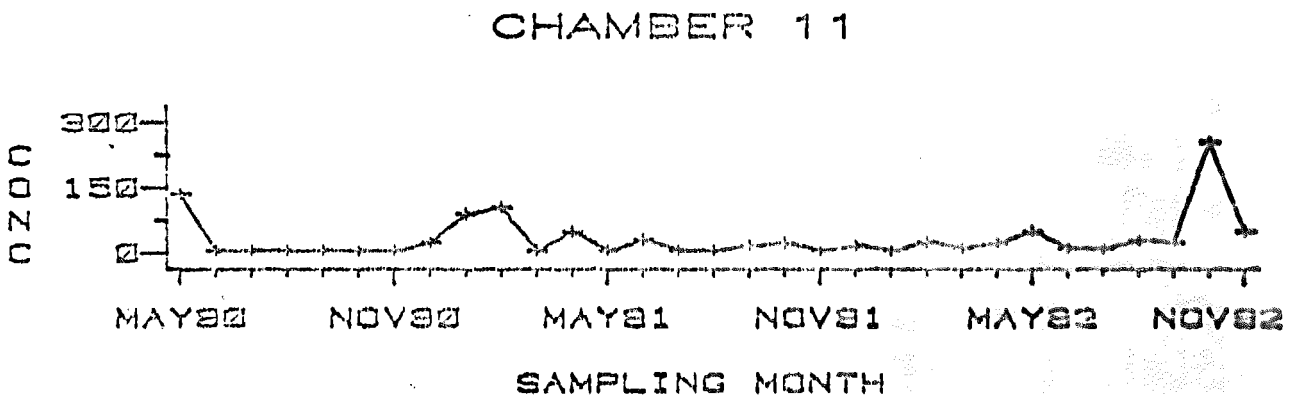


FIG.2 NDMA CONCENTRATION IN DIESEL CHAMBERS

UNITS ARE NG/CUBIC METER





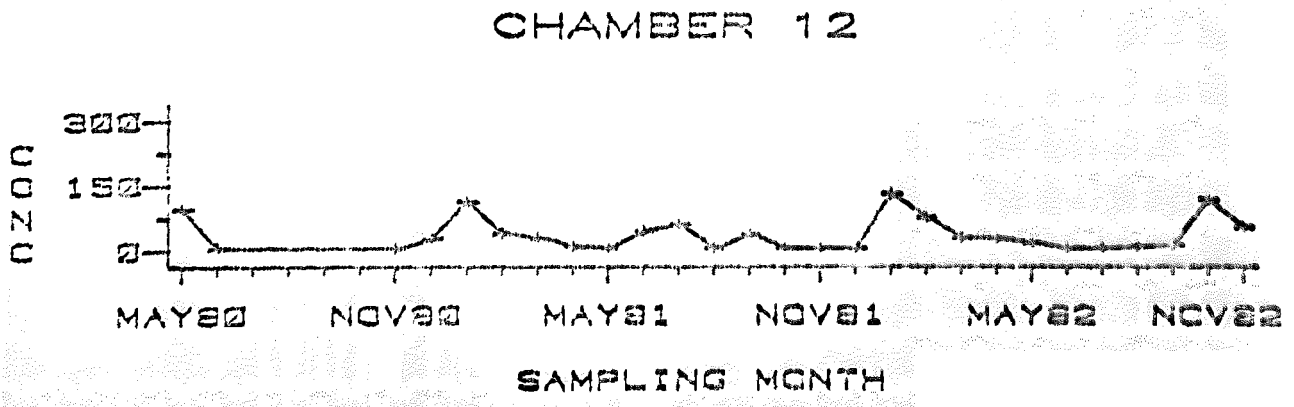
