

Hydrocarbon Gases Emitted from Vehicles on the Road. 1. A Qualitative Gas Chromatography/Mass Spectrometry Survey

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■ The gas-phase hydrocarbons $\geq C_5$ generated by motor vehicles in highway operation were surveyed in the Allegheny Mountain Tunnel of the Pennsylvania Turnpike in 1979. The samples were collected on Tenax GC polymer adsorbent and analyzed by glass-capillary gas chromatography/mass spectrometry. Approximately 400 vehicle-generated compounds were detected. Of these, over 300 were either completely or partially identified. In the various tunnel samples the same peaks are always present, with relative intensities varying according to the traffic composition. The compounds identified fall largely into homologous series of normal and branched alkanes, alkenes, and various alkyl series based on cyclopentane, cyclohexane, benzene, styrene, indan, naphthalene, and decalin. Compounds not associated with homologous series include indene, divinylbenzene, phenylacetylene, benzaldehyde, phenol, and a few halocarbons. Results from a preliminary experiment in 1977 at the Tuscarora Mountain Tunnel are also reported.

Introduction

The prospect of widespread diesel-automobile use, together with the discovery (1) of mutagenicity in bacterial bioassays of organic-solvent extracts of diesel-exhaust particulate matter, has stimulated a vigorous nationwide effort to evaluate the chemical properties and mutagenicity of exhaust particulate emissions, especially the emissions from diesels. Although mass emissions of gas-phase and particulate-phase organics from diesels are approximately comparable (2-8), the gases have attracted less attention in this recent research (9). Nevertheless a voluminous literature exists (2-8, 10-55) dealing with exhaust-gas chemical composition. The most comprehensive among these studies (21, 25, 32, 36, 37, 40, 42, 48, 53, 55) have identified between 43 and 93 compounds in the molecular weight range beginning at pentene. Only two of these studies (37, 48), however, have taken advantage of the analytical superiority of gas chromatography/mass spectrometry (GC/MS) over older techniques. The potential for misidentification when using gas chromatography alone and relying on retention time for identification, as in the case of most of the other studies, has been discussed by Dimitriadis et al. (53). Even the added assistance of mass spectral information may not always suffice for systems as complex as vehicle exhaust gas.

A number of other shortcomings in the published work can be cited. Though there are at least two field studies (56, 57) using GC/MS and in which approximately 100 vehicle exhaust species are said to have been identified, in neither case is it apparent that vehicles are actually the source. There have been only a few efforts (36, 48) to identify exhaust-gas species beyond C_{10} , whereas diesel exhaust-gas molecular weight distributions are said (5, 50) to extend much beyond C_{10} . The emphasis in identification efforts to date has been more on spark-ignition systems than on diesels. Many of the published studies made use of sampling methods (e.g., condensate traps) that cannot differentiate clearly between gas- and particulate-phase emissions. Finally, the focus on exhaust

emissions does not reflect the potential importance of other processes existing in the on-road situation—tire wear (58), crankcase blowby (50, 59), and carburetor and fuel-tank evaporative emissions (8, 50, 55).

The purpose of the present study is to identify the gases generated by motor vehicles in an on-road setting. The experiments were conducted at the Allegheny Mountain Tunnel of the Pennsylvania Turnpike in 1979 with Tenax GC polymer adsorbent trapping and computer-assisted glass-capillary GC/MS analysis. The trapping conditions dictated that compounds more volatile than pentene, approximately, were excluded from consideration.

The impetus for the study was an exploratory experiment conducted by Marano (60) in 1977 at the Tuscarora Mountain Tunnel in conjunction with an aerosol emission study (61). Marano collected gases on Tenax, found approximately 100 compounds by GC/MS, and identified some 50 of them. At that time the objective was to find a gas species unique to diesels and/or a species unique to gasoline-powered vehicles as an aid to quantitative resolution of the aerosol data. Though this objective was not realized, it became clear that a comprehensive study of gas emissions in such an on-road setting should be feasible.

The present study involved two experiments, viz., a preliminary effort in May/June 1979 to establish sampling and analysis techniques and a more comprehensive experiment in August/September 1979. These experiments were done in conjunction with studies of vehicle-aerosol properties (62-64).

The 1979 Allegheny work generally corroborates the Tuscarora results but expands the list of identified compounds approximately 6-fold. The Allegheny list (Table I), which is far more extensive than previously existed even in dynamometer studies, should provide a basis for further investigations. Quantitation and resolution into diesel and gasoline-powered vehicle contributions will be reported in a future paper.

Experimental Section

Sampling Site and General Approach. The Allegheny Tunnel sampling site and the underlying concept of experiments conducted there by this laboratory have already been described (58, 65, 66). The tunnel (Figure 1) is a four-lane dual tunnel 1850 m long, running approximately east-west (two eastbound lanes in one tunnel, two westbound lanes in the other) through Allegheny Mountain in southwestern Pennsylvania, at an elevation 707 m above sea level. The roadbed is essentially level and straight. Traffic conditions are representative of highway cruise, at speeds close to the posted 55 mile/h speed limit.

Strong diurnal and weekly traffic patterns (illustrated in Figures 2 and 3) permit sampling in periods dominated by diesels as well as periods dominated by gasoline-powered vehicles. The gasoline-powered vehicles are nearly all light-duty, predominantly passenger cars. The diesels are predominantly heavy-duty trucks, some weighing 50 tons or more (average, ~30 tons).

