ENVIRONMENTAL HEALTH SERIES

Air Pollution

EFFECTS OF THE RATIO OF HYDROCARBON TO OXIDES OF NITROGEN IN IRRADIATED AUTO EXHAUST

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE

Public Health Service

EFFECTS OF THE RATIO OF HYDROCARBON TO OXIDES OF NITROGEN IN IRRADIATED AUTO EXHAUST

Merrill W. Korth

Engineering Research and Development
Laboratory of Engineering and Physical Sciences
Robert A. Taft Sanitary Engineering Center

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Division of Air Pollution

Cincinnati, Ohio 45226

October 1966

The ENVIRONMENTAL HEALTH SERIES of reports was established to report the results of scientific and engineering studies of man's environment: The community, whether urban, suburban, or rural, where he lives, works, and plays; the air, water and earth he uses and reuses; and the wastes he produces and must dispose of in a way that preserves these natural resources. This SERIES of reports provides for professional users a central source of information on the intramural research activities of Divisions and Centers within the Public Health Service, and on their cooperative activities with State and local agencies, research institutions, and industrial organizations. The general subject area of each report is indicated by the two letters that appear in the publication number; the indicators are

AP	Air Pollution
AH	Arctic Health
EE	Environmental Engineering
FP	Food Protection
OH	Occupational Health
RH	Radiological Health
WP	Water Supply and Pollution Control

Triplicate tear-out abstract cards are provided with reports in the SERIES to facilitate information retrieval. Space is provided on the cards for the user's accession number and additional key words.

Reports in the SERIES will be distributed to requesters, as supplies permit. Requests should be directed to the Division identified on the title page or to the Publications Office, Robert A. Taft Sanitary Engineering Center, Cincinnati, Ohio 45226.

Public Health Service Publication No. 999-AP-20

FOREWORD

Vehicle exhaust is recognized as a major air pollutant. This problem has been under intensive study by government and private research agencies for several years. Basic to these studies is the determination of types and concentrations of pollutants contained in vehicular exhaust, the photochemical reactions that occur when exhaust is discharged into the atmosphere, and the products responsible for various air pollution effects.

Photochemical reactions are being studied in detail by the use of "smog" chambers in which vehicular exhaust diluted with air is irradiated to simulate the effects of sunlight in the atmosphere. This is the second of a series of reports describing irradiation chamber tests conducted by the Division of Air Pollution of the Public Health Service.* The work is performed by personnel of the Division's Laboratory of Engineering and Physical Sciences at the Robert A. Taft Sanitary Engineering Center at Cincinnati, Ohio.

Preliminary tests were conducted at the Center beginning in February 1960. The irradiation chamber tests completed between that time and May 1961 are described in PHS Publication No. 999-AP-5. The results of the series of tests conducted between May 1961 and November 1962 are presented in this report. This series investigated the effects of varying the ratio of total hydrocarbons to oxides of nitrogen in the exhaust products.

---

*Mention of commercial products used in this research does not constitute endorsement by the Public Health Service.

CONTENTS

	Page
ABSTRACT	vii
INTRODUCTION	1
TEST FACILITY AND PROCEDURES	1
TEST PARAMETERS	8
Major Independent Variables	8
Characteristics of Chamber Input	10
CHEMISTRY OF IRRADIATED EXHAUST	14
The NO NO_2 Reaction Processes	14
NO Photoxidation	14
NO_2 Formation Rate	14
CHEMICAL EFFECTS	18
Hydrocarbon Reactions	18
Aldehydes	20
Oxidant Formation	23
Percent NO_x Reacted	25
Other Products	27
BIOLOGICAL EFFECTS	28
Eye Irritation	28
Plant Injury	30
ATMOSPHERIC EFFECTS	31
STATISTICAL ANALYSIS	33
SUMMARY OF RESULTS	35
ACKNOWLEDGMENTS	38
REFERENCES	39
APPENDIX Detailed Test Data	43
Summary of Test Conditions and Run Numbers	44
Biological Data	45
Chemical Data	46
Chromatographic Data	47

ABSTRACT

As a part of a series of investigations of the problem of vehicle exhaust as an air pollutant, photochemical reactions are being studied in detail by the use of large dynamic irradiation chambers. In these studies auto exhaust, generated by test vehicles on a dynamometer, is diluted with air and irradiated to simulate the effects of sunlight under mixing conditions similar to those in the atmosphere. The irradiated mixture is used to study chemical reactions and to evaluate plant damage and human eye irritation.

In this second series of irradiation tests performed by the Public Health Service, the ratio of total hydrocarbon (HC) to oxides of nitrogen (NO_x) was varied between 1-1/2 and 24. Hydrocarbon concentrations were varied from 3 ppm to 12 ppm total carbon; oxides of nitrogen concentrations were varied from 1/4 ppm to 2 ppm.

Greatest plant damage occurred when both the HC/NO_x ratios and hydrocarbon concentrations were high. The levels of eye irritation were highest at the higher chamber hydrocarbon concentrations. For a given hydrocarbon level, chemical reaction rates were highest at the high HC/NO_x ratios.

INTRODUCTION

The growing air pollution problem resulting from automotive emissions has resulted in legislation, in certain areas, directed toward the reduction of gross hydrocarbon emissions. Although such an approach is reasonable and expedient in view of the magnitude of the problem, it was taken without complete knowledge of the effects of such a reduction on atmospheric photochemical reactions. To extend our knowledge of these reactions, we undertook a special series of tests in the PHS chamber facility for irradiation of dilute automotive exhaust. In these tests the ratios of total hydrocarbon to oxides of nitrogen were controlled and varied over a range comparable to that found in the atmosphere.

Although the processes involved in photochemical smog are much more variable in community atmospheres than in the laboratory, the findings reported herein, representing one of the most closely controlled experiments of this type completed to date, should aid materially in interpreting the effects of pollution control programs.

Air masses over urban areas continually undergo varying degrees of mixing of new pollutants with existing pollutants. The degree of mixing depends on atmospheric turbulence and on the location and movement of parcels of air with respect to pollutant sources. For study of the atmospheric photochemical oxidation of dilute automotive exhaust under conditions that simulate continuous uniform atmospheric mixing of new with old pollutants, we have used a dynamic irradiation system. In this dynamic system, dilute non-irradiated auto exhaust is continually introduced into the irradiation chamber and dilute irradiated exhaust is continually withdrawn.

TEST FACILITY AND PROCEDURES

The test facility is described in detail in earlier publications.[1, 2, 3] The equipment consists of five major components: a test vehicle operated on an automatically cycled chassis dynamometer to provide exhaust gases under simulated driving conditions, a two-stage exhaust-transfer and dilution system to dilute the raw exhaust gases to the specified concentrations, a dilution-air purification system, dynamic irradiation chambers for the irradiation of the dilute exhaust gases, and exposure facilities for evaluation of plant damage and human eye irritation.

Several changes and improvements were made in the basic irradiation facility before this test series was begun. A flywheel was installed on the dynamometer to provide a source of stored energy during deceleration in place of the slave engine used previously to simulate decelerations. The original hydraulic power absorption unit was replaced with an eddy-current power absorption unit capable of precise torque control. These modifications per-

mitted the design and use of a vehicle cycle that was more reproducible and more realistic with respect to average driving conditions than the cycle used in earlier tests. Figure 1 shows some of the major parameters of the improved test cycle.

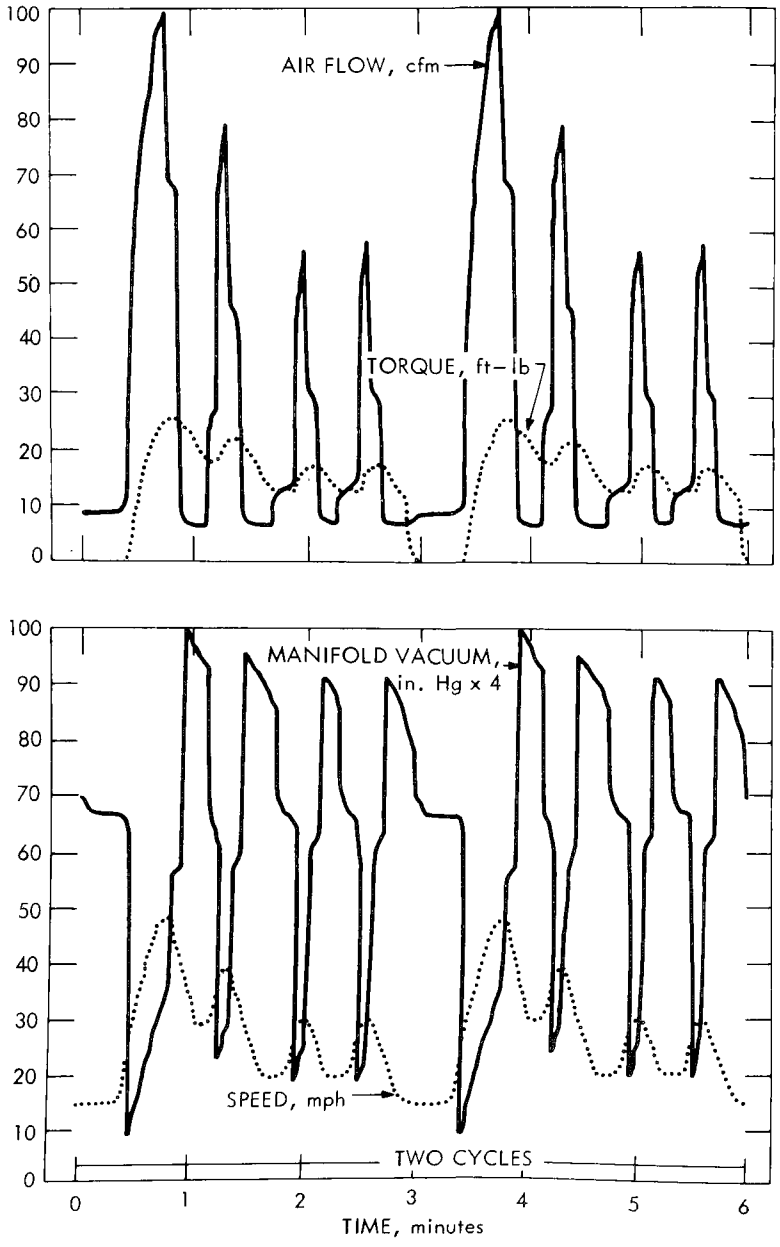

Figure 1. Automatic cycle for test vehicles.

In the irradiation chambers the original irradiation lamps were replaced with 24 fluorescent sun lamps, 36 fluorescent blue lamps, and 88 fluorescent black light lamps. This change increased the light energy in the ultraviolet region of photochemical importance. In addition, Tedlar PVF film was installed in place of Mylar for the chamber windows. The combined effect of these modifications was an improvement in the degree to which the light energy in the chamber approximated the sunlight levels in the photoreactive region of 2900 to 3800 angstroms, Figure 2. Measurement of the area under the chamber light-energy curves indicates that the present level of light intensity in the chamber is 35 percent higher than the previous level. The present light distribution closely approximates the most recently published sunlight data,[4] curve 2, in the region of 2900 to 3300 angstroms. The original sunlight distribution curve 1,[5] based on measurements made in Cleveland, Ohio, has been superseded by the generally accepted curve 2, which was developed for the Los Angeles area at a zenith angle of 20 degrees.

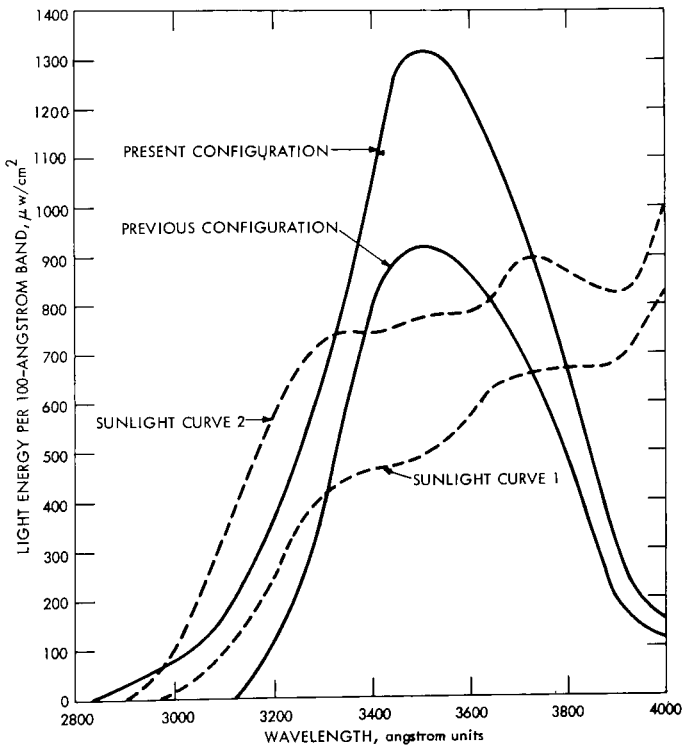

Figure 2. Light intensity in irradiation chamber.

The average irradiation time of a mixture passing through a dynamic irradiation chamber depends on the volume of the chamber and on flowrate. For the 335-cubic-foot chamber used in these experiments, flowrates of 2.79 and 1.86 cubic feet per minute produce irradiation times of 120 and 180 minutes, respectively.

Concentrations of the chemical constituents were monitored in the exhaust gas mixture after dilution and in the irradiation chamber before and during irradiation. Hydrocarbon in both the irradiated and nonirradiated exhaust gas mixture after dilution was measured with a flame ionization detector, which responds in ppm as total carbon atoms. Nitric oxide and nitrogen dioxide were measured with a continuous-recording colorimetric instrument. Because of the time-response characteristics of this instrument, a computer program was applied to convert the instrument response to instantaneous values.[1] Carbon monoxide concentrations in the irradiated gases were measured by a longpath nondispersive infrared analyzer. Oxidant concentrations were measured by a continuous-recording coulometric instrument with a neutral potassium iodide solution. Corrections for NO_2 interference were applied to the oxidant data.

Direct analyses by flame-ionization gas chromatography were made for the following aliphatic hydrocarbons: ethane, ethylene, acetylene, propane, propylene, n-butane, isobutane, and isopentane.[6] These analyses were made every 20 to 30 minutes during the experiment with a 12-foot-long silica gel column used at room temperature for separation of the components. The sample was obtained from an aluminum line, through which a portion of the contents of the irradiation chamber was drawn continuously during each experiment. Direct analyses also were made for the following aromatic hydrocarbons: benzene, toluene, ethylbenzene, m- and p-xylene, n-propylbenzene, 3- and 4-ethyltoluene, 1,3,5-trimethylbenzene and sec. and tert. butylbenzene, (reported as 1,3,5-trimethylbenzene), 1,2,4-trimethylbenzene, and styrene and 2-ethyltoluene. Analyses for aromatic hydrocarbons were made with a 15-foot-long column consisting of 5 percent 1,2,3-tris (2-cyanoethoxy) propane on 50- to 60-mesh C-22 firebrick at 50°C.[7,8] Propadiene, four- and five-carbon olefins, n-pentane, and 2-methylpentane were present in very low concentrations; these components were analyzed after a concentration step on a combination column containing a 6-foot length of bis-2 (2-methoxyethyl) adipate and a 21-foot length of dibutyl maleate on C-22 firebrick, operated at 40°C. Although all of the components listed could be analyzed at chamber concentrations of 12 ppm carbon, a number of the less abundant hydrocarbons could not be determined quantitatively at 6 and particularly at 3 ppm carbon. All gas chromatographic analyses for hydrocarbons were made with flame ionization detectors. During a few of the last experiments in this series, organic nitrates and diketones were analyzed by electron-capture gas chromotography.[9]

The spectrophotometric methods for formaldehyde by the chromotropic acid method,[10,11] acrolein by the 4-hexylresorcinol method,[12] and total aliphatic aldehydes by the 3-methyl-2-benzothiazolone hydrazone method[13,14] were used in previous irradiation studies.[2,15]

Four-carbon and higher olefins were analyzed by the dimethylaminobenzaldehyde procedure also discussed previously.[16] The bubbler containing the reagent for the olefin analysis was in series with and followed the bubbler containing the water used to collect formaldehyde from the sample stream. Nitric oxide was analyzed with bubbler samples after permanganate oxidation, and nitrogen dioxide was analyzed directly by the Saltzman[17] procedure. Oxidant was determined by the 1 percent neutral potassium iodide procedure.[18]

Samples were collected either in 10 or 20 ml of collecting solution contained in a "smog" type fritted-glass bubbler. The flowrates were kept low to insure maximum collection efficiency. Nitrogen dioxide was collected at flowrates as low as 200 cc per minute. Most of the samples were drawn through the bubblers at flowrates between 400 and 1000 cc per minute. Materials such as Tygon, Nalgon, rubber, and polyethylene were not incorporated into sampling lines to preclude losses of the more reactive substances. Teflon tubing proved satisfactory, as did glass, aluminum, and stainless steel tubing after thorough conditioning.

To obtain a test fuel having characteristics similar to the fuels used in the previous irradiation chamber studies, we blended two fuels prepared by the Western Oil and Gas Association in equal proportions. Analysis of the fuel is given in Table 1.

Table 1. PHYSICAL AND CHEMICAL PROPERTIES OF TEST FUEL

Properties	
API gravity, degrees	56.6
Reid vapor pressure, lb/in.^{2}	9.35
Distillation, °F	
Initial	95
End point	402
Research octane number, F-1	100.3
Motor octane number, F-2	89.2
Sulfur (total), weight %	0.031
Bromine no. (electrometric), g/100g	37.0
Tetraethyl lead, ml/gal	1.25
Fluorescent indicator analysis (as received), volume %	
Saturates	46
Olefins	16
Aromatics	38

For the plant-damage evaluations, plants that develop distinct types of physical injury were selected to indicate the effects of the various phytotoxicants in irradiated auto exhaust:

1. Pinto bean primary (Phaseolus vulgaris, L., var. pinto)
2. Pinto bean trifoliate (Phaseolus vulgaris, L., var. pinto)
3. Young pinto bean (Phaseolus vulgaris, L., var. pinto)
4. Tobacco wrapper C. (Nicotiana tabacum, L., var. Bel. C)
5. Tobacco smyrna (Nicotiana tabacum, L., var. Smyrna)
6. Petunia (Petunia hybrida, Vilm., var. Celestial Rose)

The plants were selected at specific stages of growth, rather than at chronological age from planting or emergence, so that some of the variability resulting from differences in environmental conditions could be avoided. Individual plants were selected for exposure on the following bases: (1) pinto bean (primary) after the first trifoliate leaf appeared and had been debudded so that only the primary leaves were present, (2) pinto bean (trifoliate) when the first trifoliate expanded and began to develop the characteristics of a mature leaf, (3) young pinto bean when the plants had fairly young primary leaves, about one-quarter the size of a mature leaf, and one unfolding trifoliate bud, (4) both tobacco varieties when the plants had 8 to 12 leaves, and (5) petunias when the plant had one stock and four to six middle-aged leaves, prior to bud development. These stages of growth were easily identified and appeared to yield tissue of fairly uniform susceptibility to irradiated auto exhaust.

All plants were grown under closely controlled greenhouse conditions. For uniform exposure, the plants were placed on a rotating table in a small exposure chamber, Figure 3, lighted by deluxe warm-white fluorescent lamps at approximately 1800 foot-candles. The 4-hour exposure of plants to irradiated auto exhaust usually began within 15 minutes after the beginning of irradiation in the irradiation chamber.

