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Project Summary

Determination of C_2 to C_{12} Ambient Air Hydrocarbons in 39 U.S. Cities, from 1984 Through 1986

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Currently more than 60 urban areas are not in compliance with the National Ambient Air Quality Standard (NAAQS) for ozone. The use of photochemical models will be necessary to forecast nonmethane organic compound (NMOC) reductions needed to attain the NAAQS. These models require knowledge of the individual organic species in ambient air. To this end, speciated hydrocarbons were determined in over 800 ambient air samples obtained from 39 U.S. cities during 1984 through 1986. Whole-air samples were collected in electropolished, stainless steel spheres on week days from 6 a.m. to 9 a.m. during June through September each year. Two gas chromatographic (GC) procedures with cryogenic sample preconcentration were employed to separate and measure C_2 to C_{12} hydrocarbon species. One, a packed silica-gel column, measured C_2 hydrocarbon species, while the second, a 60m x 0.32mm i.d. fused silica capillary column coated with a 1μm thick liquid phase, separated C_2 to C_{12} species. Menu-driven software was developed to transfer GC data to a personal computer. The GC retention time identification table shows 314 uniquely numbered peaks, 97 of which are specifically named, 214 are identified by type (olefin, paraffin, or aromatic) and 3 are unknown. The 48 compounds seen in highest concentration consisted of 25 paraffins, 15 aromatics, 7 olefins, and acetylene. Sample concentrations of the 64 most abundant species are reported.

This Project Summary was developed by EPA's Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The ozone forming potential of an air mass is strongly dependent on the ratio of nonmethane organic compounds (NMOC) to nitrogen oxides (NO_x). Reduction of this ratio by reducing NMOC emissions is believed to be the most effective means for reducing ozone levels in urban areas. Local pollution control agencies use photochemical computer models to estimate the NMOC reductions needed to achieve acceptable ozone concentrations. One of these models, the Empirical Kinetic Modeling Approach (EKMA), requires the input of local ambient NMOC and NO_x concentrations in order to achieve precise results. Therefore, accurate measurements of ambient NMOC concentrations are clearly vital to the determination of NMOC reduction estimates.

Currently in the U.S., more than 60 urban areas are not in compliance with the NAAQS for ozone (*Federal Register*, 1983). In 1984, the EPA Office of Air Quality Planning and Standards (OAQPS) began an assistance program designed to determine NMOC in participating non-

attainment cities using the new PDFID method. As part of this project, the Atmospheric Research and Exposure Assessment Laboratory (AREAL) of the EPA analyzed over 800 samples from 39 cities from 1984 through 1986 to determine the speciated hydrocarbon composition.

Experimental Methods

Sampling

Integrated whole-air samples were collected during weekdays from 6 to 9 a.m. from June through September of 1984 through 1986. Samples were pumped into evacuated, electropolished stainless steel spheres, and air-freighted to Research Triangle Park, where a contractor gave them identification numbers and analyzed them by the PDFID method. The AREAL analyzed about 15 percent of the samples to determine the detailed hydrocarbon concentrations. Table 1 lists the cities sampled with the corresponding number of samples by year.

Analysis

Two GC analyses were employed to determine the presence of C_2 to C_{12} hydrocarbons, because one column could not provide adequate separation of the C_2 hydrocarbons (ethane, ethylene, acetylene). These latter compounds were separated on a packed silica-gel column. C_2 to C_{12} hydrocarbons were separated on a 60 m x 0.32 mm i.d. fused silica-capillary column coated with a 1 µm thick coating of a cross-linked, non-polar liquid phase (DB-1, J&W Scientific, Rancho Cordova, CA). Both analyses employed the cryogenic preconcentration of about 500 ml of air prior to injection and flame ionization detection. Hydrocarbons were identified by retention time and quantified by their FID response relative to a National Institute of Standards and Technology (NIST) propane-in-air standard reference material (SRM).

Data Reduction

The large amount of data--800 samples with 120 to 240 peaks per sample--necessitated the use of a computerized data management system. Menu-driven software was developed for a personal computer (PC) to provide sample tracking and management, data acquisition from the HP-5880A GC, and report generation functions. Data were transferred bidirectionally between the GC and a PC via RS-232 interfaces and cable at 1200 bits/s.