The tunnel-air sampling was conducted in the eastbound tunnel (Figure 1). Traffic composition eastbound was determined by visual count. Traffic volume eastbound was

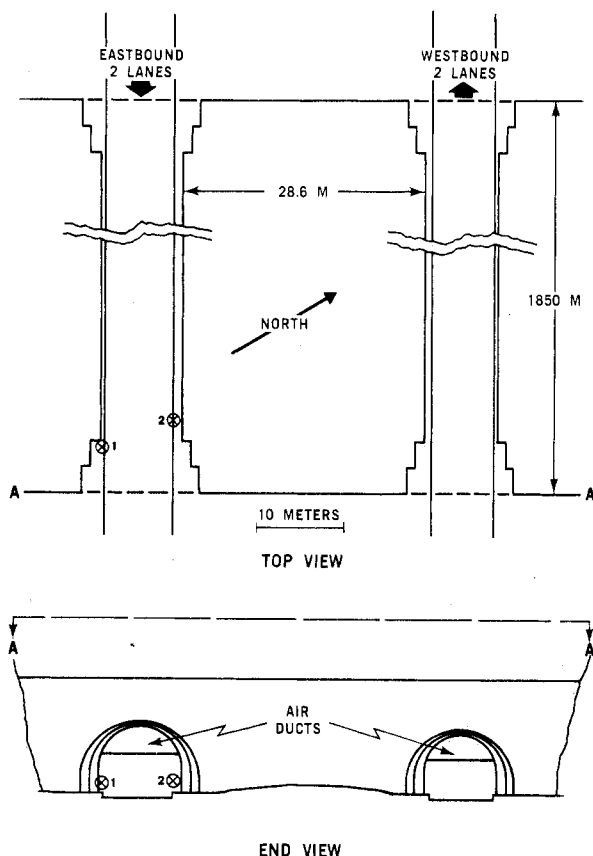


Figure 1. Allegheny Mountain Tunnel. Crosses indicate typical east portal sampling locations in eastbound tube (1 = right side, 2 = left side). Tenax cartridge samplers were on the left side between no. 2 and the portal. Overhead air ducts indicated in the end view are for intake ventilation air.

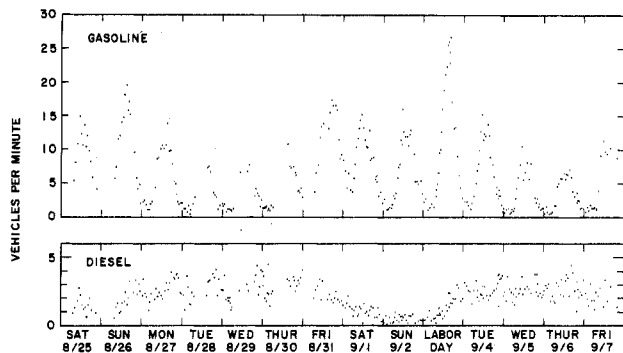


Figure 2. Visual counts of eastbound traffic through the Allegheny Mountain Tunnel during the August/September 1979 experiment: (top) gasoline-powered vehicles; (bottom) diesel vehicles.

determined by a road-tube axle counter in combination with the visual counting. The eastbound-vehicle total for a given gas-sampling run ranged from 25.4% to 93.9% gasoline powered in the two 1979 experiments.

Because of the piston effect of the traffic, reinforced by the prevailing wind, all of the air outflow from the eastbound tunnel is through the east or exit portal (at flow rates of the order of 20 000 m³/min, monitored by a Gill anemometer situated 47 m inside the east portal). Accordingly, the tunnel sampling station, located 4–4.6 m from the east portal beside the left-hand lane and 1.2–1.8 m above road level (Figure 1), registered the cumulative emissions for essentially the whole length of the tunnel. These emissions include not only the exhaust emissions but also the contributions from any other aspect of vehicle operation in the tunnel.

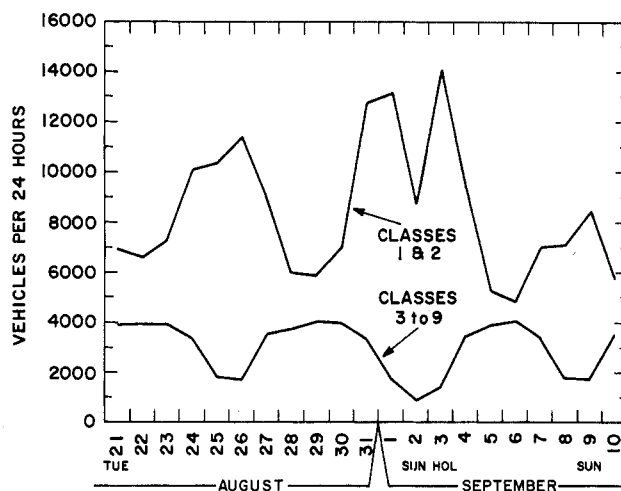


Figure 3. Eastbound 24-h traffic totals through the Allegheny Mountain Tunnel during the August/September 1979 experiment. Classes 1 and 2 encompass all vehicles up to 7.5 tons, chiefly passenger cars. Classes 3–9 encompass all vehicles heavier than 7.5 tons, chiefly diesel trucks (data courtesy of the Pennsylvania Turnpike Commission).