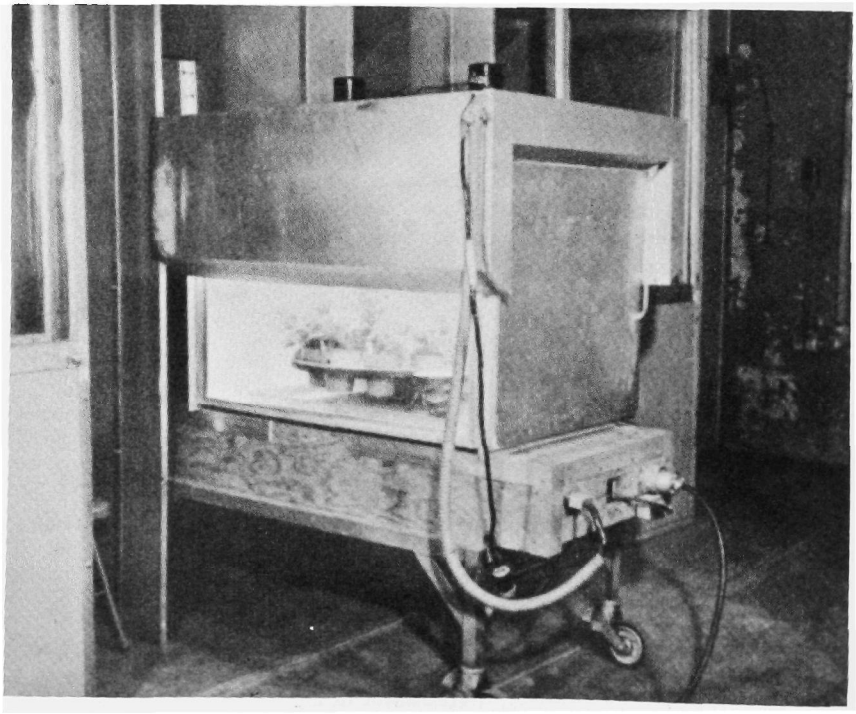

Figure 3. Plant-exposure chamber.

Microscopic examinations of the internal cell structure were made several times during the first few days after exposure to identify the phytotoxicants by the type of cell injury. The external leaf damage was estimated the third day after exposure and expressed in terms of an injury index on a scale of 0, 1, 2, 3, and 4, where 4 indicates total injury of the sensitive tissue.

Irritation of human eyes by the irradiated dilute exhaust was measured on ten volunteer panelists in the exposure facility illustrated in Figure 4. Five of the ten panelists were exposed simultaneously in five exposure booths housed in an air-conditioned enclosure.

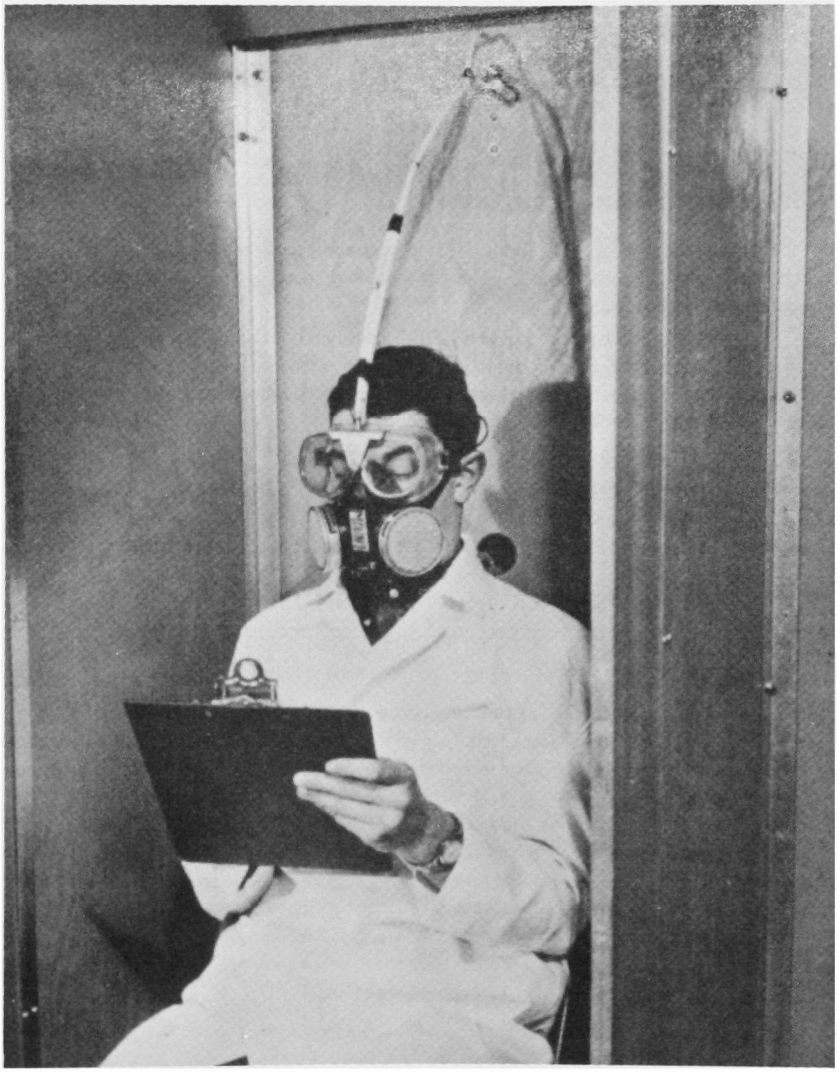

Figure 4. Eye-exposure booth.

The test atmosphere was delivered to panelists through a glass manifold connected to flexible plastic goggle-type masks with Teflon tubing. Each panelist wore a respirator with activated charcoal filters to separate any odor response from the eye irritation response. The goggle-type masks were chosen instead of the open-helmet type as a result of a series of experiments in which the distribution of gas within the masks was studied by use of probes and a flame ionization analyzer.

Each panelist reported the degree of irritation on a scale of 0 to 3 (none, light, medium, and heavy) every 30 seconds. The index number for each run was determined by adding the highest response numbers reported twice in succession by each panelist. This procedure was intended to eliminate spurious single responses by panelists.

TEST PARAMETERS

Major Independent Variables

The effects of dilute irradiated exhaust mixtures on chemical reactivity, eye irritation, and vegetation injury were studied in terms of two independent variables:

1. The initial hydrocarbon (HC) concentrations were set at 3, 6, and 12 ppm carbon.
2. Initial oxides of nitrogen (NO_x) concentrations were established at 1/4, 1/2, 1. and 2 ppm.

These ranges of concentrations, shown in Table 2, established the HC/NO_x ratios for this study at 1-1/2, 3, 6, 12, and 24. All tests were duplicated except for those at HC/NO_x ratios of 1-1/2 and 24, which were single tests undertaken to complete the test design matrix.

Table 2. PARAMETERS ESTABLISHED BY TEST DESIGN

HC concentration, ppm carbon	NO_x concentration, ppm	HC/NO_x ratio	Number of tests at 120-min AIT[a]	Number of tests at 180-min AIT[a]
3	1/4	12	2	
3	1/2	6	2	1
3	1	3	3	1
3	2	1-1/2[b]	1	
6	1/2	12	3	1
6	1	6	2	1
6	2	3	2	1
12	1/2	24[b]	1	
12	1	12	2	1
12	2	6	2	1

[a]AIT: Average irradiation time.
[b]Single tests; all others duplicated.

The concentrations and ratios in this study were intended to be comparable with those in a community atmosphere under severe photochemical conditions; therefore, data obtained by the Continuous Air Monitoring Program (CAMP) of the Public Health Service in the Los Angeles area during August and September 1962 were analyzed to determine comparability. Data for 5 days during which severe eye irritation occurred were evaluated to determine the total HC and NO_x concentrations in the atmosphere immediately before the beginning of the photochemical reaction. The highest daily atmospheric oxidant concentrations occured after the reaction was well under way. These data are presented in Table 3.

Table 3. ATMOSPHERIC DATA FROM LOS ANGELES CAMP STATION

Date	HC concentration, ppmC	NO_x concentration, ppm	HC/NO_x ratio	Maximum daily oxidant conc., pphm
8/7/62	3.2	0.32	10.0	25
8/8/62	8.0	0.59	13.5	30
8/9/62	3.0	0.32	9.4	16
8/14/62	5.0	0.45	11.1	45
9/20/62	7.0	0.62	11.3	30

Total HC concentrations were corrected for background levels by subtraction of the lowest value shown between midnight and the time of the peak HC concentration. This correction is minimal, a subtraction of 2 to 3 ppm of what is presumed to be largely methane from the total HC concentrations measured in the morning before the photochemical reaction began. Even this small correction, however, helps to relate the hydrocarbon composition of the experimental auto exhaust more nearly to that of the atmosphere. Gas chromatographic analyses were not available on these dates to permit a more detailed correction procedure. Oxidant values were corrected for interference of NO_2 and SO_2. The atmospheric HC levels, NO_x levels, and HC/NO_x ratios fall within the extremes of the test values used in this study.

Findings of the previous test series [1,2] indicated no significant effects as average irradiation time increased from 85 minutes to 120 minutes. The present series was conducted primarily at an average irradiation time of 120 minutes. There is some evidence, however, that irradiation periods exceeding 120 minutes are important for static chamber operation. Hence the average irradiation time was extended to 180 minutes in several exploratory tests, but not enough observations were made to justify statistical evaluation. Observations and conclusions presented in this paper, therefore, are based primarily on the more complete data for the 120-minute average irradiation time.

Initial HC concentrations were established above the background level observed in the dilution air. Chromatographic analysis of this background level indicated that the total concentration is about 1.5 ppmC, of which 93 percent is methane.

The statistical significance of the changes in each level of the response variable over the condition of the experiment was determined by an analysis of variance; results are reported under Statistical Analysis.

Characteristics of Chamber Input

The gas chromatographic analyses demonstrate that the detailed HC composition before irradiation was essentially constant for runs at the same total HC level and for each of the three HC levels used. Results of gas chromatographic analyses of auto exhaust samples having HC contents at one of the three concentrations normalized to the ethylene concentration are shown in Table 4. The HC concentrations used to obtain these ratios are based on average values from six to eight tests run at each concentration. The ranges of concentrations reported were not obtained by diluting an individual sample but are the results of individual tests at each concentration level and ratio. Table 4 shows that the detailed HC composition varies negligibly as the total HC level is varied. The standard deviations in percent associated with the average concentrations of various hydrocarbons are given in Table 5 to indicate the reproducibility of the entire test procedure including the gas chromatographic measurements. The standard deviations increased slightly with decreasing concentration. Figure 5 shows individual concentrations of several hydrocarbons versus total HC concentration determined with a flame ionization analyzer (as ppmC). The averages and standard deviations were obtained from six to eight tests at each of the three concentrations.

Table 4. RATIO OF CONCENTRATIONS OF VARIOUS HYDROCARBONS TO ETHYLENE

Nominal carbon, ppm	C_2H_6	C_2H_4	C_2H_2	n-C_4H_{10}	C_3H_6	C_6H_6	C_7H_8	m - and p - xylene
11.2	0.12	1.00	1.18	0.20	0.26	0.23	0.47	0.39
6.2	0.12	1.00	1.15	0.20	0.28	0.25	0.52	0.39
3.0	0.12	1.00	1.17	0.19	0.32	0.25	0.52	0.47
average	0.12	1.00	1.17	0.20	0.29	0.24	0.50	0.42
σ	±0.000		±0.015	±0.005	±0.03	±0.01	±0.03	±0.045

Table 5. REPRODUCIBILITY IN GAS CHROMATOGRAPHIC MEASUREMENTS OF INITIAL HYDROCARBON CONCENTRATIONS

	Standard Deviation ($\pm 1\sigma$) in Percent								
Initial carbon, ppm	Ethane	Ethylene	Acetylene	Propylene	n-Butane	Benzene	Toluene	m-and p-Xylene	Average
11.2	10	9	8	10	6	7	10	4	8
6.1	4	10	7	5	9	12	16	8	9
3.0	20	14	16	7	15	10	9	13	13
average	11	11	10	7	10	10	12	8	10

The extensions of each point in both directions show the one-sigma value for that point. Deviations are minimal, and the individual HC concentrations vary linearly with total HC concentration. These plots show that no significant changes occur in the detailed HC composition with variations in total HC level.

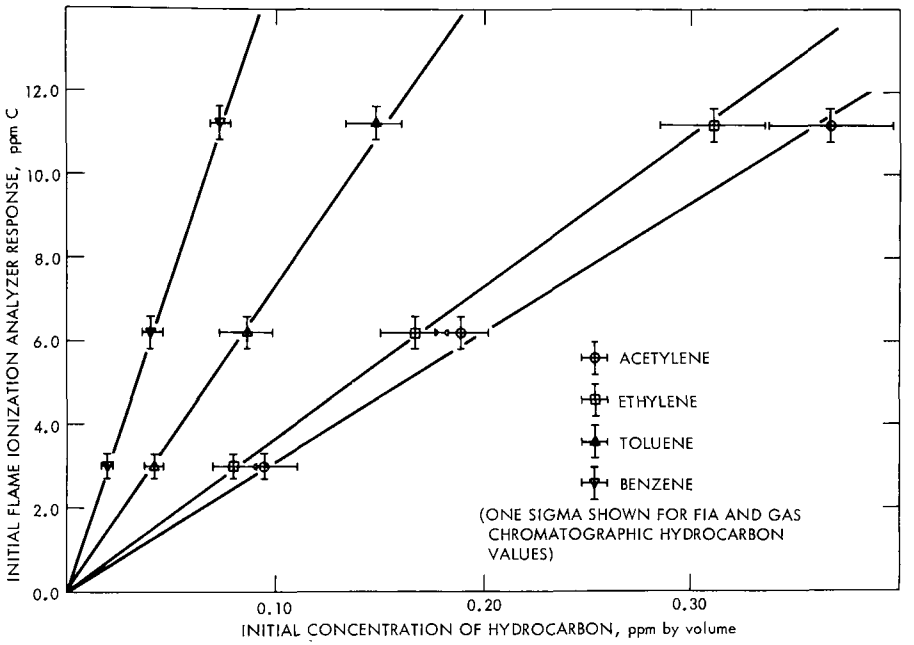

Figure 5. Relationship of individual HC concentrations to total HC concentrations determined by flame ionization analyzer.

This consistency also is evident for a single component considered in more detail. On the assumption that n-butane is a nonreactive substance and should remain constant throughout the course of a run, standard deviations were calculated by averaging all measurements made from immediately before irradiation until the end of the run. Table 6 shows the average concentration at each experimental condition, the average standard deviation, and the percent deviation. All values are averaged from data for at least two runs unless otherwise noted. The over-all average standard deviation of 7 percent is approximately twice the value considered to be a reasonable error in the instrumental reproducibility and in the measurement of peak areas with a standard butane mixture. Minor variations in the composition of the chamber input and in sampling lines probably account for the larger over-all error shown in analysis of the chamber contents.

In two experiments the chamber was charged with the charcoal-filtered air only. Analyses were performed for hydrocarbons and for the various products normally measured. Hydrocarbon contaminants in the air were present at very low levels. The background

Table 6. REPRODUCIBILITY IN GAS CHROMATOGRAPHIC MEASUREMENTS OF n-BUTANE

HC concentration, ppmC	Concentration of n-butane, ppm				Standard deviation of concentration within run			
	HC/NO_x ratio				HC/NO_x ratio			
	12/1	6/1	3/1	3/2	12/1	6/1	3/1	3/2
12	0.066	0.068			0.003	0.004		
6	0.037	0.038	0.036		0.0025	0.002	0.003	
3	0.020	0.025	0.022	0.015	0.002	0.002	0.001	0.001
	Standard Deviation, %				Avg			
12	5	5			7			
6	7	6	7		7			
3	10	8	5	7	8			
Avg	7	6	6	7	7			

levels of ethane, ethylene, acetylene, and n-butane averaged 0.008, 0.004, 0.002, and 0.006 ppm, respectively. Other hydrocarbons were present at or below their detection limits. Only for ethane was the level significant as compared to its level when the chamber was charged with diluted auto exhaust (approximately 10%). Correction for background ethane was made where necessary in the computations. The products formed from this low background of hydrocarbons were barely detectable.

A few analyses with the electron-capture detector showed that no electron-capturing products, such as organic nitrates or dicarbonyl compounds were present before irradiation, within the limits of detection of this instrument. Values obtained by wet chemical analyses for aldehydes were always below 0.1 ppm, and the aldehydes probably did not contribute any significant amount to the carbon balance before irradiation.

At the nominal 12-ppm carbon concentration a fairly complete analysis for HC content of the mixture was possible. This analysis, shown in Table 7, accounts for most of the carbon measured by the flame-ionization analyzer. Results in Table 7 are considered typical of the analysis at all concentrations in view of the high degree of consistency previously seen at all carbon concentrations for a wide variety of compounds (Tables 4, 5, and 6, Figure 5). These computations account for 92 percent of the carbon present, as determined by the flame-ionization analyzer. Since the flame-ionization analyzer does not respond equally to various classes of hydrocarbons, the two methods of measurement should not be expected to give exactly the same total concentrations. The average carbon number for the aromatics is 7.8, which is typical of a gasoline fraction, and their distribution is similar to that of gasoline. The distribution of aliphatic hydrocarbons is strongly affected by the combustion process, as would be expected, with the composition passing through a minimum concentration for the three-carbon hydrocarbons. The values for the intermediate-range aliphatic hydrocarbons may be slightly low owing to recurrent occasional minor leaks in some of the valves of the trapping apparatus used for concentration of these hydrocarbons.

The total concentration of six-carbon and higher olefins, five-carbon and higher diolefins, and four-carbon and higher acetylenes, naphthenes, and polar substances with any response on the flame-ionization detector should be less than 1 ppm carbon. If it is assumed that the average molecule for this group of substances has six carbon atoms, the maximum volume concentration of these higher-molecular-weight materials or polar substances would be approximately 0.15 ppm at the 12-carbon-ppm level in this system.

The concentrations for methane and for six-carbon and higher aliphatic hydrocarbons were estimated from the work of Hurn and coworkers on auto exhaust.[19] Since similar fuels were used in both investigations, a close similarity in detailed compostion is assumed for computation of relative concentrations of hydrocarbon classes not directly analyzed in this work.

Table 7. AVERAGE COMPOSITION OF CHAMBER AIR BEFORE IRRADIATION (at 11.2 ppm carbon concentration)

Compound	Concentration, ppm	Ppm of carbon	Ppm by carbon number
Benzene	0.073	0.438	0.073
Toluene	0.147	1.029	0.147
Ethylbenzene	0.041	0.328	0.211
m- and *p*-Xylene	0.120	0.960	
o-Xylene	0.050	0.400	
n-Propylbenzene	0.013	0.117	
3,4-Ethyltoluene	0.055	0.495	0.178
1,3,5-Trimethylbenzene + sec and tert butylbenzene	0.020	0.200	
1,2,4-Trimethylbenzene	0.070	0.630	
Styrene + 2-ethyltoluene	0.02	0.150	
Total aromatics	0.609	4.747	Avg carbon no. 7.8
Ethane	0.040	0.080	
Ethylene	0.304	0.608	0.702
Acetylene	0.358	0.716	
Propane	0.004	0.012	
Propylene	0.079	0.237	0.089
Propadiene	0.006	0.018	
Isobutane	0.009	0.036	
n-Butane	0.067	0.268	
Butene-1 and isobutene	0.032	0.128	0.147
Transbutene-2	0.006	0.024	
cis-Butene-2	0.006	0.024	
Butadiene	0.017	0.068	
Methyl acetylene	0.010	0.030	
n-Pentane	0.021	0.105	
Isopentane	0.078	0.390	
1-Pentene	0.005	0.025	0.154
2-Methylbutene-1	0.013	0.065	
2-Methylbutene-2	0.022	0.110	
Transpentene-2	0.015	0.075	
2-Methylpentane	0.042	0.252	
Total C_2-C_5 + 2-Methylpentane	1.134	3,271	Avg carbon no. 2.9
Total aromatics	0.609	4.747	
Estimated methane	0.3	0.3	
C_6 + paraffin[a]	0.33	2.0	
Total	2.37	10.3 ppm out of 11.2, or 92%	

[a]Assuming Hurn's ratio of 2.5 x concentration of C_2 through C_5 paraffins (0.89 x 2.5 = 2.2_3) less measured value of 2-methylpentane (2.2_3 - 0.2_5) 2.0).

The NO-NO_2 Reaction Processes

As demonstrated in this and earlier studies,[1,2,20] the general NO-NO_2 reaction system provides an important index for characterizing the atmospheric photochemical air pollution complex, in terms of both the rates of the over-all air pollution reaction and the degree to which the reactions proceed. This complex chemical reaction system consists of two over-all competing photochemical reaction sequences: (1) the photooxidation of NO in the presence of specific organic compounds under ultraviolet radiation below 4000 angstroms to produce NO_2 with the subsequent formation of ozone, and (2) the reaction between NO_2 and the free-radical species produced in the photooxidation of NO to form compounds such as alkyl nitrates and peroxyacyl nitrates with the subsequent reduction of NO_x (nitric oxide plus nitrogen dioxide) in the system. Since the data indicate that the chemical, physical, and biological effects can be generally correlated with measurements of the rates of photoxidation of NO, the reduction of total NO_x in the system, and the formation of ozone at equilibrium conditions, the over-all photochemical air pollution system can be characterized in terms of these parameters

NO Photoxidation

Variations both in the concentrations and ratios of HC and NO_x produce distinct differences in the general atmospheric photochemical air pollution systems, as shown in Figure 6.