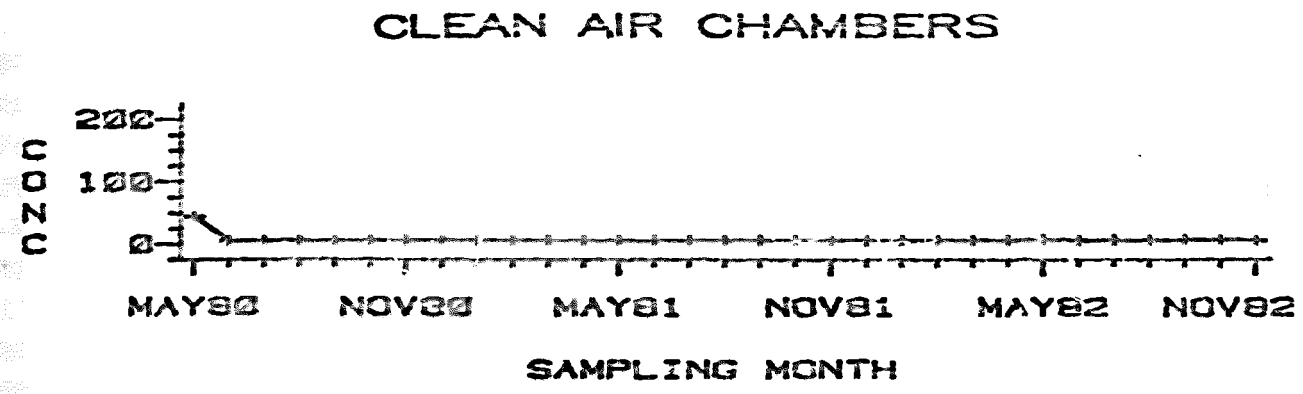
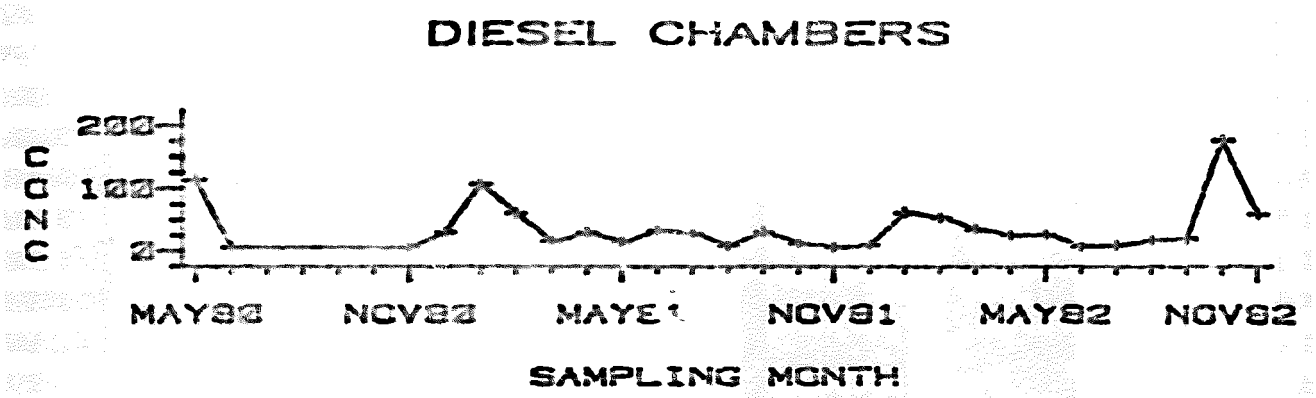
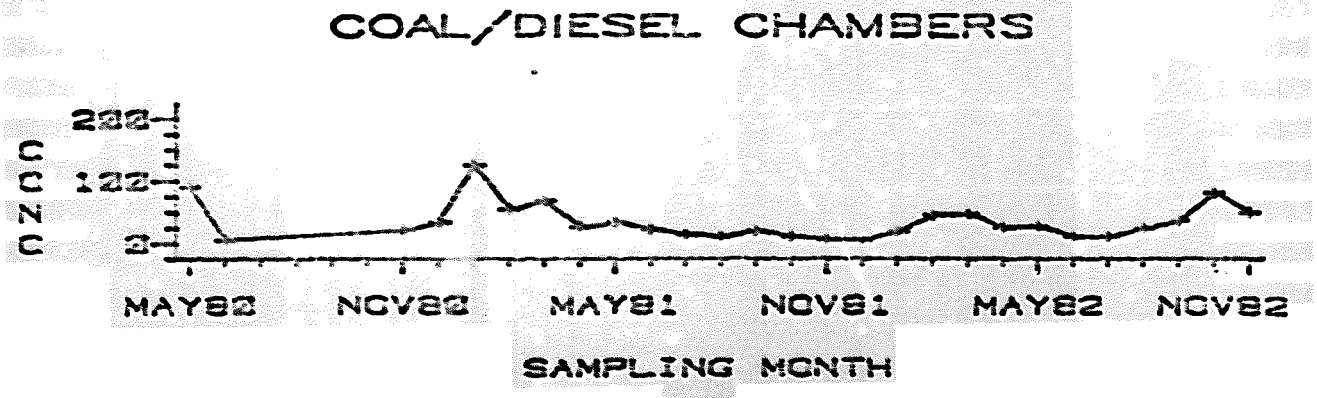