Approximately 40% of the air flow into the eastbound tunnel during these experiments entered through the west or entrance portal under the piston action of the traffic and the prevailing westerly wind. The rest of the inflow was provided by large intake fans on both sides of the mountain, which injected air through louvers in the tunnel ceiling (Figure 1). There were two stations for sampling the incoming ventilation air so that the contribution of vehicle emissions to the tunnel air could be ascertained by difference. One station was in the east intake fan room on the east side of the mountain, and the other was in the west intake fan room on the west side of the mountain.

Sampling Apparatus and Procedures. The gas-phase emissions were collected by adsorption on Tenax GC, a 2,6-diphenyl-*p*-phenylene oxide polymer. Specially designed (67) glass cartridges (10 mm o.d. × 114 mm long, 1-mm wall thickness) were packed with approximately 0.6 g of 60/80-mesh Tenax held in place by heat-treated silanized glass wool. Before being packed into the cartridges, the Tenax was subjected to a 24-h Soxhlet extraction with methanol (Burdick & Jackson "distilled in glass" UV grade) followed by vacuum drying at ~500 μmHg and 280 °C for 18–36 h to remove residual organics. Prior to sampling, each packed cartridge was thermally desorbed in a helium stream at 300 °C for 10 min and then sealed in 20 mm × 125 mm Teflon-capped culture tubes. After sampling, the cartridges were returned to the culture tubes and stored under dry ice in the dark. Cotton gloves were used in handling the cartridges.

The sampling units are described schematically in Figure 4. Each unit was designed to draw three parallel streams at 300 mL/min per stream (900 mL/min total flow per unit). Each stream was fitted with two tandem Tenax cartridges (hence, six cartridges per unit).

Sampling times were 185–240 min and were the same at all stations in a given run. Cartridge temperature during sample collection was allowed to follow the ambient temperature, which averaged 12.5 °C in May/June and 20.5 °C in August/September.

Samples were obtained in the tunnel in the August/September experiment with and without upstream filtering in order to evaluate the contribution of condensed-phase material captured in the sampling process. Filtering was accomplished by stretching a poly(tetrafluoroethylene) membrane, 0.2-μm nominal mean pore diameter, over the mouth (tapered end, ~4 mm i.d.) of the upstream car-

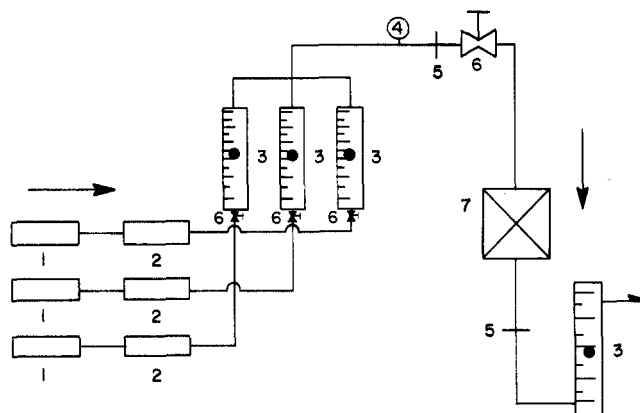


Figure 4. Flow schematic of Tenax GC air sampler. Key: (1) front Tenax cartridges, (2) backup Tenax cartridges, (3) flowmeters, (4) vacuum gauge, (5) filters (10- μ m pore diameter), (6) needle valves, (7) pump (Metal Bellows Corp. MB-41). Membrane filters (0.2- μ m pore size, PTFE) were sometimes placed on the entrances of the front Tenax cartridges.

tridge; the flow cross section through the filter was ~ 0.13 cm².

Tenax cartridges designated as controls were carried to the tunnel but not used for sampling. Some control cartridges were placed on the sampling devices. Others were left in the culture tubes used for storage and transport, with the culture tubes uncapped. Blank Tenax was also analyzed directly.

GC/MS Analysis. All samples were analyzed by GC/MS, with thermal desorption used to recover the sample from the Tenax cartridge. In addition, standards composed of *n*-alkanes, aromatic compounds, alkenes, and oxygenates were analyzed by GC/MS using liquid injection with chromatographic temperature programming identical with that used for the tunnel samples.

Prior to analysis, internal standards were added to each sample by injecting, under helium (99.999% purity) flow, 2 mL of helium containing 20.0 ppm of hexafluorobenzene (HFB) and 4.98 ppm of octafluorotoluene (OFT). The helium flow, maintained at 60 mL/min for 6 min at room temperature, served also to purge most of the CO₂ that had accumulated in the cartridge during dry-ice storage.

The main elements of the GC/MS instrumentation were (1) a Perkin-Elmer 900 gas chromatograph, fitted with a special injector port patterned after a design by Zlatkis et al. (67) to accommodate the 10-mm o.d. sample cartridges, together with a liquid-nitrogen-cooled capillary trap (type 200 nickel tubing 0.5 mm i.d. \times 50 cm long, gold plated inside) of a design described by Pellizzari et al. (68), (2) a VG Micromass MM-16 magnetic sector mass spectrometer, and (3) a Finnigan 2000 data system. The GC column was a 50 m long \times 0.25 mm i.d. silicone oil SF-96 borosilicate glass capillary (GC² Chromatography Ltd., U.K.).