The over-all reactions, as characterized by the NO_2 formation rate, the percent of the total NO_x reacting, and oxidant formation, tend to be slower and less complete as the HC/NO_x ratio is decreased from 24 to 1-1/2. The various systems studied differ significantly. At ratios of 3 and less, equilibrium is reached with free NO existing and zero reduction of the total NO_x in the system. Increasing the ratios above 3 results in both increasing NO_2 formation rates (increase in the initial slope for the NO_2 reaction) and increasing total NO_x reacting in the system at equilibrium. Oxidant level at equilibrium generally exhibits the same characteristics. As would be expected, at HC/NO_x ratios of 3 and less, where free NO exists in the system, no equilibrium oxidant concentration is found. At ratios above 3 oxidant level at equilibrium increases as the ratio increases to 24.

NO_2 Formation Rate

The effect of the initial HC and NO_x concentrations on the over-all NO-NO_2 reaction sequence is indicated by the variations in the rate of NO photooxidation. Within the limits of this study, variation of HC concentration produces the greatest single effect on NO photooxidation as measured by NO_2 formation rate; Figure 7, Table 8. Increases in HC concentration produce an increase in NO_2 formation rate consistently for each NO_x level studied; the increase is greatest at the 1-ppm NO_x level.

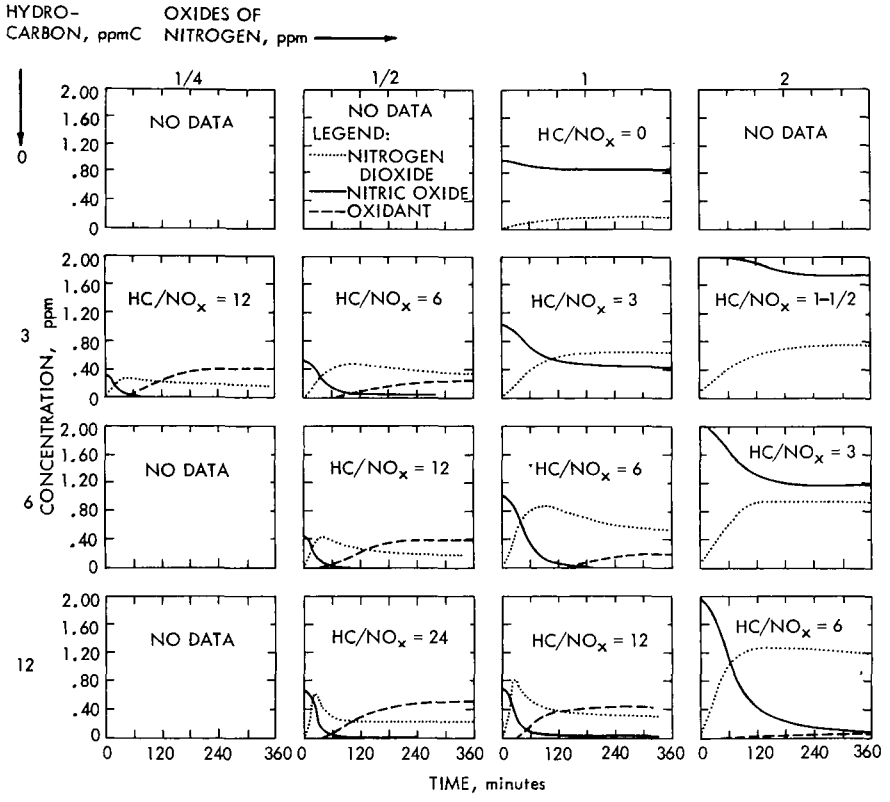

Figure 6. Reactions of NO, NO_2, and oxidant in various photochemical systems.

The effect of initial NO_x concentration on NO_2 formation rate varies depending on the HC concentration at which the measurements are made; Figure 7, Table 8. For the 12-ppmC HC level, increase in NO_x concentration from 1/2 ppm through 2 ppm results in the NO_2 formation rate initially increasing, passing through a maximum at about the 1-ppm level, and decreasing as the NO_x concentration approaches the 2-ppm level. This peaking effect becomes less pronounced with decreasing HC level at which the variation in NO_x concentration is measured. At the 3-ppmC HC level no significant change in NO_2 formation rate is noted with change in NO_x concentration.

The data in Table 8 indicate that the 180-minute average irradiation time follows the same general pattern as the 120-minute irradiation time with respect to the effects of HC and NO_x concentrations. Not enough tests were made in this exploratory phase of the study to allow the determination of statistical significance in the results, but the over-all effect appears to be a somewhat lower level of NO_2 formation rate for the longer average irradiation time.

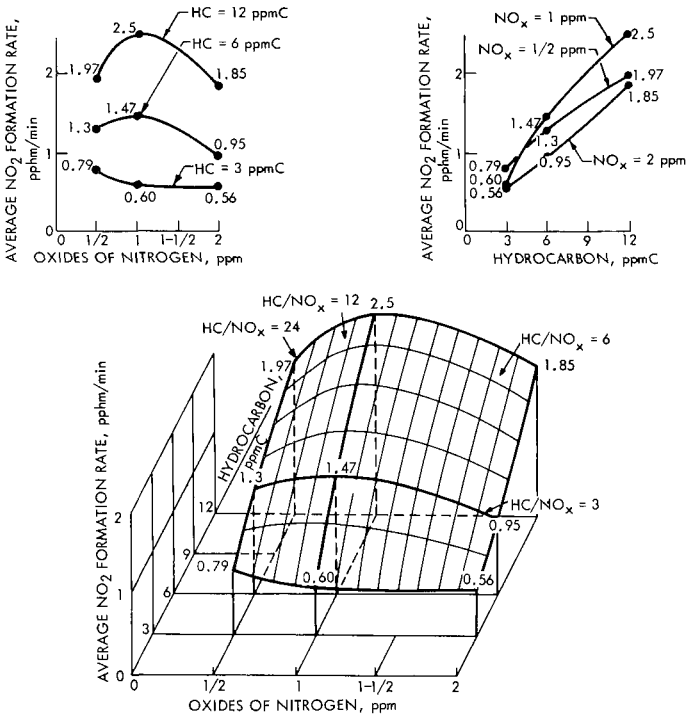

Figure 7. Average NO_2 formation rate versus HC and NO_x concentrations.

Table 8. CHEMICAL RESPONSE DATA

Average Irradiation Time, min	Test conditions: Nominal concentration HC, ppmC	Nominal concentration NO_x, ppm	Mean concentration HC, ppmC	Mean concentration NO_x, ppm	Response: NO_2 formation rate Mean, pphm/min	NO_x reacted Mean, %	Corrected oxidant Mean, pphm
120	12	2	11.2	2.00	1.85	35	7
	12	1	11.1	0.73	2.50	56	43
	12	1/2	11.7	0.65	1.97	65	52
	6	2	6.2	2.10	0.95	4	0
	6	1	5.8	1.02	1.47	42	19
	6	1/2	6.0	0.44	1.30	58	36
	3	2	2.8	2.14	0.56	0	0
	3	1	2.8	1.03	0.60	0	0
	3	1/2	3.3	0.51	0.79	23	23
	3	1/4	2.8	0.34	0.79	46	31
	0	1	0	0.97	0.15	0	0
180	12	2	11.3	1.86	1.40	8	4
	12	1	12.0	1.05	1.56	66	53
	6	2	6.6	1.96	0.69	0	0
	6	1	6.3	0.92	1.00	13	10
	6	1/2	6.1	0.47	1.31	61	41
	3	1	3.0	1.20	0.61	0	0
	3	1/2	3.2	0.47	0.70	36	25

This effect is consistent with results from the static chamber tests of fuel effects.[21] As indicated in Table 9, increase in average irradiation time from 120 minutes to its upper limit, i.e., static irradiation, yields a consistent reduction of NO_2 formation rate. This finding is also consistent with results of the first series of PHS irradiation chamber studies, which indicated no significant effect on NO_2 formation rate at the lower average irradiation times, i.e., 85-minutes and 120-minutes. These shorter irradiation times appear to be the lower limit of the effect of average irradiation time on NO_2 formation rate.

Table 9. EFFECT OF AVERAGE IRRADIATION TIME ON NO_2 FORMATION RATE

Mean concentrations[a]		Mean NO_2 formation rates, pphm/min		
HC, ppmC	NO_x, ppm	120-min[b] AIT	180-min[b] AIT	Static[a] AIT
12.9	1.01	2.65	1.66	1.59
4.6	0.97	1.10	0.84	0.61

[a]Data obtained from Reference 21.
[b]Data from Table 8 extrapolated to the HC and NO_x concentrations indicated.

Comparison of the data from the first PHS study on photoxidation of exhaust products indicates that the NO_2 formation rate at 12 ppmC HC and 1 ppm NO_x was lower in the original study. With identical fuel at 120-minute average irradiation time, the value was 1.5 pphm per minute; in the present tests, 2.5 pphm per minute. These results are not inconsistent, however, because the light intensity in the earlier tests was approximately 35 percent lower than in the present series. Based on the work of Tuesday[22] concerning the effect of light intensity on NO_2 formation for a system of 10 ppm trans-butene-2 and 4.2 ppm nitric oxide, a correction factor was applied to the NO_2 formation rate developed in the original study. Application of this factor resulted in a value of 2.3 pphm per minute, which agrees well with the level observed in the present series. Use of this correction factor assumes that the effect of light intensity on irradiated auto exhaust would be the same as that found for the butene-2 NO_x system. Unpublished work by Tuesday with other systems indicates that this assumption is reasonable at the concentrations studied.

CHEMICAL EFFECTS

Hydrocarbon Reactions

The rates of reaction of six of the more abundant hydrocarbons, analyzed by gas chromatography, are given in Table 10. The percent decrease in concentration of each hydrocarbon is computed from the difference between the average initial concentration (computed from several analyses made immediately before irradiation begins) and the average concentration at dynamic equilibrium (computed from several analyses made after about two average irradiation times—about 4 hours for an average irradiation time of 120 minutes). The percent decreases are listed as functions of both total carbon levels and total HC/NO_x ratios.

Table 10. PERCENT DECREASE IN HYDROCARBON CONCENTRATION DURING IRRADIATION[a]

Hydrocarbon, ppmC	Ratio, HC/NO_x 12/1	6/1	3/1	Ratio, HC/NO_x 12/1	6/1	3/1
	Ethylene			Propylene		
12	38	24		77	56	
6	40	27	25	76	61	52
3	36	30	20		64	57
Average	39	27	22	76	60	55
	Toluene			Ethylbenzene		
12	17	12		15	13	
6	31	15		20	17	
3	25	22	12	23	17	16
Average	24	16	12	19	16	16
	m- and *p*-Xylene			*o*-Xylene		
12	40	34		24	25	
6	47	37		34	25	
3	44	38	35		34	28
Average	44	36	35	29	26	28

[a]Percent decreases computed from differences between the average concentration immediately before irradiation began and the average concentration at dynamic equilibrium.

The percent decreases given in Table 10 for the six hydrocarbons listed occur in the same relative order as that previously reported in dynamic irradiation experiments.[15] The absolute values average somewhat higher for the current tests. The present data confirm the previously reported results on the reactivity of aromatics in irradiated exhaust.[14] Toluene and ethylbenzene are somewhat less reactive than ethylene, while the combined *m*- and *p*-xylene are somewhat more reactive than ethylene. Less extensive data for 3-ethyltoluene and 4-ethyltoluene indicated an average decrease of 45 percent during irradiation.[8] Analyses for 1, 3, 5-trimethylbenzene and 1, 2, 4-trimethylbenzene were limited to the 12-carbon-ppm level; these trimethylbenzenes decreased by over 60 percent during the irradiation,[8] and thus are consumed to the same extent as propylene.

A number of the hydrocarbons analyzed showed little or no decrease in concentration during the irradiations. The average percent decrease and standard deviations in percent were as follows: ethane, -2 ± 9; acetylene, -1 ± 5; n-butane, -8 ± 6; isobutane, -6 ± 9; and benzene, -4 ± 6. These values show that no significant changes in the concentrations of ethane, acetylene, or benzene occurred during irradiation. The butanes may have reacted very slightly. These results agree essentially with those obtained previously in a dynamic irradiation system.[15]

None of the less abundant four- and five-carbon olefins analyzed after the concentration step are listed in Table 10. The gas chromatographic data obtained are considered reliable enough to use for determining initial loadings, as in Table 7. So few analyses could be made during irradiation that the values for percent decrease in concentration are considered less reliable than values for those hydrocarbons determined by direct sampling and analysis. The average over-all decrease in the four- and five-carbon olefins was about 85 percent. The percent decreases in 1-alkenes and internally double-bonded alkenes generally agreed with the percent reductions previously reported (75% and 95-100%) for these two classes of olefins.[15]

The scatter in the values for initial olefin concentrations determined by the colorimetric olefin procedure is appreciably larger than that in the values obtained by gas chromatography (Figure 8). The over-all results appear to vary linearly with total carbon loading. The percentage decreases in four-carbon and higher olefins during the

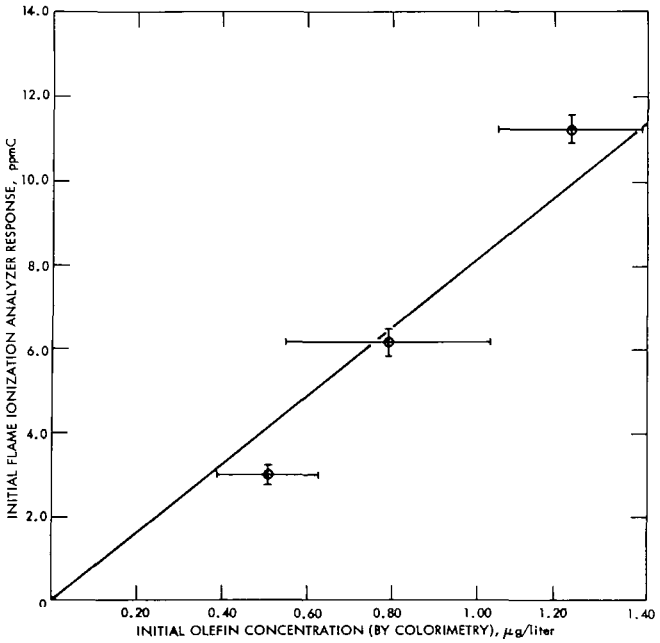

Figure 8. Relationship of olefin concentrations (colorimetry) to total HC concentrations (flame ionization analyzer).

irradiations were more consistent. The decrease for all experiments averaged 85 percent with one standard deviation being ± 5 percent. This result agreed substantially with the percent decreases determined by this procedure in previous dynamic irradiation experiments.[15]

Average irradiation times of 120 and 180 minutes show no significant effects for ethylene, propylene, toluene, ethylbenzene, and *m*-xylene and *p*-xylene. At the three nominal total concentrations, 12, 6, and 3 carbon ppm, the average differences in percent decrease at the two average irradiation times are 2, 2, and 0 percent, respectively. Similarly, no significant differences were found for olefins or aromatics considered separately with respect to the effect of average irradiation time.

If the effect of reducing initial HC concentration is considered at constant NO_x level, a marked decrease in percent HC reacted is apparent for the two olefins. For example, at an NO_x level of 1 ppm, a fourfold reduction in initial HC concentration reduced the percent ethylene reacted from 38 ± 3 percent to 20 ± 5 percent, and the percent propylene reacted from 77 ± 3 percent to 57 ± 5 percent. For the four aromatic hydrocarbons, however, varying the initial HC concentration at constant NO_x level yielded no significant effects. Since the percent decrease is a normalized rate, $\frac{\Delta C}{C_{HC}\,\Delta t}$, the actual rate of reaction for the same percent decrease in HC concentration is 4 times greater at 12 carbon ppm than at 3 carbon ppm. That is, the essentially constant percent reduction in concentration of aromatics with irradiation over a fourfold initial concentration range indicates that the rate of reaction of the aromatics is approximately a linear function of their initial concentrations. Since for olefins the percent consumed or normalized rate decreases with decreasing initial olefin concentration, the rate of reaction shows greater than a first-power relation to initial olefin concentration.

A marked effect on percent decrease in concentration of the hydrocarbons listed in Table 10 during irradiation occurs when the ratio is varied at constant HC level. A fourfold decrease in ratio, that is, a fourfold increase in NO_x, causes a 50 to 100 percent reduction in percent of HC reacted for ethylene, propylene, toluene, and ethylbenzene, and lesser reductions for the xylenes. These values show that an increase in NO_x inhibits the rate of consumption of these hydrocarbons.

Aldehydes

Formaldehyde, acrolein, and total aliphatic aldehydes were measured immediately before irradiation and during irradiation until dynamic equilibrium was nearly attained. The aldehyde concentrations reported in this investigation are net values obtained by subtracting the concentrations measured before irradiation from those measured near dynamic equilibrium. The aldehyde measured before irradiation was produced by incomplete combustion in the automobile. The various aldehydes produced by incomplete combustion constituted

10 to 20 percent of the total aldehyde measured near dynamic equilibrium. For example, at 12 carbon ppm, the formaldehyde concentrations immediately before irradiation averaged 0.06 ± 0.01 ppm, whereas at equilibrium the concentrations ranged from 0.3 to 0.4 ppm. The formaldehyde, acrolein, and total aliphatic aldehydes present before irradiation under the other experimental conditions were in approximately the same relative proportion to the gross concentrations.

The average concentrations of formaldehyde and total aliphatic aldehydes obtained from a number of experiments at each of the three concentrations are plotted in Figure 9 versus the total HC measured as ppmC by a flame-ionization analyzer. The standard deviations in the aldehyde and the HC values are indicated for each point. The yields of formaldehyde and total aliphatic aldehyde clearly are linear

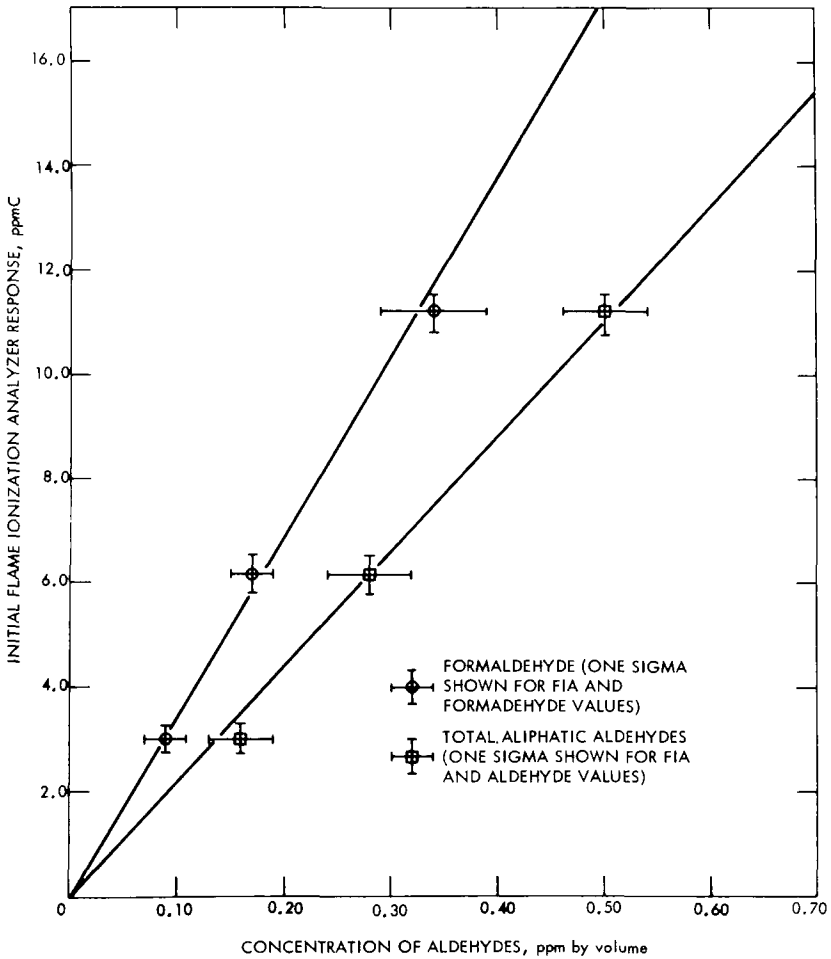

Figure 9. Relationship of aldehyde concentrations to total HC concentrations (flame ionization analyzer).

functions of the total HC concentration. This result does not imply that the aldehydes are produced from all of the hydrocarbons. Almost all of the aldehydes produced should result from the photooxidation of the olefinic and aromatic hydrocarbons, with very small yields, if any, from the paraffinic and acetylenic hydrocarbons.