Results and Discussion

The limits of detection (LOD) and quantification (LOQ) were 0.04 and 0.12 ppb as carbon (ppbC), respectively. These values are a function of the sample amount injected onto the column; however, they remain constant for all GC peaks regardless of retention time. We used an 8.22 ppmC propane-in-air SRM from the NIST for calibration. A response factor was determined using response data from several SRM analyses each year at the beginning of the study. The same response factor was used throughout the study for all compounds. The overall variation for the 1984 through 1986 period was ±12 percent. The coefficient of variation (C.V.) of the initial analyses used to determine the 1985 response factor was 1.75 percent, while the C.V. over the entire 1985 study was 3.68 percent, demonstrating that the inter-day variation was a little more than twice the intra-day variation.

The quantitative precision was determined by calculating individual peak C.V. for the 12, 1984 duplicate determinations. Concentration variability decreased (i.e., precision increased) as concentration increased. The concentration variability was typically less than 10 percent for concentrations greater than 9 ppbC. The C.V. for concentrations between 2 and 9 ppbC ranged up to 30 percent and up to 95 percent for concentrations less than 2 ppbC. No relationship was observed between concentration precision and retention time, which indicated that quantitative precision was the same for all peaks.

Retention time identifications were determined by a combination of the following: (1) Analysis of known hydrocarbons prepared by syringe injection into Tedlar bags filled with air. (2) Reference to the chromatography literature retention times. (3) Comparison to retention time results of other investigators. (4) Pre-column strippers to remove olefins and olefins plus aromatics from ambient samples. This latter approach was useful for both the confirmation of identified peaks and the determination of unidentified peaks as paraffin, olefin, or aromatic.

The accuracy of the method depends upon the peaks being properly identified. The HP-5880A GC names peaks according to a user-created calibration table of retention times, unique calibration nun bers for each peak, and an optional pea name. A retention index system based c user-identified reference peaks correct for shifting retention times. A match obtained if the corrected retention tim falls within a calibration table retentio window that consists of each retentio time plus or minus user-specifie tolerance percentages. Our experienc was that this method for naming peak worked well. A GC calibration table wa prepared that identified 314 peaks by calibration number. The table consiste of 97 peaks specifically named, 21 identified by carbon number and bon type (olefin, paraffin, or aromatic), and labeled unknown.

Since retention times are used for ider tifying peaks, it follows that retention tim precision is important. The standard de viations for the 113 most frequently ob served peaks were determined an plotted versus the mean retention time Retention time standard deviation as function of the retention time was n constant. At a retention time of 11.5 mi the standard deviation rose abruptly fro 0.015 min to 0.11 min and then gradual declined to 0.03 min at a retention time 28 min. We believe this effect is due water condensation at -50°C.

The quality of stainless steel canister as storage containers for C_2 to C_1 hydrocarbons was tested. Six ambien samples were stored after initial analysi re-analyzed once after one week, and r analyzed three consecutive times at th end of a second week. The results in dicated that the entire range of C_2 to C hydrocarbons determined by the metho presented herein was unaffected b stainless steel canister storage for up two weeks.

A statistical summary of the concentra tion results for the 48 most abunda peaks for all samples from 1984 throug 1986 is shown in Table 2. The table lis compounds in descending order of abu dance with their corresponding concen tration range statistics, which are numb of samples (n), median concentration ppbC, minimum concentration (min twenty-fifth and seventy-fifth percenti concentrations (25% and 75%), an maximum concentration (max). The 4 compounds consisted of 25 paraffins, 1 aromatics, 7 olefins, and acetylene. Thre of the aromatics were not specifical identified. The report presents tables concentrations by site of the 64 mo abundant hydrocarbons.

Table 1. *Cities Where NMOC Samples Were Collected*

EPA Region	City	Number of Samples		
		1984	1985	1986
I	Boston, MA	–	8	–
	Portland, ME	–	13	–
II	New Haven, CT	–	–	16
	Bridgeport, CT	–	–	16
	Bronx, NY	–	–	16
	Manhattan, NY	–	–	12
	Trenton, NJ	–	–	16
III	Baltimore, MD	–	–	7
	Scranton, PA	9	–	–
	Philadelphia, PA*	7	24	14
	Washington, DC	10	11	11
	Richmond, VA	10	14	–
IV	Atlanta, GA	7	–	14
	Birmingham, AL	6	–	13
	Charlotte, NC	16	–	–
	Chattanooga, TN	12	–	–
	Memphis, TN	8	–	–
	Miami, FL	3	–	–
	West Palm Beach, FL	8	–	–
V	Akron, OH	10	–	–
	Cincinnati, OH	7	–	–
	Cleveland, OH	–	17	–
	Indianapolis, IN	10	–	–
	Chicago, IL*	–	–	22
VI	Beaumont, TX	9	19	13
	Clute, TX	10	17	–
	Dallas, TX	13	23	14
	El Paso, TX	8	17	9
	Fort Worth, TX	13	19	16
	Houston, TX*	–	22	26
	Texas City, TX	13	15	–
	West Orange, TX	16	16	–
	Baton Rouge, LA	–	16	–
	Lake Charles, LA	–	16	–
	Tulsa, OK	–		12
VII	Kansas City, MO	11	18	–
	St. Louis, MO	–	18	–
	Denver, CO*	–	–	25
	Salt Lake City, UT*	–	–	27

*City had two sites.