The thermal desorption from the Tenax was conducted by back-flushing the cartridge at 300 °C in a 60 mL/min helium flow for 6 min into the liquid-nitrogen-cooled trap. Injection of the desorbed sample was accomplished by first switching a four-port valve to bring the trap in line with the column and then heating the trap with a heat gun. Efficient desorption was verified by repeating the desorption on a few of the cartridges.

The chromatographic column was held at -20 °C for 1 min and then programmed to 230 °C at a rate of 3 °C/min. Helium served as the carrier gas; the column head pressure was maintained at 24 psig to effect a linear velocity in the range of 30 cm/s. The column effluent was coupled directly to the mass spectrometer source by a heated (250 °C) transfer line of glass-lined tubing.

The mass spectrometer was exponentially downscanned from 280 to 13 amu in 0.7 s, with a total magnet cycle time of 1.0 s. The instrument was operated under standard electron-impact conditions.

Compound Identification. Compounds in the tunnel samples were identified to some degree by using techniques available through the Finnigan Incos data system (69). A modified Biller-Biemann (70) peak-finding routine was used in conjunction with spectral subtraction routines to obtain mass spectra of overlapping chromatographic peaks. Library-search algorithms matching the unknown against a 31 000-compound NBS/NIH/EPA mass spectral library (71) were used to identify compounds on the basis of probability of fit. In some cases, notably the C₇-C₁₆ alkanes, the mass fragmentation pattern of the pure compound on our GC/MS instrument was determined and used for confirmation.

However, in a very complex matrix, mass spectral analysis by itself is not sufficient for positive identification; additional criteria were needed. Aromatic and aliphatic compounds have been found to elute from the SF-96 column according to boiling point in a well-defined manner (72). It was therefore possible to specify for each class of compound a relationship between boiling point and retention time. This boiling-point criterion provided valuable supporting information for the identification of isomers exhibiting nonunique mass spectra. Advantage was taken of other thermodynamic properties inherent in gas chromatographic data to devise a new version of the classical relationship between carbon number and logarithm of retention time within a homologous series (73).

Not every compound found in the tunnel samples can be identified in the same detail. A conservative approach has been adopted in making the species assignments. A set of criteria involving boiling points, carbon-number elution profiles, and a good match (>90% probability of fit) with the mass spectral library is associated with each unique compound identification (e.g., 2,4-dimethylhexane).

Other compounds have been identified only to a limited degree (e.g., C₆ alkylbenzene, which has many possible isomers) because of insufficient boiling-point and mass spectral data.

Results

Comparison among the mass spectral reconstructed ion chromatograms (RIC's) shows that all peaks, or at least all of the readily observable ones, are always present in the tunnel samples regardless of the traffic composition. As expected, however, their relative intensities do vary with traffic composition (Figure 5). With an increase in the diesel-traffic contribution, the low-molecular-weight alkanes and the benzene- and naphthalene-series compounds all decrease relative to the heavier alkanes. The same trend was observed in the 1977 Tuscarora experiment (60).

Table I lists the vehicle-related compounds identified. For construction of this list, one data set was chosen for detailed study, namely, the samples collected in a 220-min run on Sunday September 2, 1979, beginning at 1310 EST. The eastbound traffic total during this period was 2721 vehicles, apportioned as 93.6% gasoline and 6.4% diesel. Some 400 peaks could be seen in the chromatogram, over 300 of which can be identified to some degree. A salient feature is the prevalence of homologous series, viz., *n*-alkanes (C₅-C₂₆), branched alkanes, alkylcyclopentanes, *n*-alkylcyclohexanes from methyl through *n*-heptadecyl, decalins from methyl through C₃ alkyl (though not all well enough specified to warrant listing in Table I), *n*-alkenes from 1-hexene through 1-nonene, alkyl benzenes from methyl through C₇ alkyl (again, not all listed), styrenes

Table I. Gases Detected in Allegheny Tunnel 1979 Experiments and Showing a Traffic Origin