The net concentrations of formaldehyde, acrolein, and total aliphatic aldehydes (calculated as formaldehyde) produced by photooxidation of the hydrocarbons and by subsequent secondary reactions are given in Table 11. Aldehyde yields show no significant increase when average irradiation time is increased from 120 to 180 minutes. The slight apparent average increase in aldehyde yield indicated in the tabular data can be accounted for by the 5 to 10 percent higher average HC levels at the 180-minute average irradiation time.

Table 11. CONCENTRATIONS OF FORMALDEHYDE, ACROLEIN, AND TOTAL ALIPHATIC ALDEHYDES PRODUCED DURING IRRADIATION

Aldehyde	Carbon, concentration, ppm	AIT, min	Nominal HC/NO_x ratio				
			24	12	6	3	1.5
Formaldehyde	11.2 ± 0.4	120	0.32	0.32	0.29		
	11.6 ± 0.4	180		0.36	0.40		
	6.0 ± 0.4	120		0.17	0.20	0.17	
	6.3 ± 0.2	180		0.20	0.17	0.15	
	2.9 ± 0.3	120		0.10	0.10	0.08	0.06
	3.1	180			0.10	0.09	
Acrolein	11.2 ± 0.4	120	0.029	0.031	0.028		
	11.6 ± 0.4	180		0.034			
	6.0 ± 0.4	120		0.024	0.020	0.022	
	6.3 ± 0.2	180			0.026	0.024	
Total aliphatic aldehydes	11.2 ± 0.4	120	0.46	0.45	0.50		
	11.6 ± 0.4	180		0.50	0.55		
	6.0 ± 0.4	120		0.25	0.34	0.26	
	6.3 ± 0.2	180		0.35	0.26	0.28	
	2.9 ± 0.3	120		0.17	0.19	0.15	0.12
	3.1	180			0.18	0.15	

The average formaldehyde concentration was about 60 percent of the toal aliphatic aldehyde computed as formaldehyde. As discussed in detail elsewhere,[14] the 3-methyl-2-benzothiazolone procedure is more sensitive to formaldehyde than to other aldehydes. For photochemical-smog-type reactions, a factor of 1.25 ± 0.10 is applicable. If this factor is applied to the data, the aldehyde concentrations expressed as an average aldehyde would be 25 percent higher than those listed in Table 11. Also the formaldehyde would constitute only about 50 percent of the toal aldehydes expressed as an average aldehyde. The average acrolein concentration is about 10 to 12 percent of the average formaldehyde concentration, and acrolein would constitute about 5 percent of the total aliphatic aldehydes.

The concentrations of acrolein reported are the maximum concentrations. Unlike the values for formaldehyde and total aldehydes, however, the maximum values for acrolein occurred after only about one and a half average irradiation times. Subsequently, the acrolein concentrations decreased, so that after two to three average irradiation times they averaged 25 percent less than the maximum concentration. The formaldehyde concentrations did not tend to decrease during irradiation. In about one-third of the experiments, the concentrations of total aldehydes did decrease after two average irradiation times. The decrease was slight, averaging about 5 percent for all of the experiments. Since formaldehyde makes up half of the total aldehydes, concentrations of the higher aldehydes that make up the other half may have decreased as much as 10 percent. Since acrolein constitutes only 5 percent of total aldehydes or about 10 percent of the higher aldehydes, the decrease in acrolein accounts for only about 2 percent of a 10 percent decrease.

These results for the reactions of the aldehydes are qualitatively reasonable. Formaldehyde is produced from almost all olefins and aromatics, including those that react rapidly and those that react slowly. In addition, many higher aldehydes that photooxidize produce some formaldehyde. Although formaldehyde slowly disappears by photooxidation, it is being produced also. The higher aldehydes are mostly produced from hydrocarbons that are largely consumed early in the irradiation; as a result, a net loss of higher aldehydes might be expected. Acrolein probably is produced in significant amounts only from a single hydrocarbon, 1,3-butadiene, which rapidly reaches its low equilibrium concentration with irradiation. Acrolein is being produced from this small equilibrium level of 1,3-butadiene much less rapidly than the acrolein is being consumed by photooxidation. Hence, acrolein disappears at an appreciable rate during the later stages of the irradiation.

The aldehyde yields vary with HC/NO_x ratio at constant HC level. This effect is obvious when the averaged data at each concentration level for formaldehyde and total aliphatic aldehydes are plotted against ratio (Figures 10 and 11). At the highest concentration a range of actual ratios between 22 and 6 is covered. At ratios over 12 the aldehyde yield increases slightly and then levels off. At ratios below 6 the yield definitely decreases. The decreases in concentrations of formaldehyde and aliphatic aldehydes occur consistently at ratios below 6 in all four of the curves for which experimental data are available.

Oxidant Formation

A plot of the mean value for oxidant at equilibrium against initial concentrations of HC and NO_x, Figure 12, and values given in Table 8 indicate that the formation of oxidant is strongly influenced by the HC/NO_x ratio, consistently decreasing with decreasing HC/NO_x ratio when measured at a constant level of either HC or NO_x. This trend is further established by one additional oxidant value at 31 pphm

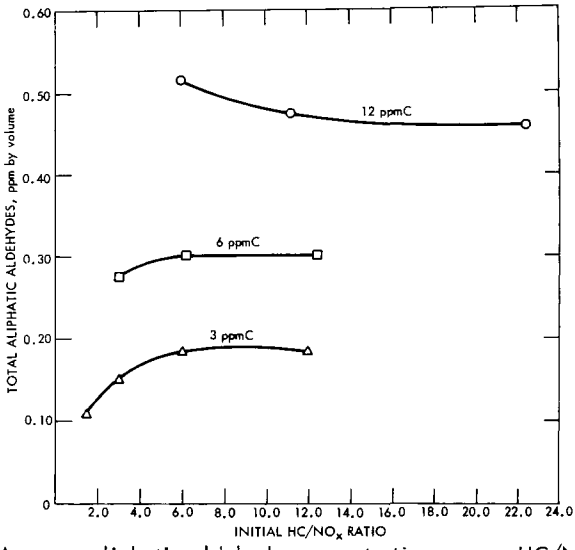

Figure 10. Average aliphatic aldehyde concentrations versus HC/NO_x ratio.

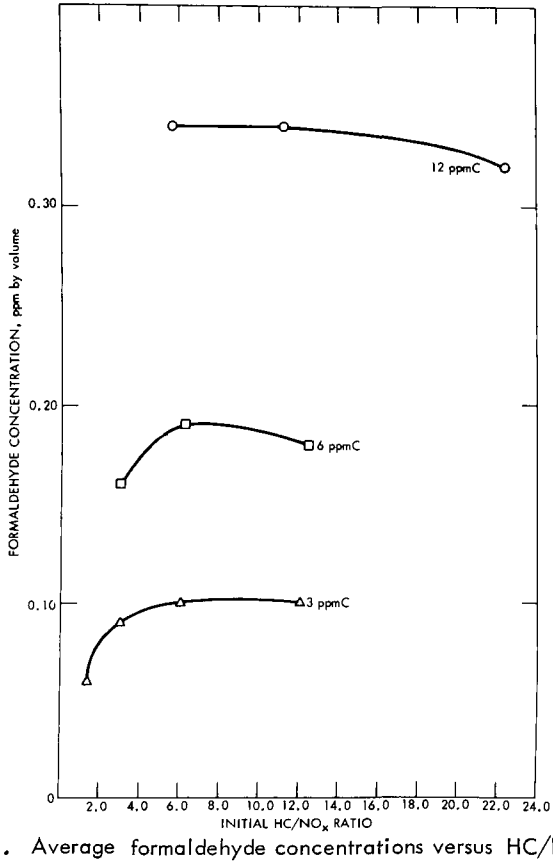

Figure 11. Average formaldehyde concentrations versus HC/NO_x ratio.

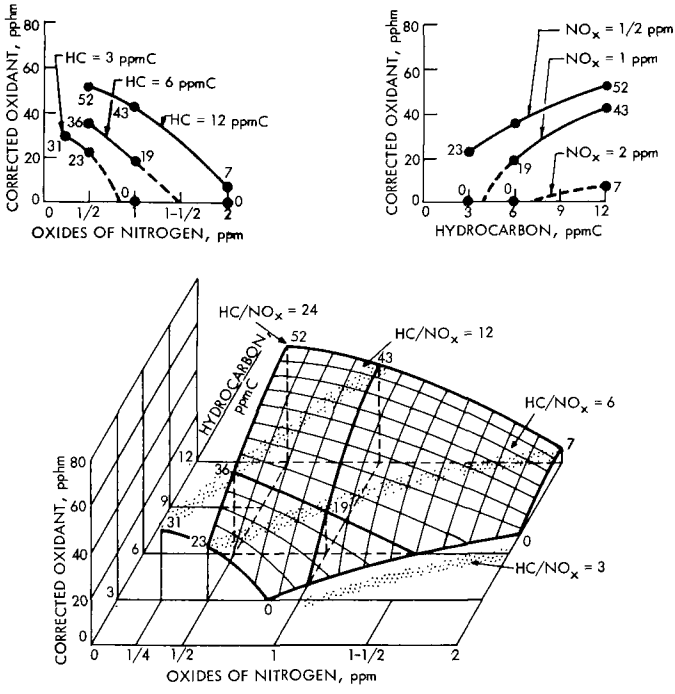

Figure 12. Oxidant concentrations at equilibrium versus HC and NO_x concentrations (120-min AIT).

for the 12:1 HC/NO_x ratio at 3 ppmC HC and 1/4 ppm NO_x. The effect of HC/NO_x ratio also is reflected in the individual effects of HC and NO_x concentrations on oxidant formation: oxidant concentration increases with increasing HC and decreasing NO_x concentrations, when measured at constant NO_x and HC levels, respectively. The data in Table 8 indicate no effect of increased irradiation time.

Appreciable oxidant concentrations will exist at HC levels below 3 ppmC and NO_x levels below 1/2 ppm, if the HC/NO_x ratio is 6 or higher. Within the concentration range studied, HC/NO_x ratios below 3 produced no free oxidant in the system. Oxidant concentration should approach zero as NO_x level approaches zero, and the test data indicate that oxidant concentration increases as NO_x decreases to 1/2 ppm levels; therefore, a peak in oxidant formation must occur at NO_x concentrations below 1/2 ppm (below 1/4 ppm at 3 carbon ppm). Additional work in this concentration range is required to establish this relationship.

Percent NO_x Reacted

Percent of NO_x reacted at equilibrium generally parallels the trends exhibited by oxidant formation concerning the effects produced by the HC/NO_x ratio, initial HC concentration, and initial NO_x con-

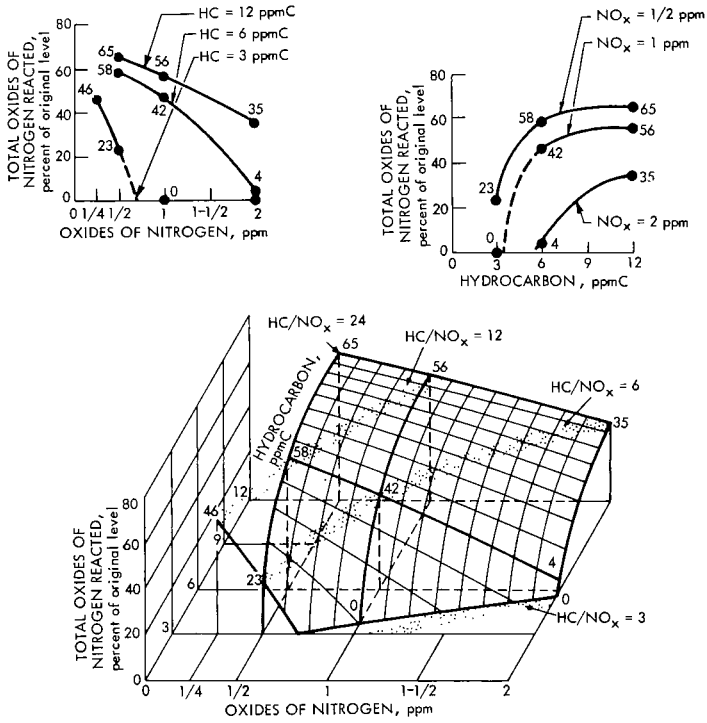

Figure 13. Percent total NO_x reacted versus HC and NO_x concentrations (120-min AIT).

centration, Figure 13, Table 8. Again the data indicate that the HC/NO_x ratio exerts the greatest effect on the percent NO_x reacted within the system. The plot shows a consistent increase in percent NO_x reacted at equilibrium with increasing HC/NO_x ratio, ranging from a low of zero reaction at a ratio of 3 to 65 percent reaction at a ratio of 24. This trend is reflected in the decrease in percent NO_x reacted with decreasing initial HC concentration and in the increase in percent NO_x reacted with decreasing initial NO_x concentration.

Within the limits of this study, a maximum is indicated in the total NO_x reacted at equilibrium as the over-all concentrations of HC and NO_x are increased at constant HC/NO_x ratios. This maximum occurs at approximately the 6-ppmC HC level at a ratio of 6 (where sufficient data are available to determine such a trend), decreasing with either increase or decrease in HC concentration. The initial irradiation study confirms this trend, in that the percent of NO_x reacted at a HC concentration of 12 ppmC for the HC/NO_x ratio of 12 corresponded to values obtained in the present study, and decreased as the over-all concentration was increased to the 33-ppmC HC level.

Other Products

Toward the end of this series of tests an electron-capture detector was acquired and put into operation. For use with this detector a 21-foot, 1/8-inch-OD column was packed with 5 percent 1, 2, 3-tris (2-cyanoethoxyl)-propane on Chromosorb-W and operated at 75°C. Since the detector was not sensitive to the hydrocarbon components of the system, analysis for the organic nitrates was possible. Figure 14 shows the variations of the organic nitrates with time for a single chamber run at an HC concentration of 3 ppmC and an HC/NO_x ratio of 3. Since this analysis was not quantitated, the results are reliable only on an area basis. The interesting features are the initial increase in concentration beginning at zero time for the alkyl nitrates (except propyl nitrate), and the continued increase during the irradiation period with a plateau usually near dynamic equilibrium. The irradiation also produced biacetyl, which started to form only after the irradiation had proceeded for some time, rapidly reached a maximum, and then decreased in concentration. Biacetyl was found in all analyses.

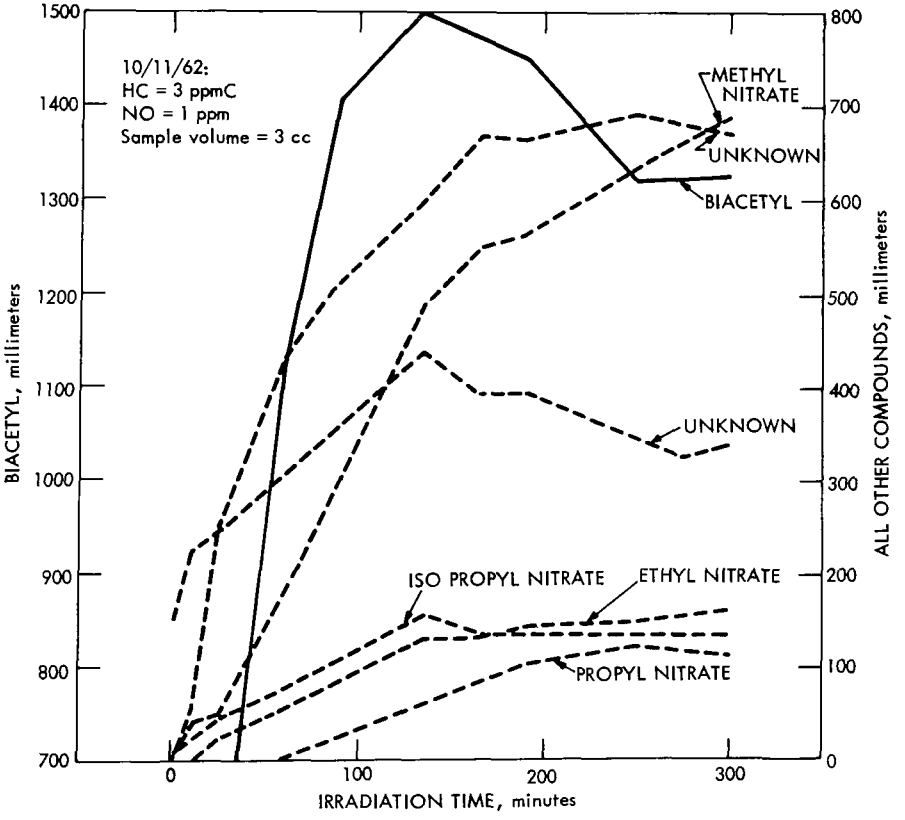

Figure 14. Variations of organic nitrate concentrations as measured by electron-capture detector.

Biacetyl may be formed in the irradiation by the recombination of acetyl radicals, although this appears to be an unfavored process. The disappearance of biacetyl is to be expected, since biacetyl readily undergoes photolysis in the presence of visible and ultraviolet radiation.

The extreme sensitivity of the gas chromatographic analytical method is indicated in Figure 14. Results from these analyses were compared with those obtained by flame ionization on a similar column used for aromatic hydrocarbon analysis. Comparison indicated no significant overlap or interference of the hydrocarbons in the electron-capture analysis, nor conversely of the organic nitrates and biacetyl in the aromatic hydrocarbon analysis with the flame-ionization detector.

BIOLOGICAL EFFECTS

Eye Irritation

A plot of eye irritation versus the two independent variables, initial concentrations of NO_x and HC, is shown in Figure 15; values are presented in Table 12. Within the concentration ranges of this study, the data indicate that HC concentration produces the greatest single effect on the production of materials causing eye irritation. Increase in HC level produces an increase in eye irritation, which is consistent at each NO_x level studied.

When NO_x concentration is increased above 1/2 ppm, eye irritation initially increases to a maximum at 1 ppm and decreases as the NO_x level reaches 2 ppm. This effect is consistent for each HC concentration at which effect of the variation in NO_x concentration was measured. It is significant that eye irritation occurs at HC/NO_x ratios of 3 and lower, in contrast to the zero responses for both oxidant concentration and percent of NO_x reacted in the system at these lower ratios.

Earlier measurements of eye irritation from irradiated auto exhaust[23] in general confirm these findings. The data reported here indicate a decrease in eye irritation with decreasing HC concentrations measured at constant NO_x levels and a peaking of eye irritation at an NO_x concentration of approximately 1 ppm, measured at constant HC concentrations.

The effect of increasing average irradiation time from 120 minutes to 180 minutes is even less definitive for eye irritation than for NO_2 formation rate, oxidant formation, and percent of NO_x reacted in the system. Eye irritation is a highly subjective measurement, and as such is most variable. The data indicate that eye irritation responses follow the same general pattern for the 180-minute and the 120-minute average irradiation times.

Table 12. BIOLOGICAL RESPONSE DATA (120-min AIT)

Test conditions				Response			
Nominal concentration		Mean concentration		Eye irritation	Mean plant injury[b]		
HC, ppmC	NO_x, ppm	HC, ppmC	NO_x, ppm	Mean index[a]	Young pinto bean	Tobacco wrapper	Petunia
12	2	11.2	2.0	5.5	0	0	0
12	1	11.1	0.73	10.2	3.5	0.1	3.0
12	1/2	11.7	0.65	7	3.0	0.2	2.0
6	2	6.2	2.10	2	0	0	0
6	1	5.8	1.02	7.5	1.0	0	1.3
6	1/2	6.0	0.44	5.7	2.0	0.3	2.6
3	2	2.8	2.14	1	0	0	0
3	1	2.8	1.03	5.4	0	0	0
3	1/2	3.3	0.51	3.2	0.1	0	1.2
3	1/4	2.8	0.34	3.3	0.4	0.5	1.1
0	1	0	0.97	6	0	0	0

[a]Panelists reported irritation response on scale of 0 (none) to 3 (heavy); index determined by adding nighest response numbers reported twice by each of ten panelists.