Table 2. *Concentration* Statistics for Most Abundant Compounds*

Compound	N	Median	Min.	25%	75%	Max.
Isopentane	832	45.3	1.4	26.2	71.6	3393
n-Butane	833	40.3	4.5	23.9	65.5	5448
Toluene	836	33.8	2.7	20.6	56.6	1299
Propane	835	23.5	1.8	12.2	45.2	393
Ethane	830	23.3	0.6	12.4	41.0	470
n-Pentane	834	22.0	1.0	12.5	36.0	1450
Ethylene	707	21.4	1.2	13.2	35.8	1001
m&p-Xylene	836	18.1	1.3	11.3	30.0	338
2-Methylpentane	836	14.9	1.2	8.5	23.5	647
Isobutane	835	14.8	1.4	8.4	28.6	1433
Acetylene	709	12.9	**	7.3	23.2	114
Benzene	835	12.6	1.0	7.9	19.9	273
n-Hexane, 2-Ethyl-1-Butene	836	11.0	0.8	6.2	18.4	601
3-Methylpentane	831	10.7	0.1	6.4	16.6	351
1,2,4-Trimethylbenzene	828	10.6	**	6.7	17.1	81
Propylene	835	7.7	0.4	4.3	14.3	455
2-Methylhexane	763	7.3	0.2	4.5	11.7	173
o-Xylene	831	7.2	0.9	4.7	11.6	79
2,2,4-Trimethylpentane	835	6.8	0.4	3.9	11.6	106
Methylcyclopentane	834	6.4	0.5	3.7	10.3	293
3-Methylhexane	828	5.9	0.3	3.5	9.7	168
2-Methylpropene, Butene-1	827	5.9	**	3.8	9.8	365
Ethylbenzene	836	5.9	0.7	3.6	9.8	159
m-Ethyltoluene	832	5.3	0.1	3.3	8.6	83
n-Heptane	831	4.7	0.1	2.8	8.2	233
2,3-Dimethylbutane	834	3.8	0.3	2.3	6.1	177
c-2-Pentene	750	3.6	**	1.9	6.0	339
1,2,3-Trimethylbenzene	758	3.4	0.1	1.6	5.7	1701
Methylcyclohexane	836	3.4	0.3	2.0	6.0	184
n-Decane	835	3.3	0.2	1.9	6.0	138
1,3,5-Trimethylbenzene	825	3.0	0.3	2.0	5.1	51
C11 Aromatic	773	3.0	0.2	1.8	4.7	71
t-2-Pentene	807	2.9	0.1	1.5	4.7	291
o-Ethyltoluene	836	2.9	0.2	1.9	4.6	54
p-Ethyltoluene	831	2.8	0.1	1.8	4.7	54
C10 Aromatic	832	2.8	0.2	1.8	4.5	235
n-Octane	799	2.6	0.2	1.6	4.6	163
2-Methyl-1-Butene	822	2.6	0.1	1.4	4.4	242
1,2-Dimethyl-3-Ethylbenzene	756	2.5	0.2	1.6	4.3	149
t-2-Butene	811	2.5	0.1	1.4	4.2	337
2,3,4-Trimethylpentane	833	2.5	0.1	1.5	4.4	78
2-Methylheptane	820	2.5	0.1	1.3	4.2	75
1,4-Diethylbenzene	821	2.4	0.1	1.5	4.0	33
3-Methylheptane	832	2.2	0.1	1.4	3.9	109
n-Nonane	821	2.2	0.2	1.3	4.2	89
Cyclohexane	817	2.2	0.2	1.1	4.8	409
2,4-Dimethylpentane	827	2.2	0.2	1.3	3.8	72
Cyclopentane	823	2.1	0.1	1.2	3.2	104

* All concentrations are parts-per-billion as carbon.
** Concentrations below the limit of quantification (0.1 ppbC).

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The complete report, entitled "Determination of C_2 to C_{12} Ambient Air Hydrocarbons in 39 U.S. Cities, from 1984 Through 1986," (Order No. PB 89-214 142/AS; Cost: $42.95, subject to change) will be available only from:

National Technical Information Service
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