scan no.	criteria ^a		scan no.	criteria ^a	
		Alkanes			
364	ACD	2-methylbutane	2240		branched C ₁₃ alkane
377	ACD	<i>n</i> -pentane	2252		branched C ₁₃ alkane
428	ACD	2-methylpentane	2296		branched C ₁₃ alkane
441	ACD	3-methylpentane	2307		branched C ₁₃ alkane
464	ACD	<i>n</i> -hexane	2311		branched C ₁₃ alkane
506	ACD	2,4-dimethylpentane	2326		branched C ₁₃ alkane
573	ACD	2,3-dimethylpentane	2339		branched C ₁₃ alkane
575	ACD	2-methylhexane	2354		branched C ₁₃ alkane
592	ACD	3-methylhexane	2367		branched C ₁₃ alkane
614		alkane ^b	2436	ABCD	<i>n</i> -tridecane ^h
650	ABCD	<i>n</i> -heptane	2461		branched C ₁₄ alkane
654		branched C ₈ alkane	2482		branched C ₁₄ alkane
726	AD	2,5-dimethylhexane	2508		branched C ₁₄ alkane
729	AD	2,4-dimethylhexane	2539		branched C ₁₄ alkane
762	A	2,3,4-trimethylpentane	2558		branched C ₁₄ alkane
762	A	2,3,3-trimethylpentane	2568		branched C ₁₄ alkane
803	AD	2,3-dimethylhexane	2575		branched C ₁₄ alkane
828	AD	2-methylheptane	2587		branched C ₁₄ alkane
848	AD	3-methylheptane	2601		branched C ₁₄ alkane
875	A	(2,2,5-?) trimethylhexane	2616		branched C ₁₄ alkane
930	ABCD	<i>n</i> -octane	2637		branched C ₁₄ alkane
966	AC	2,3,5-trimethylhexane	2694	ABCD	<i>n</i> -tetradecane ^h
994	ACD	2,4-dimethylheptane	2705		branched C ₁₅ alkane
1016	AC	2,6-dimethylheptane	2718		branched C ₁₅ alkane
1036	AC	2,5-dimethylheptane	2816		branched C ₁₅ alkane
1067		branched C ₉ or C ₁₀ alkane	2824		branched C ₁₅ alkane
1108	ACD	2,3-dimethylheptane	2836		branched C ₁₅ alkane
1120	AC	4-ethylheptane	2851		branched C ₁₅ alkane
1134	AC	4-methyloctane	2864		branched C ₁₅ alkane
1139	ACD	2-methyloctane	2892		branched C ₁₅ alkane
1162	ACD	3-methyloctane	2938	ABCD	<i>n</i> -pentadecane ^h
1170	C	3,3-diethylpentane	3046		branched C ₁₆ alkane
1180	A	(-, -, -)trimethylheptane	3052		branched C ₁₆ alkane
1232	A	(-, -, -)trimethylheptane	3060		branched C ₁₆ alkane
1250	ABCD	<i>n</i> -nonane	3072		branched C ₁₆ alkane
1284		branched C ₁₀ alkane	3086		branched C ₁₆ alkane
1294		branched C ₁₀ alkane	3092		branched C ₁₆ alkane
1321		branched C ₁₀ alkane	3100		branched C ₁₆ alkane
1329		branched C ₁₀ alkane	3152		branched C ₁₆ alkane
1345	A	(2,5-?) dimethyloctane	3170	ABCD	<i>n</i> -hexadecane ^h
1358	A	2,6-dimethyloctane	3270		branched C ₁₇ alkane
1377		branched C ₁₀ alkane	3285		branched C ₁₇ alkane
1487	ACD	3-methylnonane	3297		branched C ₁₇ alkane
1547		branched C ₁₀ alkane	3309		branched C ₁₇ alkane
1576	ABCD	<i>n</i> -decane ^h	3324		branched C ₁₇ alkane
1588		branched C ₁₁ alkane	3390	ACD	<i>n</i> -heptadecane ^h
1601		branched C ₁₁ alkane	3408		branched C ₁₈ alkane ^c
1618		branched C ₁₁ alkane	3483		branched C ₁₈ alkane ^c
1626		branched C ₁₁ alkane	3522		branched C ₁₈ alkane ^c
1644		branched C ₁₁ alkane	3597	CD	<i>n</i> -octadecane ^h
1695		branched C ₁₁ alkane	3798	CD	<i>n</i> -nonadecane ^{c,d,h}
1728		branched C ₁₁ alkane	3989	CD	<i>n</i> -eicosane ^{c,d}
1733		branched C ₁₁ alkane	4171	CD	<i>n</i> -heneicosane ^{c,d}
1770	D	methyldecane	4345	CD	<i>n</i> -docosane ^{c,d}
1803		branched C ₁₁ alkane	4514	CD	<i>n</i> -tricosane ^{c,d}
1878	ABCD	<i>n</i> -undecane ^h	4676	CD	<i>n</i> -tetracosane ^{c,d}
1920		branched C ₁₂ alkane	4834	CD	<i>n</i> -pentacosane ^{c,d}
1930		branched C ₁₂ alkane	4983	CD	<i>n</i> -hexacosane ^{c,d}
2007		branched C ₁₂ alkane			Cycloparaffins
2020		branched C ₁₂ alkane	492	ACD	cyclohexane
2027		branched C ₁₂ alkane	601	AC	1,3-dimethylcyclopentane
2038		branched C ₁₂ alkane	606	AC	1,2-dimethylcyclopentane
2048		branched C ₁₂ alkane	675	ACD	methylcyclohexane ^h
2061	D	methylundecane	708	A	ethylcyclopentane
2078		branched C ₁₂ alkane	734	A	(1,2,4-?) trimethylcyclopentane
2120		branched C ₁₂ alkane	753	A	(-, -, -)trimethylcyclopentane
2164	ABCD	<i>n</i> -dodecane ^h	836	A	1,2-dimethylcyclohexane
2194		branched C ₁₃ alkane	866	A	1-ethyl-3-methylcyclopentane
2205		branched C ₁₃ alkane			(cis or trans)
2214		branched C ₁₃ alkane	872	A	1-ethyl-3-methylcyclopentane
2223		branched C ₁₃ alkane			(trans or cis)