[b]On a scale of 0 to 4; 4 maximum damage.

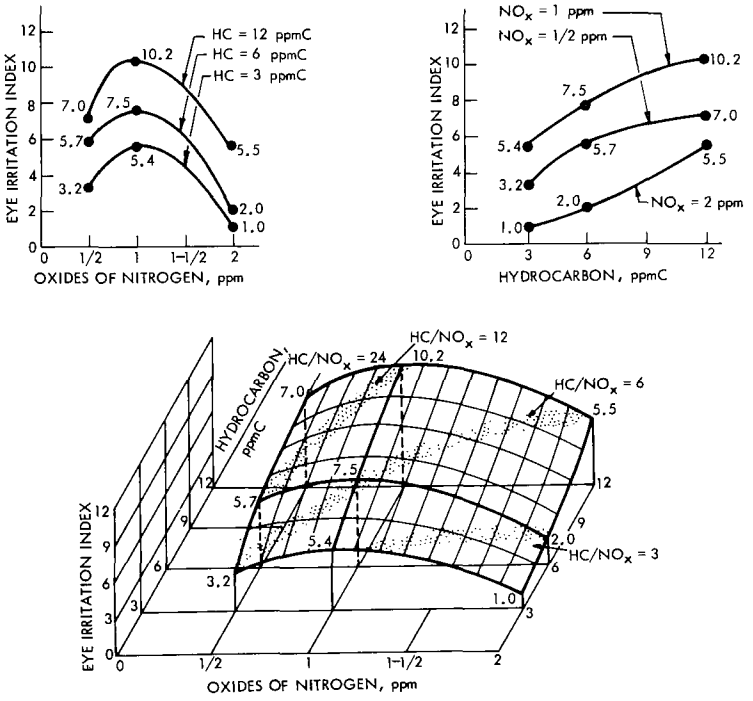

Figure 15. Eye-irritation responses versus HC and NO_x concentrations.

Plant Injury

Microscopic examination of plant tissues and observation of injury patterns indicate that the irradiated exhaust contains at least three distinct phytotoxicants that produce the sequence of anatomical and morphological changes observed.[24, 25]

The first toxicant causes glazing and silvering of the lower surface of young primary leaves of the pinto bean used as the indicator. These symptoms are similar to the injury developed under field conditions in the Los Angeles area[26] and to the symptoms develped on young pinto bean plants exposed to peroxyacetyl nitrate.[27]

The injury pattern of the second toxicant exhibits itself as dehydrated, bleached sunken spots on the upper surfaces of middle-aged leaves and tends to be random on the leaf surface. The middle-aged leaves of tobacco wrapper C are used to indicate this type of toxicant. The symptoms are similar to tobacco-fleck type of injury, which is known to be caused by ozone and which is common in the northeast area of the United States.[24, 28] In this type of injury, only the palisade cell is typically affected.

The injury pattern of the third toxicant also involves the palisade cells but occurs on younger leaves than is typical of the ozone-type injury. Initially a water-logged appearance develops on the upper surface of the leaf; later the injured tissue becomes reddish brown and finally develops a tan or bronze color, depending on the environmental conditions in which the plants are grown. This type of injury develops (1) near the tip of the very young petunia leaf, (2) more toward the base on slightly older leaves, and (3) at the base of the newly expanded leaf. Petunia also responds to all types of toxicants and as used here reflects the total phytotoxic development, regardless of type.

The results of the plant exposures to dilute irradiated auto exhaust gases are shown in Table 13 A, B, C. The data, Table 13 A, C, for injury of the lower-surface glazing type (young pinto bean) and for the total injury response (petunia) indicate a decrease in severity of injury as the HC/NO_x ratio decreases to 3, at which level no injury is observed. Increase in HC concentration produces an increase in severity of injury for all conditions except the 12 ppmC HC and 1/2 ppm NO_x concentrations for the general injury, Table 13 C. This would be expected, since the generalized type of injury appears to be produced by several phytotoxicants while the under-surface glazing type appears to be specific for one phytotoxicant. The severity of these two types of plant injury generally follows the trends indicated by the percent of total NO_x reacting in the system. Since some plant damage has been attributed to compounds formed from reactions between free radicals and NO_2 produced in the photooxidation process, this correlation is expected.

The ozone-type damage, Table 13 B, as might be expected, appears to be related to the oxidant concentration in the system. Further, no injury of this type was observed at oxidant levels below 30 pphm.

Table 13. PLANT INJURY RESPONSE DATA[a]

HC, ppmC	NO_x, ppm 1/4	1/2	1	2
0				
3	0.4	0.1	0	
6		2.0	0	0
12		3.0	3.5	0
A Young pinto bean: lower-surface-glazing type injury				
0			0	
3	0.5	0	0	0
6		0.3	0	0
12		0.2	0.1	0
B Tobacco wrapper: upper-surface type injury to middle-aged leaves (ozone)				
0			0	
3	1.1	1.2	0	0
6		2.6	1.3	0
12		2.0	3.0	0
C Petunia: total injury (all phytotoxicants)				

[a]On a scale of 0 to 4; 4 maximum damage.

ATMOSPHERIC EFFECTS

While the effects of variations in initial HC concentration, initial NO_x concentration, and HC/NO_x ratio on the response variables cannot be extrapolated directly to atmospheric effects, sound judgment allows an extension of the more definitive effects, within the limitations of the experimental design. Differences of initial concentrations, variability of the concentrations during irradiation, levels and variability of irradiation intensity, and rate of ventilation of a given air mass all can produce significant differences between the experimental work performed under controlled laboratory conditions and community atmospheric conditions. Within these limitations, extensions of the chamber work to atmospheric conditions will give some indication of the effects of HC reduction on the atmospheric response variables.

Reduction in atmospheric HC concentration should result in a reduction of oxidant formed and a reduction in eye irritation produced by the atmospheric photochemical $NO-NO_2$ reaction system. At HC/NO_x ratios below 3, no oxidant should be produced and free NO should exist in the atmosphere. Experimental data on eye irritation, however, indicate that lower but significant eye irritation levels will exist, particularly at the low concentration ranges of both initial HC and NO_x.

Data on plant injury generally indicate the same over-all trends. Reduction in atmospheric HC concentration should reduce the severity of lower-surface glazing and the total phytotoxicant injury (young pinto bean and petunia), to the HC/NO_x ratio of 3, at which level no injury is produced for the response conditions investigated. For the upper-surface type of injury to middle-aged leaves (tobacco wrapper) no injury should be produced at oxidant concentrations below 30 pphm, since this type of plant injury appears to be oxidant-dependent.

The reduction of NO_x concentrations to 1/2 ppm at HC levels of 6 and 12 ppmC and to 1/4 ppm at 3 ppmC does not appear to reduce the amount of HC consumption, the amount of oxidant or aldehyde formed, or the degree of plant damage. Although the levels of chemical and biological activity should decrease to zero at zero NO_x concentrations, it appears that a maximum occurs at NO_x concentrations below those used in the present study. If so, a very large percentage decrease in NO_x may be necessary to produce an appreciable effect. More recent studies do not include plant-damage measurements but tend to confirm the chemical results.[29, 30]

Schuck and coworkers[31] used the atmospheric flame-ionization and NO_x analyzer measurements recently available and compared these levels with the oxidant levels and smog days reported during the same period of time. Their curves for oxidant versus NO_x were of the same general shape as those in the present study. Oxidant levels reached a maximum at 0.15 ppm NO_x. Furthermore, the number of smog days also reached a maximum at about 0.15 ppm NO_x. This work by Schuck and others[31] was preliminary and involved many assumptions about reactive hydrocarbons, meteorological parameters, and pollutant charging conditions. The results also were not subject to statistical evaluation. The difference between a maximum at 1 ppm NO_x for eye irritation in the present study and 0.15 ppm NO_x with atmospheric data represents a large variation in results. The difference may be attributed to many factors, including the wide difference in the eye irritation measures used, the difference between a stirred dynamic flow reactor and the actual atmospheric conditions, differences in reactive HC concentrations, statistical considerations, etc. Only further experimental work can resolve just at what point eye irritation and other effects should maximize with variations in NO_x concentration in polluted atmospheres.

There has been some concern about the effects of a reduction of gross atmospheric HC concentration on the average and the instantaneous NO_2 concentrations in the atmosphere. To explore this phenomenon, average NO_2 concentrations were developed from the initial data by integration over the first 4 hours and over the first 10 hours after the start of irradiation, Figures 16 and 17. These average NO_2 concentrations were calculated by integrating the concentration with respect to time for the time interval shown and expressing this integral in terms of unit time to establish the average NO_2 concentration. These data indicate a general reduction of average NO_2 concentration with decreasing atmospheric HC concentrations, except for NO_x concentrations in the region of 1 ppm and below. For this range the trend indicates that a reduction in concentration of

atmospheric HC could initially produce an increase in average NO_2 concentrations. With continued reduction, however, an over-all decrease for both time periods studied is indicated.

STATISTICAL ANALYSIS

The effects on six response variables due to changes in the initial concentrations of HC and NO_x were evaluated statistically. Replicate tests were conducted for each of the nine combinations of HC and NO_x concentrations resulting from the three levels of each pollutant, except at the upper and lower extremes of HC/NO_x ratio, where only one test was run at each extreme (Table 2). The statistical significance of changes in the level of each response variable over the conditions of the experiment was determined by an analysis of variance. The statistical model was a two-way classification, in which the main effects of HC and NO_x concentrations and the interactions between them (HC/NO_x ratio) were evaluated. Results are shown in Table 14.

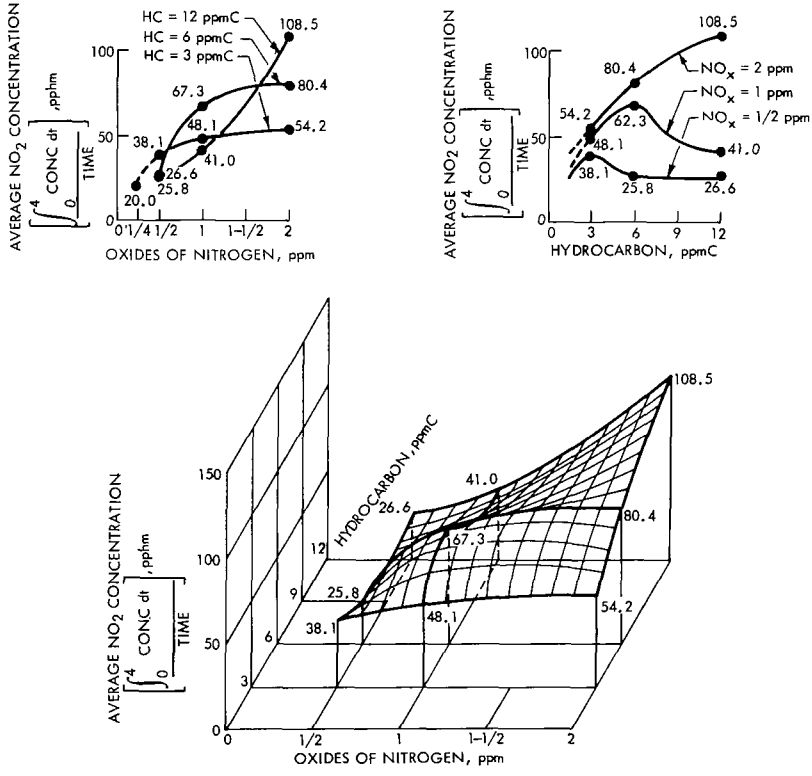

Figure 16. Average NO_2 concentration versus HC and NO_x concentrations (first 4 hours; 120-min AIT).

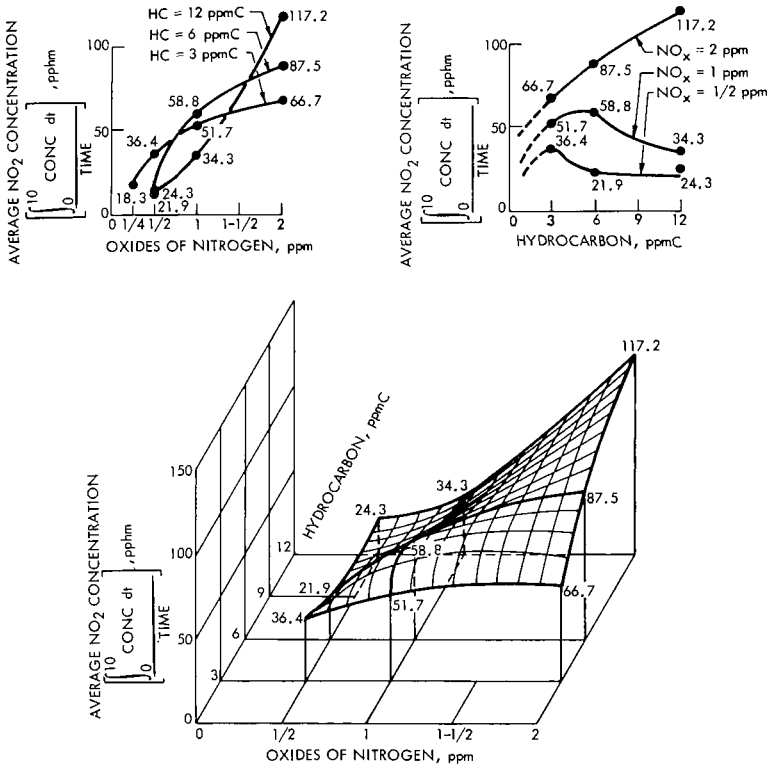

Figure 17. Average NO_2 concentration versus HC and NO_x concentrations (first 10 hours; 120-min AIT).

Table 14. RESULTS OF STATISTICAL ANALYSIS

	Due to HC change	Due to NO_x change	Interaction (HC/NO_x)
NO_2 formation rate	**	*	**
Oxidant	**	**	**
Percent NO_x reacting	**	**	*
Eye irritation	*	*	
Average NO_2 exposure (0 to 4 hours)	*	**	**
Average NO_2 exposure (0 to 10 hours)	*	**	*

Blank Difference in level of response variable not significant.
* Difference in level of response variable significant at 5% level.
** Difference in level of response variable significant at 1% level.

SUMMARY OF RESULTS

The concentrations of individual hydrocarbons in the diluted auto exhaust were well within the concentrations reported for the same hydrocarbons in Los Angeles. Ethylene concentrations before irradiation averaged from 0.31 ppm at the highest total HC concentration (12 ppmC) to 0.08 ppm at the lowest concentration (3 ppmC). The average initial concentrations of several other hydrocarbons at the highest and lowest total carbon concentrations were as follows: acetylene, 0.36 and 0.10 ppm; propylene, 0.08 and 0.023 ppm; benzene, 0.07 and 0.02 ppm; toluene, 0.15 and 0.04 ppm; and xylenes, 0.17 and 0.05 ppm. The atmospheric levels of these substances reported in Los Angeles either by Neligan during 1960[32] or Altshuller and Bellar in 1961[33] fall into this range of values. The concentrations of formaldehyde and total aliphatic aldehydes produced at 6 and 3 ppmC are also within the range of atmospheric concentrations reported for Los Angeles during 1960 and 1961.[33,34]

The effects of ratios on aldehyde concentrations (Table 11, Figures 10 and 11) are reasonable in terms of general photochemical knowledge. At very high HC/NO_x ratios, insufficient NO_x is available for complete reaction to end products; hence, the slight decrease in yield. The decrease in yield at ratios below 6 probably results from the inhibition of the HC reaction by excess NO_x.

The variations of aldehydes with NO_x concentration contrast with the eye-irritation data (Table 12), which show a maximum at 1 ppm nitric oxide. No such maximum occurs in the aldehyde yields. These results substantiate the previous suggestions that while formaldehyde and acrolein (along with PAN) are known eye irritants, they do not play an exclusive role in causing eye irritation.[34,35] Other species probably depend strongly upon the NO_x concentrations, and these species determine the specific shape of the eye irritation response curves (Figure 15).

The relative concentrations of individual hydrocarbons are independent of auto exhaust concentration before irradiation in dynamic irradiation experiments. The absolute concentrations of the individual hydrocarbons are linearly related to total HC concentration.

In general, increasing average irradiation time showed no effect except on the NO_2 formation rate, which appeared somewhat lower for the exploratory 180-minute average irradiation time.

The effects of changes in initial HC concentration, initial NO_x concentration and HC/NO_x ratio are summarized in terms of the individual response variables.

1. Variation both in the initial concentrations of HC and NO_x and in the HC/NO_x ratio produced distict differences in the over-all NO-NO_2 reaction system. Over-all reaction rates were slower and less complete with decrease in the HC/NO_x ratio. At ratios of 3 and less, equilibrium was reached with free NO existing and zero reduction of the total NO_x in the system.

2. The greatest single effect on NO_2 formation rate resulted from variation in initial HC concentrations. Increase in initial HC concentrations produced a consistent increase in NO_2 formation rate, greatest at 1 ppm NO_x. The effects of initial HC concentration on NO_2 formation rate differed from those produced by initial NO_x concentration in that the increase in initial NO_x concentration from the 1/2-ppm level resulted in an increase in NO_2 formation rate, peaking at 1 ppm NO_x and decreasing as the concentration approached 2 ppm. Peaking effect was greatest at 12 ppmC hydrocarbon, decreasing with decrease in HC concentration. Longer average irradiation time caused a somewhat lower NO_2 formation rate.
3. A fourfold reduction in initial HC concentration at constant HC/NO_x ratio caused a slight increase in the relative amounts (percent) of HC consumed during irradiation. The same fourfold reduction in initial HC concentration at constant NO_x level resulted in a decrease in the percent of olefins reacted, but did not affect the percent of aromatics reacted. When the HC level was kept constant, an increase in NO_x level caused a marked reduction in the percent of olefinic and aromatic hydrocarbons reacted during irradiation.
4. The aldehyde yields are linearly related to the total HC level. No significant effect on aldehyde yields was found when the average irradiation time was varied from 120 to 180 minutes. The aldehyde yields decreased both at very high and very low HC/NO_x ratios.
5. Oxidant formation was strongly influenced by the HC/NO_x ratio, consistently decreasing with decreasing ratio. At ratios below 3 no free oxidant formed in the system. The effect of HC/NO_x ratio on oxidant formation was reflected in the effects of individual HC and NO_x concentrations; oxidant concentration increased with increasing HC and decreasing NO_x concentrations.
6. Percent NO_x reacted also was strongly influenced by the HC/NO_x ratio, decreasing consistently with decreasing ratio. No reduction in NO_x was indicated at ratios of 3 or below. Variations in initial HC and NO_x concentrations, as reflected by HC/NO_x ratio, indicated an increase in percent NO_x reacted with increasing initial HC concentration and decreasing NO_x concentration.
7. Average NO_2 concentration increased and passed through a maximum as the initial HC level was decreased from 12 ppm to 3 ppm at NO_x concentrations in the region of 1 ppm and below. With further reduction in HC level below 3 ppm, a decrease in average NO_2 concentration may be expected at all NO_x levels studied.
8. Variations in initial HC concentration produced the greatest single effect on eye irritation, i.e., increase in HC level produced a consistent increase in eye irritation response.

Increase in NO_x concentration from the 1/2-ppm level resulted in eye irritation response initially increasing to a maximum at 1 ppm and decreasing as the NO_x concentration reached 2 ppm. Although the aldehydes may be responsible in part for the eye irritation, the presence of other eye-irritating species must be postulated to explain the shape of the eye-irritation response curves when plotted against NO_x concentration, since aldehyde yields are linearly related to the total HC level.

9. Three distinct types of plant injuries were produced by the irradiated exhaust gases: (1) glazing and silvering of the lower surface of the young primary leaves of the pinto bean; (2) dehydrated bleached sunken spots on the upper surface of middle-aged leaves of the tobacco wrapper C; and (3) tan or bronze discolorations of the upper surface of the petunia plant. Each of the first two types of plant injury is attributed to a different single phytotoxicant, whereas the third type appears to reflect the total phytotoxic development. The undersurface glazing and the total phytotoxic injury were related to HC/NO_x ratio, decreasing with decrease in ratio. No injury of these types was observed at ratios of 3 or lower. The second type of injury is related to toal oxidant in the system. No plant damage was observed at total oxidant concentrations below 30 pphm.
10. As average irradiation time was reduced from static to 85 minutes, the NO_2 formation rate reached a maximum in the region of 120 minutes. The decrease in the concentration of reactive hydrocarbons during irradiation was independent of whether a 120- or a 180-minute average irradiation time was used.