FIG.3 AVERAGE NDMA CONCENTRATION PER CHAMBER TYPE

UNITS ARE NG/CUBIC METER

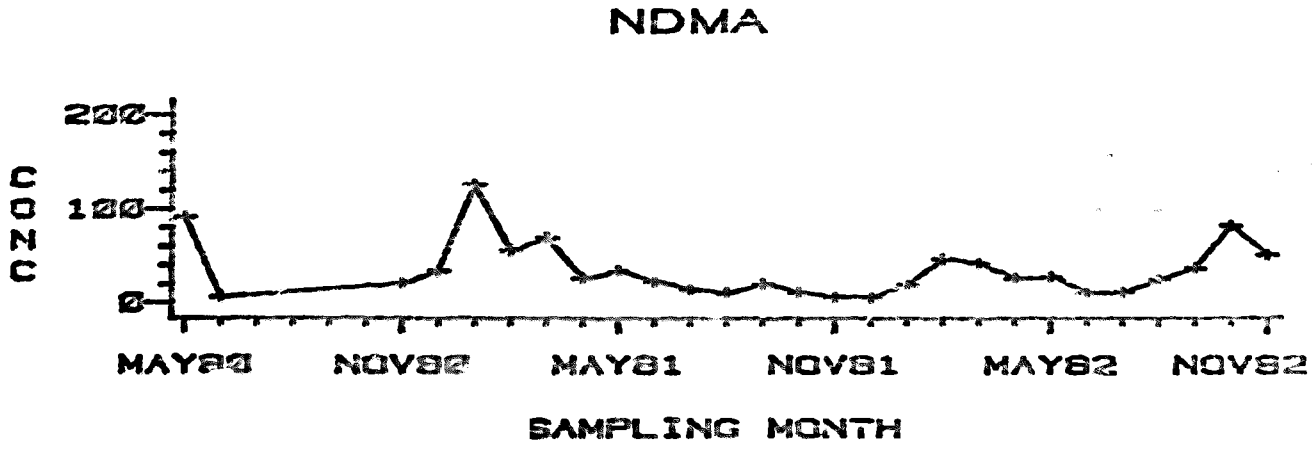


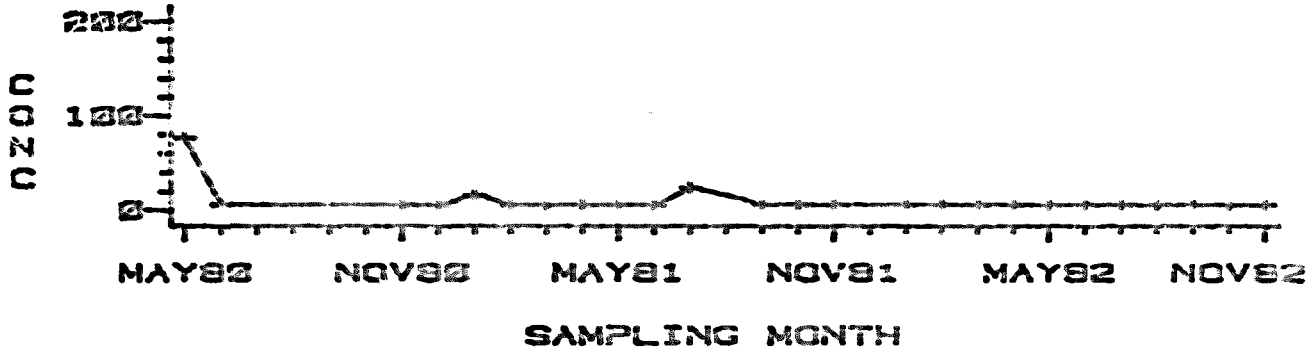




G.4 NITROSAMINE CONCENTRATIONS IN COAL/DIESEL CHAMBERS

UNITS ARE NG/CUBIC METER





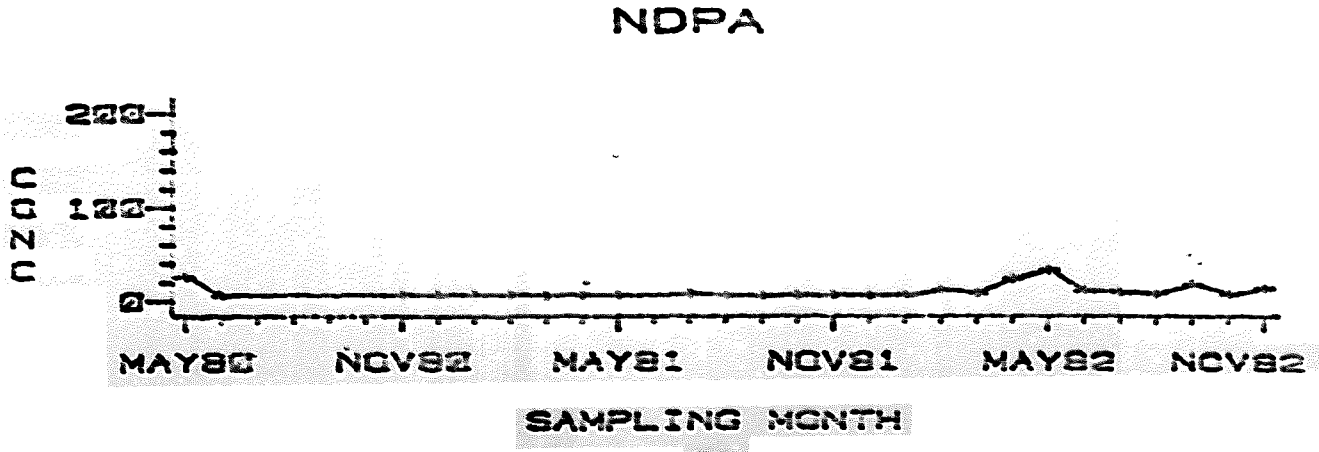


FIG.5 NITROSAMINE CONCENTRATIONS IN DIESEL CHAMBERS

UNITS ARE NG/CUBIC METER