Table I (Continued)

scan no.	criteria ^a		scan no.	criteria ^a	
882	A	dimethylcyclohexane	1613	AC	indene ^h
905	A	dimethylcyclohexane	1624	AC	1-methyl-2-isopropylbenzene
958	A	ethylmethylcyclopentane	1663	AC	1,3-diethylbenzene
969	A	dimethylcyclohexane	1674	AC	1-methyl-3- <i>n</i> -propylbenzene
988	A	ethylcyclohexane	1685	ACD	<i>n</i> -butylbenzene
994	A	(<i>n</i> -?) propylcyclopentane	1685	AC	1-methyl-4- <i>n</i> -propylbenzene
1005	A	1,1,3-trimethylcyclohexane	1685	AC	1,2-diethylbenzene
1178		substituted cyclohexane ^e	1699	AC	1,3-dimethyl-5-ethylbenzene
1229		substituted cyclohexane ^e	1699	AC	1,4-diethylbenzene
1266	A	(isopropylcyclohexane) ^f	1713	AC	1-methyl-2- <i>n</i> -propylbenzene
1304	ACD	<i>n</i> -propylcyclohexane	1737		C ₃ alkylstyrene
1526		substituted cyclohexane ^e	1753	AC	1,4-dimethyl-2-ethylbenzene
1539	A	<i>tert</i> -butylcyclohexane	1766	ACD	1-methylindan
1550		substituted cyclohexane ^e	1773	AC	1,3-dimethyl-4-ethylbenzene
1597		substituted cyclohexane ^e	1782	AC	1,2-dimethyl-4-ethylbenzene
1633	ACD	<i>n</i> -butylcyclohexane	1782	AC	1,3-dimethyl-2-ethylbenzene
1672	AC	decalin	1785	AC	2-methylindan
1847	AC	methyldecalin	1799		C ₂ alkylstyrene
1891	AC	methyldecalin	1810		C ₂ alkylstyrene
1943	ACD	<i>n</i> -pentylcyclohexane	1820	AC	1,2-dimethyl-3-ethylbenzene
1990		substituted cyclohexane ^e	1823		C ₅ alkylbenzene
2109		substituted cyclohexane ^e	1830		C ₅ alkylbenzene
2151		substituted cyclohexane ^e	1838		C ₅ alkylbenzene
2238	ACD	<i>n</i> -hexylcyclohexane	1843		C ₅ alkylbenzene
2274		substituted cyclohexane ^e	1846	A	(1,3-?) diethenylbenzene
2416	A	(1,2,3-trimethylcyclohexane) ^f	1859	AC	1,2,4,5-tetramethylbenzene
2516	ACD	<i>n</i> -heptylcyclohexane	1863		(C ₂ alkylstyrene) ^f
2673	ACD	substituted cyclohexane ^e	1871	AC	1,2,3,5-tetramethylbenzene
2780	ACD	<i>n</i> -octylcyclohexane	1877		C ₂ alkylstyrene
3029	ACD	<i>n</i> -nonylcyclohexane	1898		(C ₂ alkylstyrene) ^f
3266	ACD	<i>n</i> -decylcyclohexane	1907	AC	5-methylindan
3489	ACD	<i>n</i> -undecylcyclohexane ^c	1925		C ₅ alkylbenzene
3705	CD	<i>n</i> -dodecylcyclohexane ^c	1932	AC	4-methylindan
3904	CD	<i>n</i> -tridecylcyclohexane ^c	1945		C ₅ alkylbenzene
4099	CD	<i>n</i> -tetradecylcyclohexane ^c	1946		C ₅ alkylbenzene
4281	CD	<i>n</i> -pentadecylcyclohexane ^c	1953	AC	1,2,3,4-tetramethylbenzene
4458	CD	<i>n</i> -hexadecylcyclohexane ^c	1956	ACD	tetrahydronaphthalene (Tetralin)
4627	CD	<i>n</i> -heptadecylcyclohexane ^c	1971		C ₅ alkylbenzene
Alkenes			1984		C ₅ alkylbenzene
450	ACD	1-hexene	2000		C ₅ alkylbenzene
471	A	2- or 3-hexene (cis or trans)	2010		C ₅ alkylbenzene
483	A	2-hexene (trans or cis)	2014		C ₅ alkylbenzene
621	ACD	1-heptene	2017	ACD	naphthalene ^h
661	A	2-heptene (cis or trans)	2032		C ₅ alkylbenzene
796	A	methylheptene	2053		C ₃ alkylstyrene or C ₂ alkylindan
891	ACD	1-octene	2063		C ₅ alkylbenzene
940	A	4-octene	2072		C ₅ alkylbenzene
1209	ACD	1-nonene	2095		C ₅ alkylbenzene
Aromatic Hydrocarbons			2098		C ₅ alkylbenzene
535	ACD	benzene	2122		C ₅ alkylbenzene
789	ACD	toluene ^h	2140		C ₅ alkylbenzene
1061	ACD	ethylbenzene ^h	2173		C ₆ alkylbenzene
1105	AC	<i>p</i> -xylene	2175		ethyl- or dimethylindan
1105	AC	<i>m</i> -xylene	2184		C ₅ alkylbenzene
1111	A	ethynylbenzene	2185		C ₆ alkylbenzene
1156	ACD	styrene	2208		C ₆ alkylbenzene
1168	AC	<i>o</i> -xylene	2212		C ₅ alkylbenzene
1264	AC	isopropylbenzene (cumene)	2219		ethyl- or dimethylindan
1358	ACD	<i>n</i> -propylbenzene	2234		C ₆ alkylbenzene
1398	AC	1-methyl-3-ethylbenzene	2256		ethyl- or dimethylindan
1398	AC	1-methyl-4-ethylbenzene	2258		C ₆ alkylbenzene
1420	AC	1,3,5-trimethylbenzene	2269		C ₆ alkylbenzene
1442	AC	1-methyl-2-ethylbenzene	2284		C ₆ alkylbenzene
1490	AC	1,2,4-trimethylbenzene	2297		ethyl- or dimethylindan
1506	ACD	methylstyrene	2303		C ₆ alkylbenzene
1533	AC	isobutylbenzene	2315		C ₆ alkylbenzene
1541	AC	<i>sec</i> -butylbenzene	2322	ACD	2-methylnaphthalene ^h
1570	AC	1,2,3-trimethylbenzene	2358	ACD	1-methylnaphthalene ^h
1585	AC	1-methyl-3-isopropylbenzene	2363	CD	dimethyltetrahydronaphthalene
1590	AC	1-methyl-4-isopropylbenzene	2451		C ₇ alkylbenzene
1593	ACD	indan	2471		C ₇ alkylbenzene
			2519		C ₇ alkylbenzene