ACKNOWLEDGMENTS

The following organizations and people assisted in the work reported in this publication:

LABORATORY OF ENGINEERING AND PHYSICAL SCIENCES BRANCH

CHEMICAL RESEARCH AND DEVELOPMENT SECTION

Dr. A.P. Altshuller, J.E. Sigsby, Jr.
P.W. Leach, L.J. Leng, T.A. Bellar

PHYSICAL RESEARCH AND DEVELOPMENT SECTION

Dr. H.J.R. Stevenson

ENGINEERING RESEARCH AND DEVELOPMENT SECTION

A.H. Rose, Jr.
R.C. Stahman
R.P. Lauch

LABORATORY OF MEDICAL AND BIOLOGICAL SCIENCES BRANCH

AGRICULTURAL SECTION

Dr. C.S. Brandt
Dr. I.J. Hindawi

CLINICAL RESEARCH SECTION

Dr. D.W. Lockwood

REFERENCES

1. M. W. Korth, "Dynamic Irratiation Chamber Tests of Automotive Exhaust," U.S. Public Health Service Publication No. 999-AP-5, Robert A. Taft Sanitary Engineering Center, Cincinnati, Ohio, 1963.

2. A.H. Rose, Jr., R.C. Stahman, M.W. Korth, "Dynamic Irradiation Chamber Tests of Automotive Exhaust, Part I," J. Air Pollution Control Association, 12:468 (1962).

3. M.W. Korth, A.H. Rose, Jr., R.C. Stahman, "Effects of Hydrocarbon to Oxides of Nitrogen Ratios on Irradiated Auto Exhaust, Part I," J. Air Pollution Control Association, 14:168, (1964).

4. General Motors Research Laboratories, "Search," September, 1962.

5. M. Luckiesh, "Applications of Germicidal, Erythemal and Infrared Energy," D. Van Nostrand Company, Inc., 1946.

6. T. Bellar, J.E. Sigsby, Jr., C.A. Clemons, and A.P. Altshuller, "Direct Application of Gas Chromatography to Atmospheric Pollutants," Anal. Chem. 34:763 (1962).

7. C.A. Clemons, P.W. Leach, and A.P. Altshuller, "1,2,3-Tris (2-cyano-ethoxy) Propane as a Stationary Phase in the Gas Chromatographic Analysis of Aromatic Hydrocarbons," Anal. Chem., 35:1546 (1963).

8. A.P. Altshuller and P.W. Leach, "Reactivity of Aromatic Hydrocarbons in Irradiated Automobile Exhaust," Intern. J. Air and Water Pollution, 8:37 (1964).

9. T. Bellar and J.E. Sigsby, Jr., "Application of the Electron Capture Detector to Gas Chromatography in Air Pollution," presented at 144th Annual Meeting American Chemical Society, March 31-April 5, 1963, Los Angeles, California.

10. A.P. Altshuller, D.L. Miller, and S.F. Sleva, "Determination of Formaldehyde in Gas Mixtures by the Chromotropic Acid Method," Anal. Chem. 33:621 (1961).

11. A. P. Altshuller, L. J. Leng, and A. F. Wartburg, "Source and Atmospheric Analysis for Formaldehyde by Chromotropic Acid Procedures," Intern. J. Air and Water Pollution 6:381 (1962).

12. I. R. Cohen and A. P. Altshuller, "A New Spectrophotometric Method for the Determination of Acrolein in Combustion Gases and in the Atmosphere," Anal. Chem. 33:726 (1961).

13. E. Sawicki, T. R. Hauser, T. W. Stanley, and W. C. Elbert, "The 3-Methyl-2-Benzothiazolone Hydrazone Test," Anal. Chem. 33:93 (1961).

14. A. P. Altshuller and L. J. Leng, "Application of the 3-Methyl-2-Benzothiazolone Hydrazone Method to Analysis of Aliphatic Aldehydes in the Vapor State," Anal. Chem., 35 (1963).

15. J. E. Sigsby, Jr., T. A. Bellar, and L. J. Leng, "Dynamic Irradiation Chamber Tests of Automotive Exhaust, Part II," J. Air Pollution Control Assoc., 12:522 (1962).

16. A. P. Altshuller, L. J. Leng, and S. F. Sleva, "Determination of Olefins in Combustion Gases and in the Atmosphere," Am. Ind. Hyg. Assoc. J. 23:289 (1962).

17. B. E. Saltzman, "Colorimetric Microdetermination of Nitrogen Dioxide in the Atmosphere," Anal. Chem. 26:1949 (1954).

18. D. H. Byers and B. E. Saltzman, "Determination of Ozone in Air by Neutral and Alkaline Iodide Procedures," Advances in Chemistry Series No. 21:93-101, (1959).

19. R. W. Hurn, C. L. Dozois, J. O. Chase, C. F. Ellis, and P. E. Ferrin, "The Potpourri that is Exhaust Gas," 27th Midyear Meeting, American Petroleum Institute's Division of Refining, San Francisco, Calif., May 17, 1962.

20. E. R. Stephans, "The Reactions of Auto Exhaust in Sunlight," presented at the Air Pollution Research Conferences on "Atmospheric Reactions of Constituents of Motor Vehicle Exhaust," Los Angeles, California, December, 1961.

21. W. J. Hamming, P. P. Mader, S. W. Nicksic, J. C. Romanovsky, and L. G. Wayne, "Gasoline Composition and the Control of Smog," Western Oil and Gas Association and Los Angeles County Air Pollution Control District, Los Angeles, California, 1961.

22. C. S. Tuesday, "The Atmospheric Photooxidation of trans-Butene-2 and Nitric Oxide" from "Chemical Reactions in the Lower and Upper Atmosphere," J. Wiley and Sons, New York, 1961.

23. W.L. Faith, N.A. Renzetti, L.H. Rogers, "Fourth Technical Progress Report, No. 22," Air Pollution Foundation, San Marino, California, 1958.

24. I.J. Hindawi, J.A. Dunning, and C.S. Brandt, "Morphological and Anatomical Response of Tobacco Wrapper C., Pinto Bean, and Petunia Plants Exposed to Irradiated Auto Exhaust" (Abstract), Submitted to Ohio Academy of Science, 1963.

25. I.J. Hindawi, J.A. Dunning, and C.S. Brandt, "Microscopical Changes of Pinto Bean Leaf Exposed to Irradiated Auto Exhaust" (Abstract), American Journal of Botany 49 (part 2):660, (1962).

26. R.A. Bobrov, "Tha Anatomical Effects of Air Pollution on Plants," Proc. Second National Air Pollution Symposium, Stanford Research Institute, 129-134, (1952)

27. E.R. Stephens, E.F. Darley, O.C. Tayler, and W.E. Scott, "Photochemical Reaction Products in Air Pollution," Proc. Am. Petroleum Institute 40, III, (1960).

28. A.C. Hill, M.R. Pack, M. Treshow, R.J. Downs, and L.G. Transtrum, "Plant Injury Induced by Ozone," Phytopathology 51:356-363, (1961).

29. A.P. Altshuller and I.R. Cohen, "Atmospheric Photooxidation of the Ethylene-Nitric Oxide System," Int. J. Air and Water Poll., 8:611-632 (1964).

30. W.A. Glasson and C.S. Tuesday, "Inhibition of the Atmospheric Photooxidation of Hydrocarbon by Nitric Oxide," presented at 148th National Meeting, American Chemical Society, Chicago, Ill., Aug. 30 Sept. 4, 1964.

31. E.A. Schuck, J.N. Pitts, Jr., J.K.S. Wan, "Atmospheric Analytical Data and Photooxidation of Nitrogen Oxides," presented at 148th National Meeting, American Chemical Society, Chicago, Ill, Aug. 30 - Sept. 4, 1964.

32. R.E. Neligan, "Hydrocarbons in the Los Angeles Atmosphere," Arch. Environ. Health 5:581 (1962).

33. A.P. Altshuller and T.A. Bellar, "Gas Chromatographic Analyses in the Los Angeles Atmosphere," J. Air Pollution Control Assoc. 13:81 (1963).

34. N.A. Renzetti and R.J. Bryan, "Atmospheric Sampling for Aldehydes and Eye Irritation in Los Angeles Smog 1960," J. Air Pollution Control Assoc. 11:421 (1961).

35. A. P. Altshuller and S. P. McPherson, "Spectrophotometric Analysis of Aldehydes in the Los Angeles Atmosphere," J. Air Pollution Control Assoc. 13:109 (1963).

36. P. W. Leach, L. J. Leng, T. A. Bellar, J. E. Sigsby, Jr. and A. P. Altshuller, "Effects of Hydrocarbon to Oxides of Nitrogen Ratios on Irradiated Auto on Exhaust, Part II," J. Air Pollution Control Assoc. 14:168 (1964).

APPENDIX

DETAILED TEST DATA

Table A1. SUMMARY OF TEST CONDITIONS AND RUN NUMBERS

Hydrocarbon Hydrocarbon (HC), ppmC	Oxides of nitrogen (NO_x), ppm	HC/NO_x ratio	Average irradiation time (AIT), minutes	Run number
12	1/2	24	120	132
12	1	12	120	142
12	1	12	120	143
12	2	6	120	136
12	2	6	120	138
6	1/2	12	120	125
6	1/2	12	120	128
6	1/2	12	120	167
6	1	6	120	140
6	1	6	120	141
6	2	3	120	137
6	2	3	120	139
3	1/4	12	120	146
3	1/4	12	120	147
3	1/2	6	120	148
3	1/2	6	120	150
3	1	3	120	149
3	1	3	120	151
3	1	3	120	161
3	2	1-1/2	120	159
	1		120	160[a]
12	1	12	180	156
12	2	6	180	154
6	1/2	12	180	158
6	1	6	180	155
6	2	3	180	157
3	1/2	6	180	153
3	1	3	180	152
6	2	3	0	165[b]

[a]Background air (no auto exhaust).
[b]Static run (no plant data).

Table A2. BIOLOGICAL DATA

Run number	Eye irritation response: Clean air	Eye irritation response: Irradiated exhaust	Eye irritation response: Index[a]	Plant damage index[b]: Tobacco wrapper "C"	Plant damage index[b]: Tobacco smyrna	Plant damage index[b]: Pinto bean trifoliate T	Plant damage index[b]: Pinto bean trifoliate P	Plant damage index[b]: Pinto bean (primary)	Plant damage index[b]: Young pinto bean	Plant damage index[b]: Petunia
125	8.0	11.0	3.0	1	1	0	0	0	1	1
128	5.0	13.0	8.0	4	4				4	
132	7.0	14.0	7.0	4	3	3	0	0	3	2
136	3.0	9.0	6.0	0	0	0		0	0	0
137	6.0	9.0	3.0	0	0	0		0	0	0
138	7.0	12.0	5.0	0	0	0		0	0	0
139	8.0	9.0	1.0	0	0	0		0	0	0
140	2.0	11.0	9.0	0	0	1	0	0	2	2
141	5.0	11.0	6.0	0	0	1	0	0	2	2
142	8.6	15.7	7.1	c	c	3	0	1	3	3
143	10.0	23.3	13.3	2	2	3	0	0	3	3
146	4.3	7.1	2.8	c	0	0		0	c	c
147	3.6	7.5	3.9	2	c	1	0	0	1	2
148	7.0	10.0	3.0	0	0	0		0	c	c
149	5.6	10.0	4.4	0	0	0		0	0	0
150	5.6	8.9	3.3	0	0	0		0	0	1
151	8.6	15.0	6.4	0	0	0		0	0	0
152	6.7	11.6	4.9	0	0	0		0	0	0
153				0	0	0		0	c	1
154				0	0	0		0	0	0
155				0	0	0		0	0	0
156	5.0	21.4	16.4	2	1	2	0	0	3	3
157	4.4	8.9	4.5	0	0	0		0	0	0
158	7.0	12.0	5.0	3	3	2	0	0	3	3
159	6.0	7.0	1.0	0	0	0		0	0	0
160	6.0	12.0	6.0	0	0	0		0	0	0
161				0	0	0		0	0	0
165	4.4	7.7	3.3							
167	5.0	11.0	6.0	1	2	3	1	0	4	3

[a]Panelists reported irritation response on scale of 0 (none) to 3 (heavy); index determined for each run by adding highest response numbers reported twice by each of ten panelists.
[b]On a scale of 0 to 4; 4 maximum damage.
[c]Trace.

Table A3. RESULTS OF CHEMICAL ANALYSES

Run number	Actual concentrations before irradiation: Hydrocarbon (FIA), ppmC	NO_x, ppm	NO_2 formation rate, pphm/min	NO_x reacted, %	Oxidant (corrected for NO_2), pphm: Wet	Oxidant (corrected for NO_2), pphm: Mast	Olefin, g/l: Before irrad	Olefin, g/l: After irrad	Formaldehyde, ppm: Before irrad	Formaldehyde, ppm: After irrad	Acolein, ppm: Before irrad	Acolein, ppm: After irrad	Total aldehydes (as formaldehyde), ppm: Before irrad	Total aldehydes (as formaldehyde), ppm: After irrad
125	5.7	0.53	1.30	41	42	28	0.56	0.09	0.02	0.21		0.017	0.10	0.37
128	5.8	0.38	1.36	71	47	44	0.78	0.13	0.04	0.17		0.027	0.12	0.35
132	11.7	0.65	1.97	65	52			0.15		0.37		0.025		0.52
136	10.7	1.90	1.75	42	7	10	1.20	0.23	0.06	0.28		0.027	0.09	0.55
137	6.6	2.20	0.84	8	3	0	0.46	0.05	0.02	0.20		0.032	0.03	0.21
138	11.6	2.10	1.94	27	3	4	1.45	0.24	0.07	0.40		0.025	0.04	0.64
139	5.8	2.00	1.05	0		0	0.43	0.09	0.01	0.18		0.018	0.03	0.28
140	5.9	1.02	1.38	40	19		1.10	0.12	0.04	0.22		0.018	0.03	0.37
141	5.7	1.02	1.55	43	19		0.51	0.03	0.04	0.26		0.016	0.03	0.34
142	11.1	0.74	2.50	51	39	40	1.17	0.01	0.05	0.35		0.017	0.05	0.48
143	11.1	0.72	2.50	60	47	46	1.12	0.22	0.04	0.38		0.035	0.05	0.53
146	2.8	0.33	0.86	47	49	32	0.63	0.08	0.02	0.12			0.01	0.18
147	2.7	0.34	0.72	44	50	30	0.34	0.05	0.02	0.12				0.19
148	3.6	0.53	0.78	26	27	22	0.54	0.07	0.04	0.13			0.06	0.25
149	2.7	1.05	0.52	0	0	0	0.50	0.09	0.02	0.08			0.03	0.17
150	3.0	0.48	0.79	20		23				0.13				
151	3.0	1.05	0.60	0	8	0	0.43	0.12	0.01	0.09			0.00	0.20
152	3.0	1.20	0.61	0	0	0	0.53	0.08	0.01	0.10			0.03	0.19
153	3.2	0.47	0.70	36	25	25	0.63	0.11	0.01	0.11			0.00	0.17
154	11.3	1.86	1.40	8	0	4	1.20	0.29	0.07	0.47			0.06	0.65
155	6.3	0.92	1.00	0	3	10	0.76	0.11	0.05	0.22		0.028	0.03	0.27
156	12.0	1.05	1.56	68	67	53		0.14	0.05	0.40		0.017	0.10	0.58
157	6.6	1.96	0.69	0	0	0	0.72	0.16	0.02	0.18		0.024	0.12	0.40
158	6.1	0.47	1.31	61	53	41	0.82	0.32	0.02	0.23			0.02	0.36
159	2.8	2.14	0.56	0	0	0	0.32	0.03	0.02	0.07			0.00	0.12
160		0.97	0.15	0	0	0		0.03	0.00	0.01			0.02	0.03
161	2.7	0.99	0.67	7	0	0	0.63	0.08					0.02	0.14
165	5.0	2.15	0.95	13	0	0	0.42	0.00	0.00	0.13		0.012	0.02	0.27
167	6.5	0.41	1.23	63	42	35	1.00	0.27	0.07	0.25		0.017	0.09	0.34

Table A4. CHROMATOGRAPHIC DATA: Run 132, Light Hydrocarbons

Time	Ethane	Ethylene	Propane	Acetylene	Isobutane	*n*-Butane	Propylene
10:00	0.039	0.328	0.004	0.360	0.016	0.068	0.092
10:30	0.041	0.362	0.007	0.407	0.010	0.068	0.088
11:05	0.042	0.369	0.006	0.405	0.010	0.069	0.091
11:30	0.042	0.353	0.006	0.405	0.012	0.070	0.088
12:15	0.043	0.310	0.006	0.435	0.014	0.069	0.039
1:00	0.043	0.036	0.007	0.431	0.012	0.072	0.027
1:30	0.044	0.276	0.005	0.434	0.012	0.074	0.025
2:00	0.044	0.271	0.005	0.442	0.014	0.071	0.041
2:30	0.044	0.263	0.006	0.448	0.007	0.064	0.020
3:00	0.043	0.259	0.006	0.441	0.011	0.068	0.023
3:30	0.044	0.250	0.006	0.429	0.010	0.062	0.025

Table A5. CHROMATOGRAPHIC DATA: Run 137, Light Hydrocarbons

Time	Ethane	Ethylene	Propane	Acetylene	Isobutane	*n*-Butane	Propylene
9:25	0.024	0.164	0.004	0.177	0.005	0.033	0.037
9:50	0.024	0.177	0.003	0.199	0.010	0.034	0.038
10:30	0.024	0.189	0.003	0.221	0.007	0.040	0.049
11:00	0.025	0.192	0.004	0.223	0.007	0.039	0.051
11:30	0.025	0.187	0.004	0.212	0.008	0.038	0.044
12:30	0.024	0.177	0.003	0.208	0.004	0.040	0.036
1:00	0.024	0.155	0.003	0.195	0.005	0.037	0.026
2:00	0.025	0.158	0.003	0.196	0.003	0.038	0.030
2:40	0.023	0.152	0.002	0.185	0.005	0.035	0.023
3:20	0.023	0.147	0.002	0.187	0.005	0.038	0.024
3:45	0.022	0.138	0.002	0.178	0.005	0.041	

Table A6. CHROMATOGRAPHIC DATA: Run 138

Time	Ethane	Ethylene	Propane	Acetylene	Isobutane	*n*-Butane	Propylene	Isopentane
10:15	0.040	0.315	0.004	0.337	0.011	0.070	0.082	0.095
10:45	0.040	0.318	0.004	0.336	0.012	0.071	0.092	0.101
11:20	0.043	0.322	0.004	0.349	0.013	0.071	0.087	0.089
12:15	0.042	0.285	0.004	0.343	0.009	0.068	0.053	0.076
1:45	0.039	0.243	0.004	0.322	0.009	0.075	0.046	0.077
2:30	0.039	0.245	0.004	0.325	0.006	0.069	0.046	0.088
2:45	0.039	0.250	0.003	0.337	0.009	0.066	0.038	0.083
3:40	0.039	0.242	0.003	0.338	0.008	0.063	0.043	0.077

Aromatic Hydrocarbons[a]

Time	Benzene	Toluene	Ethyl-benzene	*m*-and *p*-xylene	Comp'd X	*o*-Xylene	*n*-Propyl-benzene	3 and 4 Ethyl-toluene
9:45	0.029	0.061	0.010	0.032	0.016	0.016		0.014
10:15	0.066	0.128	0.038	0.114	0.031	0.042	0.011	0.049
10:50	0.067	0.126	0.039	0.116	0.033	0.042	0.015	0.045
11:20	0.069	0.123	0.034	0.098	0.027	0.037	0.010	0.033
12:15	0.070	0.119	0.037	0.094	0.033	0.038	0.008	0.045
1:45	0.065	0.106	0.030	0.067	0.028	0.030	0.007	0.033
2:30	0.061	0.102	0.030	0.067	0.031	0.031	0.007	0.032
3:00	0.065	0.109	0.030	0.073	0.035	0.033	0.011	0.030
3:40	0.062	0.103	0.031	0.067	0.030	0.032	0.010	0.031

[a]Isopropylbenzene not detected.