Table I (Continued)

scan no.	criteria ^a	scan no.	criteria ^a
2543	C ₇ alkylbenzene	2998	C ₃ alkyl-naphthalene
2543	A (biphenyl) ^f	3240	C ₄ alkyl-naphthalene
2565	C ₆ alkylbenzene		Halocarbons
2580	C ₂ alkyl-naphthalene	2002	A trichlorobenzene ^d
2613	C ₂ alkyl-naphthalene	2089	A trichlorobenzene ^d
2643	C ₂ alkyl-naphthalene		Sulfur Compounds
2651	C ₂ alkyl-naphthalene		(ethylthiophene) ^f
2692	C ₂ alkyl-naphthalene	833	A
2725	C ₂ alkyl-naphthalene		Oxygenates
2860	C ₃ alkyl-naphthalene	340	AB (butanol) ^f
2890	C ₃ alkyl-naphthalene	1355	A benzaldehyde ^{d,h}
2924	C ₃ alkyl-naphthalene	g	A phenol
2955	C ₃ alkyl-naphthalene	3411	A methyltetradecanoate
2969	C ₃ alkyl-naphthalene		

^a Criteria used in establishing compound identification (see text): (A) mass fragmentation pattern has >90% probability of fit to NBS/NIH/EPA library spectrum; (B) matches mass fragmentation pattern of external standard; (C) meets boiling point vs. retention time criterion; (D) follows plot of carbon number vs. retention time in homologous series. ^b This species is in a region where the relationship between boiling point and retention time changes slope. Criterion C would be met by 3-ethylpentane or by 2,2-dimethylhexane. Criterion A is met by both 2,2-dimethylhexane and by 2,2,4-trimethylpentane (isooctane). ^c Ambiguity about how much is in the gas phase; see text. ^d Exists in the particulate phase, at least in part, in ambient air according to ref 74. ^e There is a homologous series of substituted cyclohexanes at scans 1178, 1229, 1526, 1550, 1597, 1990, 2109, 2151, 2274, 2673, and other scans—up to 40 species—that cannot be identified. They possess distinctive and similar mass spectra, consistent with methylethylcyclohexanes or methylbromocyclohexanes. ^f Tentative. ^g Broad band from scans 1700 to 2900, approximately. ^h This species was identified also in the 1977 Tuscarora Mountain Tunnel experiment (ref 60). In addition to the compounds designated by this footnote, the following were reported in ref 60: Two of the xylenes, one dimethylstyrene, one unidentified *n*-alkane, five unidentified branched alkanes >C₁₆, five unidentified C₃ alkylbenzenes, nine unidentified C₄ alkylbenzenes, seven unidentified C₅ alkylbenzenes, two unidentified C₆ alkylbenzenes, and two unidentified C₂ alkyl-naphthalenes. In addition, dimethyloctanol was reported in ref 60 but is not confirmed in the 1979 Allegheny work.

through C₄ alkyl (not all listed), indans through C₄ alkyl (not all listed), naphthalenes through C₄ alkyl.

To first approximation, the intake-air contribution to the organics in the tunnel was insignificant (Figure 6). The same was true in the 1977 Tuscarora experiment (60). Nevertheless, among the less abundant compounds there were a few that had essentially the same concentrations in the intake air as in the tunnel air and that therefore cannot be legitimately ascribed to vehicles on the basis of the present experiments. These are listed in Table II and are excluded from Table I even though vehicles probably do emit some of them (e.g., 2,3-dimethyloctane). All together some 100 compounds were detected, and 69 of them were identified in the intake samples in amounts exceeding their control-cartridge and blank Tenax amounts. Recirculation of tunnel air into the intake fan rooms is responsible for some of them; average fan-room concentrations of Pb and CO attributable to the Turnpike traffic emissions were ~6% of the tunnel concentrations.

There are a few compounds found in the control Tenax cartridges (Figure 6, bottom) in amounts comparable to the amounts found in the tunnel samples. These too are listed in Table II and are excluded from Table I.