Table A7. CHROMATOGRAPHIC DATA: Run 140

Light Hydrocarbons

Time	Ethane	Ethylene	Propane	Acetylene	Isobutane	n-Butane	Propylene	Isopentane	n-pentane
9:30	0.030	0.057	0.004	0.064	0.018	0.042	0.017	0.041	
10:00	0.035	0.034	0.017	0.038	0.071	0.180	0.017	0.123	0.072
11:00	0.024	0.171	0.003	0.211	0.012	0.039	0.047	0.57	
11:30	0.023	0.167	0.003	0.211	0.013	0.040	0.038	0.061	
12:30	0.026	0.144	0.004	0.203	0.015	0.044	0.026	0.053	
1:30	0.027	0.130	0.004	0.200	0.016	0.044	0.021	0.050	
2:00	0.029	0.130	0.004	0.201	0.007	0.041	0.020	0.054	
2:45	0.027	0.121	0.004	0.200	0.010	0.038	0.014	No peak	
3:30	0.028	0.115	0.005	0.196	0.006	0.038	0.017	0.042	

Aromatic Hydrocarbons[a]

Time	Benzene	Toluene	Ethylbenzene	and p-Xylene	Comp'd X	o-Xylene	n-Propylbenzene	Ethyl-3 and 4 toluene
9:30	0.043	0.072	0.018	0.043	0.042	0.020	0.012	
10:00	0.038	0.057	0.015	0.042	0.029	0.014	0.009	
10:30	0.047	0.093	0.022	0.067	0.037	0.021	trace	0.031
11:00	0.054	0.094	0.025	0.068	0.036	0.025	trace	0.027
11:30	0.054	0.092	0.025			0.026	trace	0.038
12:30	0.052	0.084	0.023	0.048	0.046	0.024	trace	0.022
1:00	0.050	0.089	0.020	0.045	0.039	0.024	trace	0.022
1:30	0.049	0.083	0.017	-.044	0.040	0.022	trace	0.016
2:00	0.050	0.080	0.020	0.042	0.035	0.021	trace	0.026
2:45	0.049	0.079	0.017	-.036	0.035	0.021	trace	
3:30	0.048	0.075	0.023	0.042	0.043	0.024	trace	0.031

[a]Isopropylbenzene not detected.

Table A8. CHROMATOGRAPHIC DATA: Run 141

Light Hydrocarbons

Time	Ethane	Ethylene	Propane	Acetylene	Isobutane	n-Butane	Propylene	Isopentane
10:15	0.026	0.162	0.004	0.185	0.008	0.038	0.027	0.054
10:45	0.026	0.169	0.004	0.196	0.007	0.038	0.044	0.048
11:15	0.026	0.164	0.004	0.192	0.006	0.039	0.042	0.052
12:15	0.026	0.141	0.004	0.189	0.008	0.037	0.022	0.047
12:45	0.025	0.137	0.004	0.181	0.006	0.036	0.022	0.044
1:30	0.025	0.125	0.004	0.185	0.007	0.039	0.018	0.047
2.00	0.026	0.115	0.004	0.183	0.006	0.037	0.017	0.040
2:30	0.025	0.113	0.004	0.183	0.007	0.037	0.018	0.041
3.00	0.025	0.117	0.004	0.190	0.008	0.036	0.014	0.041
3:30	0.026	0.113	0.005	0.191	0.007	0.038	0.019	0.044

Aromatic Hydrocarbons[a]

Time	Benzene	Toluene	Ethylbenzene	m- and p-Xylene	Comp'd X	o-Xylene	n-Propylbenzene	3 and 4 Ethyltoluene
10:15	0.040	0.071	0.024	0.064	0.033	0.023	trace	0.046
10:45	0.040	0.070	0.020	0.055	0.034	0.021	trace	0.024
11:15	0.040	0.075	0.024	0.066	0.031	0.026	0.029	0.039
12:15	0.040	0.069	0.019	0.048	0.036	0.028	trace	0.024
12:45	0.040	0.071	0.020	0.047	0.034	0.028	trace	0.031
1:30	0.037	0.061	0.018	0.039	0.034	0.022	trace	0.015
2;00	0.038	0.062	0.017	0.038	0.032	0.020	trace	0.020
2:30	0.039	0.062	0.014	0.034	0.035	0.020	trace	0.021
3:00	0.038	0.062	0.020	0.036	0.037	0.020	trace	0.015
3:30	0.039	0.061	0.016	0.035	0.038	0.019	trace	0.021

[a]Isopropylbenzene not detected.

Table A9. CHROMATOGRAPHIC DATA: Run 142

Light Hydrocarbons

Time	Ethane	Ethylene	Propane	Acetylene	Isobutane	-Butane	Proylene	Isopentane
10:30	0.033	0.289	0.004	0.349	0.007	0.058	0.072	0.081
11:00	0.033	0.295	0.003	0.363	0.007	0.060	0.071	0.083
11:30	0.034	0.301	0.004	0.367	0.007	0.063	0.072	0.079
1:00	0.034	0.236	0.003	0.360	0.006	0.060	0.036	0.083
1:35	0.038	0.212	0.004	0.362	0.007	0.060	0.023	0.075
2:15	0.035	0.197	0.003	0.356	0.007	0.054	0.020	0.067
2:45	0.036	0.187	0.004	0.353	0.007	0.055	0.020	0.070
3:30	0.036	0.181	0.003	0.357	0.007	0.057	0.021	0.061

Aromatic Hydrocarbons[a]

Time	Benzene	Toluene	Ethyl-benzene	*m*-and *p*-Xylene	Comp'd X	*o*-Xylene	*n*-Propyl-benzene	3 and 4 Ethyl-toluene
10:30	0.078	0.154	0.045	0.121	0.031	0.042	0.012	0.066
11:00	0.081	0.168	0.048	0.127	0.037	0.059	0.028	0.052
11:30	0.080	0.164	0.043	0.131	0.041	0.086	0.029	0.056
1:00	0.074	0.137	0.039	0.091	0.036	0.043	0.011	0.034
1:35	0.079	0.141	0.050	0.095	0.043	0.046		0.039
2:15	0.073	0.124	0.031	0.067	0.031	0.046	0.010	0.035
2:45	0.078	0.135	0.036	0.077	0.031	0.038	0.013	0.038

[a]Isopropylbenzene not detected.

Table A10. CHROMATOGRAPHIC DATA: Run 143

Light Hydrocarbons

Time	Ethane	Ethylene	Propane	Acetylene	Isobutane	*n*-Butane	Propylene	Isopentane
9:50	0.035	0.248	0.004	0.299	0.009	0.053	0.062	0.075
10:20	0.035	0.284	0.004	0.340	0.007	0.058	0.074	0.078
10:55	0.035	0.298	0.003	0.362	0.009	0.064	0.074	0.071
11:25	0.036	0.293	0.003	0.365	0.009	0.065	0.064	0.077
12.30	0.037	0.234	0.004	0.373	0.008	0.062	0.030	0.080
1:00	0.038	0.215	0.004	0.372	0.007	0.057	0.025	0.073
2:10	0.038	0.197	0.004	0.370	0.008	0.058	0.019	0.075
2:35	0.038	0.194	0.003	0.374	0.009	0.061	0.019	0.073
3:00	0.037	0.191	0.004	0.379	0.008	0.056	0.016	0.076
3:30	0.038	0.189	0.004	0.377	0.008	0.056	0.021	0.069

Aromatic Hydrocarbons

Time	Benzene	Toluene	Ethyl-benzene	*m*-and *p*-Xylene	Comp'd X	Isopropyl-benzene	*o*-Xylene	*n*-Propyl-benzene	3 and 4 Ethyl-toluene
9:50	0.068	0.138	0.036	0.101	0.031	trace	0.039	0.007	0.043
10:20	0.075	0.156	0.043	0.128	0.034	trace	0.046	0.012	0.051
10:55	0.077	0.164	0.045	0.143	0.037	trace	0.046	0.010	0.053
11:25	0.078	0.164	0.043	0.120	0.035	trace	0.056	0.012	0.054
12:30	0.079	0.153	0.048	0.105	0.033	trace	0.053	0.022	0.040
1:00	0.078	0.150	0.037	0.089	0.031	trace	0.051	0.025	0.044
2:10	0.080	0.145	0.047	0.092	0.047	trace	0.042	0.015	0.041
2:35	0.080	0.145	0.038	0.084	0.039	trace	0.042	0.022	0.033
3:00	0.080	0.147	0.042	0.084	0.036	trace	0.044	0.009	0.038
3:30	0.080	0.145	0.044	0.087	0.043	trace	0.049	0.014	0.027

Table A11. CHROMATOGRAPHIC DATA· Run 146

Light Hydrocarbons

Time	Ethane	Ethylene	Propane	Acetylene	Isobutane	n-Butane	Propylene	Isopentane
9:20	0.025	0.063	0.005	0.074	0.010	0.020	0.021	0.024
10:20	0.016	0.076	0.003	0.095	0.006	0.019	0.017	0.024
10:52	0.020	0.056	0.004	0.066	0.005	0.042	0.019	0.034
11:25	0.014	0.075	0.002	0.092	0.005	0.022	0.018	trace
11:55	0.013	0.071	0.002	0.090	0.005	0.022	0.022	0.018
12:38	0.012	0.058	0.002	0.083	0.003	0.018	0.013	trace
1:10	0.013	0.056	0.002	0.086	0.004	0.017	0.009	trace
2:30	0.013	0.051	0.002	0.090	0.005	0.021	trace	trace
3:00	0.015	0.049	0.003	0.088	0.003	0.019	none	trace

Aromatic Hydrocarbons[a]

Time	Benzene	Toluene	Ethyl-benzene	m-and p-xylene	Comp'd X	o-Xylene	n-Propyl-benzene	3 and 4 Ethyl-toluene
9:20	0.019	0.042	0.010	0.028	0.034	0.014	trace	0.023
10:20	0.022	0.044	0.018	0.043	0.029	0.018	0.015	0.016
10:52	0.022	0.042	0.013	0.035	0.035	0.011	trace	
11:25	0.022	0.041	0.012	0.051	0.036	0.012	trace	0.017
11:55	0.021	0.042	0.014	0.041	0.037		trace	0.026
12:38	0.018	0.037	0.018	0.042	0.034	0.011	trace	0.008
1:10	0.020	0.034	0.020	0.029	0.032	0.012	trace	trace
2:30	0.018	0.033	0.012	0.024	0.027	0.009	trace	trace
3:00	0.020	0.032	0.009	0.021	0.031	trace	trace	trace

[a]Isopropylbenzene not detected.

Table A12. CHROMATOGRAPHIC DATA· Run 147

Light Hydrocarbons[a]

Time	Ethane	Ethylene	Acetylene
10:00	0.011	0.066	0.075
10:30	0.012	0.071	0.087
11:00	0.011	0.074	0.085
11:30	0.011	0.071	0.079
12:30	0.011	0.058	0.079
1:00	0.013	0.045	0.067
2:00	0.012	0.049	0.077
2:30	0.012	0.048	0.079
3:00	0.011	0.045	0.077
3:30	0.011	0.045	0.079

[a]No measurements of propane, isobutane, n-butane, propylene, or isopentane because of baseline fluctuation caused by temperature change in room.

Aromatic Hydrocarbons[a]

Time	Benzene	Toluene	Ethyl-benzene	m-and p-Xylene	Comp'd X	o-Xylene	n-Propyl-benzene	3 and 4 Ethyl-toluene
10:30	0.019	0.038	0.017	0.053	0.037	0.028	trace	0.018
11:00	0.020	0.039	0.014	0.036	0.033		trace	
11:30	0.020	0.036	0.014	0.037	0.025		trace	
12:30	0.019	0.032	0.009	0.024	0.036	0.019	trace	0.007
1:00	0.022	0.030	0.017	0.029	0.025	0.009	trace	
2:00	0.018	0.028	0.008	0.016	0.024	0.019	trace	0.024
2:30	0.016	0.027	0.011	0.018	0.027		trace	
3:00	0.019	0.028	0.014	0.022	0.031	0.007	trace	0.017

[a]Isopropylbenzene not detected.

Table A13. CHROMATOGRAPHIC DATA: Run 149

Light Hydrocarbons

Time	Ethane	Ethylene	Propane	Acetylene	Isobutane	*n*-Butane	Propylene
9:30	0.015	0.057	0.006	0.065	0.012	0.022	0.018
10:30	0.013	0.072	0.004	0.087	0.010	0.024	0.024
11:10	0.013	0.075	0.004	0.088	0.005	0.025	0.027
12:40	0.013	0.071	0.003	0.088	0.005	0.025	0.019
1:10	0.013	0.067	0.003	0.086	0.006	0.020	0.010
1:40	0.013	0.066	0.002	0.087	0.007	0.022	0.012
2:10	0.012	0.063	0.002	0.087	0.004	0.022	0.012
3:00	0.013	0.062	0.003	0.087	0.004	0.018	0.010
3:30	0.012	0.060	0.003	0.081	trace	0.021	0.009

Aromatic Hydrocarbons

Time	Benzene	Toluene	Ethyl-benzene	*m*-and *p*-Xylene	Comp'd X	Isopropyl-benzene	*o*-Xylene	*n*-Propyl-benzene	3 and 4 Ethyl-toluene
10:30	0.018	0.034	0.008	0.032	0.026		0.018	0.031	trace
11:10	0.018	0.039	0.008	0.028	0.025	trace	0.020	0.016	trace
11:40	0.018	0.042	0.012	0.032	0.021	trace	0.013	0.019	trace
12:40	0.019	0.038	0.012	0.029	0.024	trace	0.015	0.019	trace
1:10	0.018	0.038	0.012	0.026	0.027	trace	0.016	0.013	trace
1:40	0.017	0.034	0.008	0.020	0.022	trace	0.019	0.015	trace
2:10	0.017	0.034	0.008	0.027	0.027		0.016	0.012	trace
3:00	0.017	0.034	0.007	0.022	0.026	trace	0.011	0.011	trace
3:30	0.017	0.034	0.009	0.021	0.024	trace	0.015	0.013	trace

Table A14. CHROMATOGRAPHIC DATA: Run 150

Light Hydrocarbons

Time	Ethane	Ethylene	Propane	Acetylene	Isobutane	-Butane	Propylene
10:10	0.019	0.083	0.004	0.098	trace	0.023	0.024
10:40	0.020	0.088	0.004	0.104	0.005	0.024	0.031
11:10	0.019	0.087	0.004	0.102	0.006	0.023	0.025
12:10	0.018	0.080	0.005	0.101	0.005	0.020	0.018
12:50	0.017	0.072	0.003	0.102	0.004	0.021	0.012
1:20	0.015	0.063	0.004	0.103	0.005	0.020	0.012
1 50	0.015	0.065	0.003	0.102	0.008	a	a
2:20	0.015	0.065	0.004	0.104	0.004	0.022	a
3.00	0.016	0.065	0.003	0.108	0.005	0.022	0.012
3:40	0.015	0.062	0.002	0.102	0.005	0.020	0.009

[a]Not measurable.

Aromatic Hydrocarbons

Time	Benzene	Toluene	Ethyl-benzene	*m*-and *p*-Xylene	Comp'd X	Isopropyl-benzene	*o*-Xylene	-Propyl-benzene	3 and 4 Ethyl-toluene
10:40	0.022	0.045	0.013	0.042	0.038		0.016	0.030	0.020
11:10	0.022	0.046	0.012	0.039	0.037	trace	0.012	0.031	0.019
11:40	0.023	0.046	0.012	0.033	0.044		0.024	0.027	0.021
12:50	0.022	0.039	0.011	0.032	0.048		0.011	0.011	trace
1:20	0.022	0.039	0.017	0.029	0.043	trace	0.010	0.017	trace
1:50	0.021	0.039	0.012	0.027	0.040		0.012		trace
2:20	0.022	0.037	0.008	0.024	0.041		0.010	0.009	trace
3:00	0.022	0.036	0.012	0.028	0.047		0.011	0.010	trace
3:40	0.020	0.035	0.009	0.017	0.037				

Mid-range Hydrocarbons

Time 11:00 - 11:30

COMPOUND	PPB
acetylene	
ethylene	
ethane	
methyl acetylene	2.5
propadiene	0.8
propylene	
propane	
butadiene	1.95
butene-1, Isobutylene	5.3
cis-butene-2	trace
trans-butene-2	trace
pentene-1	1.3
cis-pentene-2	trace
trans-pentene-2	trace
2-methylbutene-2	4.4
2-methylbutene-1	1.7
iso-pentane	18.4
n-pentane	6.8
2-methylpentane	10.1

Table A15. CHROMATOGRAPHIC DATA: Run 151

Light Hydrocarbons

Time	Ethane	Ethylene	Propane	Acetylene	Isobutane	n-Butane	Propylene
9:02	0.013	0.053	0.002	0.060	a	0.016	0.018
9:33	0.014	0.078	0.002	0.093	0.005	0.021	0.024
10:05	0.015	0.086	0.002	0.102	0.003	0.020	a
10:35	0.013	0.089	0.003	0.109	0.007	0.022	0.027
11:04	0.013	0.092	0.002	0.106	0.008	0.021	0.024
12:35	0.013	0.080	0.002	0.103	a	0.022	0.030
2:37	0.012	0.073	0.002	0.103	trace	0.018	a
3:10	0.012	0.075	0.002	0.106	trace	a	a
3:50	0.013	0.074	0.002	0.107	trace	0.019	0.012

[a]Not measured because of temperature fluctuations.

Aromatic Hydrocarbons

Time	Benzene	Toluene	Ethyl-benzene	m-and p-Xylene	Comp'd X	Isopropyl-benzene	o-Xylene	n-Propyl-benzene	3 and 4 Ethyl-toluene
9:02	0.017	0.028	0.012	0.028	0.028	0.005	0.014	trace	trace
9:33	0.022	0.043	0.015	0.034	0.033	trace	0.015	0.016	trace
10:05	0.023	0.044	0.012	0.030	0.028	trace	0.020	0.018	0.016
10:35	0.025	0.047	0.021	0.048	0.033	trace	0.026	0.017	0.023
11:04	0.025	0.050	0.018	0.041	0.032	trace	0.021	0.021	trace
11:35	0.024	0.044	0.014	0.040	0.030	trace	0.017	0.017	trace
12:35	0.023	0.045	0.013	0.031	0.032		0.016	0.016	trace
2:10	0.023	0.041						0.013	trace
2:37	0.022	0.045	0.019	0.051	0.033		0.018	trace	trace
3:10	0.022	0.042	0.018	0.032	0.033		0.011	trace	trace
3:50	0.022	0.041	0.015	0.031	0.028		0.015		

Mid-range Hydrocarbons

Time 11:00 - 11:30

COMPOUND	PPB
acetylene	
ethylene	
ethane	
methyl acetylene	doublet
propadiene	2.9
propylene	
propane	
butadiene	Bad peak
butadiene	
butene-1, Isobutylene	9.1
cis-butene-2	trace
trans-butene-2	trace
trans-butene-2	trace
iso-butane	2.7
n-butane	16.7
pentene-1	trace
cis-pentene-2	trace
trans-pentene-2	trace
2-methylbutene-2	6.8
2-methylbutene-1	trace
iso-pentane	22.0
n-pentane	7.1
2-methylpentane	11.5

Table A16. CHROMATOGRAPHIC DATA: Run 152

Light Hydrocarbons

Time	Ethane	Ethylene	Propane	Acetylene	Isobutane	n-Butane	Propylene
9:00	0.017	0.057	0.002	0.069	0.005	0.014	0.040
9:30	0.017	0.076	0.002	0.094	0.008	0.019	0.016
10:00	0.016	0.086	0.002	0.101	0.010	0.016	0.023
10:30	0.017	0.090	0.002	0.106	trace	0.018	0.028
11:05	0.016	0.092	0.002	0.111	trace	0.018	0.022
11:30	0.016	0.091	0.003	0.113	trace	0.023	0.028
12:10	0.016	0.084	0.002	0.115	trace	0.018	0.014
12:40	0.016	0.080	0.002	0.114	0.005	0.022	0.016
1:15	0.016	0.077	0.002	0.114	trace	0.020	0.016
1:45	0.017	0.077	0.002	0.113	trace	0.023	0.016
2:25	0.016	0.077	0.002	0.111	trace	0.019	0.015
3:00	0.015	0.077	0.002	0.118	trace	0.020	0.016
3:30	0.016	0.075	0.002	0.112	trace	0.021	0.014

Aromatic Hydrocarbons

Time	Benzene	Toluene	Ethyl-benzene	m-and p-Xylene	Comp'd X	Isopropyl-benzene	o-Xylene	n-Propyl-benzene	3 and 4 Ethyl-toluene
10:30	0.020	0.040	0.018	0.041	0.031	trace	0.015	0.013	0.028
11:05	0.021	0.041	0.014	0.040	0.028	trace	0.017	0.022	trace
11:30	0.021	0.039	0.017	0.038	0.031		0.017	0.020	trace
12:10	0.020	0.038	0.017	0.036	0.034	trace	0.012	0.010	trace
12:40	0.020	0.037	0.013	0.029	0.028	trace	0.015	0.011	trace
1:15	0.021	0.036	0.013	0.030	0.029		0.010	0.013	trace
1:45	0.021	0.039	0.011	0.029	0.033		0.011	0.016	trace
2:25	0.020	0.037	0.015	0.032	0.029				
3:00	0.020	0.037	0.014	0.023	0.023	trace	0.016	0.009	trace
3:30	0.021	0.038	0.013	0.025	0.026		0.009	0.013	0.014

Table A17. CHROMATOGRAPHIC DATA: Run 153

Light Hydrocarbons

Time	Ethane	Ethylene	Propane	Acetylene	Isobutane	n-Butane	Propylene
10:00	0.034	0.092	0.010	0.120	0.006	0.030	0.021
10:30	0.025	0.093	0.007	0.119	0.005	0.033	0.024
11:00	0.023	0.094	0.005	0.125	0.007	0.026	0.025
11:30	0.022	0.091	0.005	0.122	0.005	0.024	0.019
12:30	0.020	0.075	0.004	0.115	0.010	0.023	0.013
1:00	0.020	0.070	0.004	0.113	0.006	0.021	0.020
1:30	0.019	0.067	0.004	0.110	0.006	0.023	0.016
2:00	0.019	0.064	0.004	0.114	0.004	0.020	0.008
2:30	0.019	0.065	0.004	0.113	0.005	0.021	0.011
3:00	0.019	0.061	0.004	0.112	trace	0.020	0.007

Aromatic Hydrocarbons

Time	Benzene	Toluene	Ethyl-benzene	m-and p-Xylene	Comp'd X	Isopropyl-benzene	o-Xylene	n-Propyl-benzene	3 and 4 Ethyl-toluene
10:00	0.023	0.042	0.011	0.037	0.027	trace	0.015	0.028	trace
10:30	0.023	0.042	0.010	0.034	0.030	trace	0.015	0.016	trace
11:00	0.021	0.044	0.010	0.035	0.027	trace	0.014	0.023	trace
11:30	0.021	0.041	0.009	0.035	0.030	trace	0.013	0.023	0.020
12:30	0.021	0.037	0.009	0.027	0.026	0.021	0.011	0.014	trace
1:00	0.019	0.034	0.010	0.020	0.030	0.007	0.012	0.014	trace
1:30	0.020	0.037	0.011	0.024	0.029	trace	0.010	0.014	trace
2:00	0.020	0.035	0.011	0.021	0.030	trace	0.008	0.022	trace
2:30	0.019	0.034	0.010	0.018	0.028	trace	0.011	0.012	trace
3:00	0.019	0.032	0.012	0.024	0.029		0.009	0.018	trace

Table A18. CHROMATOGRAPHIC DATA: Run 154

Light Hydrocarbons

Time	Ethane	Ethylene	Propane	Acetylene	Isobutane	-Butane	Propylene
9:45	0.039	0.267	0.005	0.314	0.010	0.060	0.074
10:15	0.041	0.288	0.006	0.342	0.011	0.070	0.082
10:45	0.045	0.307	0.005	0.353	0.008	0.077	0.088
11:20	0.043	0.308	0.005	0.364	0.010	0.067	0.079
12:00	0.044	0.297	0.005	0.371	0.009	0.068	0.067
12:30	0.046	0.287	0.005	0.374	0.011	0.069	0.055
1:00	0.044	0.278	0.005	0.379	0.011	0.071	0.055
1:30	0.045	0.271	0.005	0.380	0.012	0.074	0.048
2:05	0.046	0.263	0.006	0.384	0.012	0.070	0.043
2:35	0.048	0.258	0.006	0.382	0.011	0.070	0.037
3:05	0.046	0.246	0.006	0.371	0.009	0.067	0.038
3:35	0.048	0.235	0.006	0.371	0.011	0.064	0.039

Aromatic Hydrocarbons

Time	Benzene	Toluene	Ethyl-benzene	*m*-and *p*-Xylene	Isopropyl-benzene	*o*-Xylene	*n*-Propyl-benzene	3 and 4 Ethyl-toluene
9:45	0.062	0.116	0.035	0.101	trace	0.044	0.009	0.043
10:15	0.063	0.116	0.036	0.097	trace	0.044	0.015	0.050
10:45	0.068	0.134	0.039	0.111	trace	0.053	0.014	0.054
11:20	0.070	0.138	0.037	0.114	trace	0.052	0.014	0.064
12:00	0.071	0.136	0.040	0.109	0.004	0.045	0.014	0.053
12:30	0.071	0.135	0.040	0.105	0.011	0.055	0.010	0.056
1:00	0.072	0.135	0.043	0.101	trace	0.042	0.013	0.051
1:30	0.073	0.131	0.036	0.083	trace	0.046	0.015	0.059
2:05	0.072	0.131	0.037	0.088	0.004	0.037	0.014	0.051
2:35	0.072	0.130	0.037	0.086	trace	0.042	0.013	0.045
3:05	0.072	0.130	0.037	0.078	trace	0.039	0.014	0.046
3:35	0.072	0.127	0.035	0.081	trace	0.041	0.017	0.052

Table 19. CHROMATOGRAPHIC DATA: Run 155

Light Hydrocarbons

Time	Ethane	Ethylene	Propane	Acetylene	Isobutane	*n*-Butane	Propylene
10:00	0.026	0.170	0.005	0.196	0.007	0.037	0.048
10:30	0.026	0.170	0.005	0.195	0.006	0.043	0.041
11:00	0.025	0.171	0.005	0.191	0.008	0.045	0.051
11:30	0.025	0.166	0.004	0.196	0.008	0.039	0.042
12:15	0.025	0.151	0.004	0.190	0.007	0.039	0.031
1:15	0.026	0.142	0.003	0.197	0.006	0.037	0.026
1:55	0.024	0.140	0.004	0.195	0.008	0.041	0.023
2:25	0.026	0.138	0.003	0.203	0.006	0.036	0.021
3:00	0.026	0.137	0.004	0.208	0.006	0.036	0.020
3:30	0.026	0.137	0.004	0.207	0.004	0.038	0.022

Aromatic Hydrocarbons

Time	Benzene	Toluene	Ethyl-benzene	*m*-and *p*-Xylene	Isopropyl-benzene	*o*-Xylene	*n*-Propyl-benzene	3 and 4 Ethyl-toluene
10:00	0.041	0.078	0.018	0.063	trace	0.023	0.006	0.037
10:30	0.039	0.080	0.017	0.059	trace	0.029	0.006	0.036
11:00	0.039	0.079	0.022	0.065	trace	0.028	0.009	0.036
11:30	0.039	0.078	0.021	0.061	trace	0.028	0.005	0.035
12:15	0.036	0.072	0.018	0.050	trace	0.024	0.004	0.038
1:15	0.038	0.070	0.029	0.060	trace	0.026	0.007	0.016
1:55	0.040	0.073	0.016	0.049	trace	0.021	0.007	0.027
2:25	0.039	0.072	0.022	0.041	trace	0.020	0.008	0.019
3:00	0.039	0.071	0.019	0.041	trace	0.020	0.005	0.022
3:30	0.039	0.070	0.024	0.045	trace	0.025	trace	0.016

Table A20. CHROMATOGRAPHIC DATA: Run 156

Light Hydrocarbons

Time	Ethane	Ethylene	Propane	Acetylene	Isobutane	*n*-Butane	Propylene
9:40	0.046	0.251	0.008	0.286	0.010	0.059	0.067
10:15	0.046	0.298	0.006	0.347	0.010	0.072	0.083
10:45	0.046	0.313	0.006	0.367	0.012	0.074	0.082
11:15	0.046	0.322	0.005	0.367	0.012	0.072	0.070
11:45	0.046	0.307	0.004	0.375	0.014	0.074	0.070
12:22	0.047	0.284	0.005	0.389	0.014	0.074	0.049
12:50	0.046	0.265	0.005	0.388	0.011	0.068	0.030
1:20	0.048	0.247	0.005	0.391	0.013	0.077	0.025
1:50	0.045	0.226	0.004	0.384	0.011	0.070	0.019
2:25	0.043	0.208	0.004	0.375	0.008	0.067	0.018
3:00	0.044	0.189	0.003	0.357	0.010	0.067	0.018
3:30	0.043	0.177	0.004	0.347	0.008	0.066	0.012

Aromatic Hydrocarbons

Time	Benzene	Toluene	Ethyl-benzene	*m*-and *p*-Xylene	Isopropyl-benzene	*o*-Xylene	*n*-Propyl-benzene	3 and 4 Ethyl-toluene
10:15	0.069	0.136	0.036	0.102	0.005	0.046	0.010	0.054
10:45	0.071	0.144	0.035	0.124	trace	0.046	0.008	0.059
11:15	0.074	0.149	0.041	0.121	trace	0.050	0.010	0.059
11:45	0.072	0.143	0.042	0.116	trace	0.049	0.012	0.051
12:22	0.075	0.145	0.039	0.096	trace	0.050	0.010	0.048
12:50	0.073	0.134	0.033	0.086	trace	0.037	0.011	0.037
1:20	0.074	0.137	0.039	0.084	trace	0.038	0.017	0.046
1:50	0.073	0.133	0.035	0.075	trace	0.042	0.020	0.043
2:25	0.070	0.125	0.033	0.064	trace	0.034	0.010	0.032
3:00	0.068	0.121	0.032	0.067	trace	0.029	0.010	0.030
3:30	0.065	0.111	0.030	0.067	trace	0.026	0.007	0.026

Table A21. CHROMATOGRAPHIC DATA: Run 158

Light Hydrocarbons

Time	Ethane	Ethylene	Propane	Acetylene	Isobutane	*n*-Butane	Propylene
9:30	0.019	0.122	0.003	0.143	0.004	0.031	0.034
10:00	0.022	0.147	0.003	0.175	0.007	0.036	0.034
10:30	0.023	0.157	0.004	0.190	0.006	0.040	0.042
11:02	0.024	0.159	0.004	0.189	0.008	0.041	0.042
11:31	0.024	0.147	0.003	0.196	0.008	0.039	0.029
12:35	0.025	0.119	0.004	0.190	0.006	0.038	
1:00	0.025	0.112	0.004	0.194	0.008	0.040	0.012
1:30	0.025	0.106	0.004	0.193	0.006	0.036	0.012
2:00	0.025	0.096	0.003	0.186	0.006	0.039	0.009
2:30	0.024	0.089	0.004	0.174	0.004	0.038	0.010
3:00	0.024	0.086	0.003	0.177	0.006	0.038	trace
3:35	0.024	0.085	0.004	0.177	0.006	0.033	trace

Aromatic Hydrocarbons

Time	Benzene	Toluene	Ethyl-benzene	*m*-and *p*-Xylene	Isopropyl-benzene	*o*-Xylene	*n*-Propyl-benzene	3 and 4 Ethyl-toluene
10:00	0.037	0.076	0.018	0.058	none	0.023	0.009	0.025
10:30	0.038	0.080	0.022	0.064	none	0.024	0.007	0.034
11:02	0.038	0.081	0.020	0.059	trace	0.025	0.013	0.021
11:31	0.039	0.078	0.021	0.053	trace	0.026	0.007	0.032
12:35	0.040	0.070	0.020	0.044	trace	0.020	0.008	0.020
1:00	0.039	0.068	0.018	0.031	trace	0.019	0.009	0.019
1:30	0.038	0.068	0.017	0.038	trace	0.020	0.005	0.014
2:00	0.037	0.062	0.019	0.041	trace	0.016	0.004	0.022
2:30	0.037	0.060	0.014	0.033	trace	0.015	0.007	0.018
3:00	0.035	0.057	0.016	0.032	trace	0.015	0.008	0.027
3:35	0.035	0.058	0.016	0.026	trace	0.020	0.003	0.013

Table A22. CHROMATOGRAPHIC DATA: Run 160

Light Hydrocarbons

Time	Ethane	Ethylene	Propane	Acetylene	Isobutane	*n*-Butane	Propylene
9:30	0.021	0.014	0.005	0.018	none	0.008	none
10:00	0.018	0.011	0.005	0.015	0.004	0.008	none
10:30	0.017	0.010	0.004	0.013	trace	0.011	none
11:03	0.015	0.009	0.004	0.011	trace	0.014	none
11:35	0.013	0.009	0.003	0.010	trace	0.010	none
12:13	0.011	0.006	0.003	0.007	trace	0.008	none
12:43	0.010	0.005	0.003	0.007	0.004	0.008	none
1:13	0.009	0.004	0.003	0.006	trace	0.007	none
1:43	0.008	0.004	0.003	0.004	trace	0.006	none
2:13	0.008	0.004	0.002	0.005	trace	0.006	none
2:43	0.007	0.003	trace	0.005	trace	0.004	none
3:15	0.007	0.004	0.002	0.007	trace	0.006	none
3:30	0.007	0.003	0.002	0.004	trace	0.005	none

Aromatic Hydrocarbons

Small traces of benzene and toluene were present throughout the day (amounts less than 0.001 ppm). Ethylbenzene, *m*- and *p*-xylene, isopropylbenzene, *o*-xylene, *n*-propylbenzene, and 3- and 4-ethyltoluene were not detectable even in trace amounts.

Table A23. CHROMATOGRAPHIC DATA: Run 161

Light Hydrocarbons

Time	Ethane	Ethylene	Propane	Acetylene	Isobutane	*n*-Butane	Propylene
10:30	0.016	0.060	0.003	0.067	a	0.024	0.015
11:08	0.017	0.065	0.002	0.077	0.003	0.019	0.019
11:37	0.016	0.060	0.002	0.075	0.003	0.023	0.011
12:16	0.016	0.053	0.003	0.074	a	0.018	0.010
1:55	0.013	0.049	0.002	0.073	trace	0.023	0.019
2:28	0.012	0.048	0.002	0.071	a	0.016	trace
3:28	0.013	0.045	0.002	0.074	a	0.016	0.008

[a]Impossible to measure because of irregular base.

Aromatic Hydrocarbons

Time	Benzene	Toluene	Ethylbenzene	*m*-and *p*-Xylene	Isopropylbenzene	*o*-Xylene	*n*-Propylbenzene	3 and 4 Ethyltoluene
10:30	0.018	0.035	0.007	0.025	None	0.009	trace	0.011
11:08	0.017	0.037	0.011	0.033	None	0.010	trace	0.018
12:16	0.017	0.035	0.012	0.024	None	0.018	trace	0.011
1:55	0.016	0.033	0.013	0.024	None	0.009	trace	0.009
2:28	0.017	0.030	0.010	0.020	None	0.009	trace	trace
3:30	0.017	0.033	0.007	0.020	None	0.006	trace	0.011

Table A24. CHROMATOGRAPHIC DATA: Run 165

Light Hydrocarbons

Time	Ethane	Ethylene	Propane	Acetylene	Isobutane	-Butane	Propylene
9:30	0.014	0.071	0.002	0.049	0.004	0.032	0.020
10:00	0.015	0.082	0.003	0.059	0.005	0.032	0.030
11:00	0.014	0.089	0.002	0.060	0.003	0.033	0.034
11:30	0.015	0.088	0.002	0.064	0.004	0.032	0.029
12:36	0.015	0.074	0.002	0.056	0.004	0.030	0.017
1:07	0.014	0.066	0.002	0.056	0.006	0.029	0.021
1:48	0.014	0.063	0.002	0.050	trace	0.026	0.018
2:06	0.014	0.060	0.002	0.052	0.005	0.029	0.016
2:40	0.014	0.051	0.002	0.048	trace	0.024	trace
3:05	0.013	0.047	0.001	0.049	trace	0.023	trace
3:33	0.013	0.044	0.002	0.048	0.004	0.024	0.009
4:06	0.013	0.045	0.002	0.044	not recorded	not recorded	

Aromatic Hydrocarbons[a]

Time	Benzene	Toluene	Ethyl-benzene	*m*-and *p*-Xylene	Isopropyl-benzene	*o*-Xylene	-Propyl benzene	3 and 4 Ethyl-toluene
10.00	0.022	0.058	b	b	b			
11:00	0.023	0.061	0.022	0.054	trace	0.022	trace	0.019
11:30	0.023	0.059	0.019	0.051	trace	0.022	trace	0.022
12:36	0.020	0.054	0.021	0.042	trace	0.020	trace	0.024
1:07	0.021	0.050	0.023	0.041	trace	0.021	0.008	0.020
1:48	0.021	0.049	0.016	0.060 ?	trace	0.019	0.008	0.018
2:06	0.020	0.047	0.008	0.025	trace	0.017	trace	0.023
2:40	0.019	0.043	0.014	0.024	trace	0.018	trace	0.011
3:05	0.018	0.041	0.014	0.017	trace	0.012	trace	0.011
3:33	0.016	0.037	0.014	0.013	trace	0.013	trace	0.013
4:06	0.016	0.038	0.014	0.013	trace			

[a]1, 3, 5-trimethylbenzene and sec- and tert-butylbenzene were not recorded in the first and last runs; irregular baseline contact occurred in all other runs.
[b]bad baseline.

Table A25. CHROMTOGRAPHIC DATA: Run 167

Light Hydrocarbons

Time	Ethane	Ethylene	Propane	Acetylene	Isobutane	*n*-Butane	Propylene
9:41	0.030	0.123	0.006	0.153	trace	0.040	0.028
10:11	0.029	0.136	0.006	0.176	0.004	0.044	0.029
10:43	0.030	0.142	0.006	0.176	0.005	0.047	0.040
11:13	0.029	0.137	0.005	0.178	0.006	0.039	0.039
11:43	0.028	0.123	0.005	0.175	0.005	0.040	0.024
12:14	0.027	0.113	0.004	0.174	0.005	0.034	0.014
12:43	0.026	0.104	0.003	0.171	trace	0.038	trace
1:14	0.026	0.099	0.003	0.172	0.006	0.034	0.013
1:45	0.024	0.096	0.003	0.172	trace	0.036	0.017
2:17	0.024	0.091	0.003	0.166	trace	0.032	trace
2:47	0.024	0.090	0.003	0.166	0.004	0.030	trace
3:37	0.023	0.086	0.003	0.165	0.004	0.032	trace

Aromatic Hydrocarbons

Time	Benzene	Toluene	Ethyl-benzene	m-and p-Xylene	Isopropyl-benzene	o-Xylene	-Propyl-benzene	3 and 4 Ethyl-toluene	1, 3, 5-Tri-methyl-benzene	1, 2, 4-Tri-methyl-benzene
9:41	.0.039	0.102	0.022	0.060	trace	0.019	0.007	0.036	0.024	0.040
11:11	0.041	0.109	0.026	0.069	trace	0.034	0.008	0.031	0.023	0.057
10:43	0.044	0.106	0.026	0.076	trace	0.031	0.013	0.037	0.029	0.051
11:13	0.041	0.104	0.021	0.069	trace	0.032	0.011	0.050	trace	0.035
11:43	0.040	0.094	0.023	0.066	trace	0.023	0.012	0.028	trace	0.047
12:14	0.040	0.091	0.020	0.050	trace	0.030	0.009	0.027	trace	0.046
12:43	0.040	0.087	0.022	0.049	trace	0.020	0.011	0.035	trace	0.028
1:14	0.039	0.081	0.019	0.046	trace	0.022	0.011	0.031	trace	0.043
1:45	0.037	0.076	0.019	0.032	trace	0.019	0.020	0.036	trace	0.023
2:17	0.039	0.075	0.023	0.039	trace	0.030	0.017	0.026	trace	0.019
2:47	0.038	0.073	0.021	0.044	trace	0.022	0.010	0.027	trace	off scale
3:37	0.039	0.066	0.019	0.034	trace	0.017	0.013	0.036	trace	

☆ U. S. GOVERNMENT PRINTING OFFICE: 1968 O - 308-671