Comparison between tunnel samples with and without prefilters showed no demonstrable effect of filtering on the alkanes through hexadecane (C₁₆H₃₄). However, anomalies become evident when front and backup cartridges from filtered and unfiltered units are compared with reference to alkanes in the region from nonadecane through hexacosane. Accordingly (and as noted in Table I), some ambiguity exists beyond octadecane as to how much of a given compound is actually in the gas phase. Molecular weight distributions in dichloromethane extracts of filter samples collected in these experiments (62) at the same time as the Tenax sampling show detectable particulate-phase organics beginning at C₁₄. Black and High (5) in dynamometer experiments also have reported difficulty in differentiating by filtration between gas and particulate organics in the

Table II. Gases Detected in Allegheny Tunnel 1979 Experiments but Associated Mainly with Tenax Control Cartridges^a or Intake-Fan-Room Air^b

scan no. ^c		
336	difluorodimethylsilane	a
354	acetic acid	a
370	trichlorofluoromethane (Freon-11)	a
380	fluorotrimethylsilane	a
380	(1,4?) pentadiene (or possibly furan)	a
396	1,1,2-trichloro-1,2,2-trifluoroethane	a
510	1,1,1-trichloroethane	a
898	tetrachloroethene	b
1045	hexamethylcyclotrisiloxane	a
1423	branched C _{≥10} alkane	b
1433	branched C _{≥10} alkane	b
1446	2,2,3,3-tetramethylhexane	b
1452	2,3-dimethyloctane	b
1461	2-methylnonane	b
1633	octamethylcyclotetrasiloxane	a
1751	branched C _{≥11} alkane	b
1763	branched C _{≥11} alkane	b
1772	branched C _{≥11} alkane	b
1788	branched C _{≥11} alkane	b

^a Many other compounds were observed. Listed here are only the ones whose amounts appear able to account for the amounts seen in the tunnel samples, judging from analysis of several control cartridges and blank Tenax samples. Levels among controls were extremely variable.

^b Approximately 100 compounds (not all identified) were observed in the intake-fan-room air. Listed here are only the ones whose amounts were sufficient to account for substantially all that is seen in the tunnel samples and whose amounts at the same time were in excess of the amounts in the controls. ^c Normalized to the scan numbers of Table I.

high-molecular-weight range, likewise without being able to learn the cause. Ambient-air data on more than 100 gas-phase compounds are said (74) to show significant

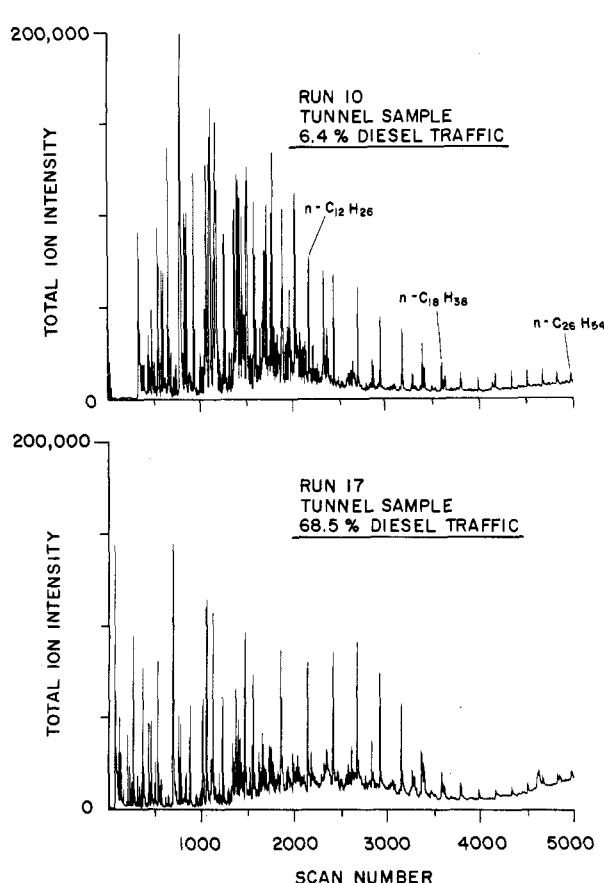


Figure 5. GC/MS total-ion-current (RIC) chromatograms of gas samples collected in the Allegheny Tunnel, eastbound tube, August/September 1979 experiment, east portal sampling station. All sample streams were unfiltered. All sampling rates were 300 mL/min. Run 10 (220 min) beginning 1310 EST Sunday September 2, 1979, traffic composition 6.41% diesel, traffic total 2721 vehicles. Run 17 (240 min) beginning 2140 Wednesday September 5, 1979, traffic composition 68.5% diesel, traffic total 1065 vehicles. Scan number is equal to retention time in seconds.

partitioning to the particulate phase beginning at C_{19} (5% in the particulate phase), perhaps consistent with the foregoing.

Discussion

The consistency between the Tuscarora results (60) and the present results is particularly noteworthy since there were substantial procedural differences between the Tuscarora experiments and the Allegheny experiments. Sample volumes at Tuscarora were approximately 40 times those at Allegheny. The Tuscarora Tenax samples were Soxhlet extracted with pentane and injected as the solution into the GC/MS, and a different type of GC column was used.

Approximately 200 gas-phase organic species represented in the literature as emanating from vehicles (including exhaust, blowby, and fuel evaporation) cannot be confirmed at Allegheny. These "missing" species are listed in Table III. This table should not be interpreted simply as a catalog of discrepancies between Allegheny and the literature, for four reasons. First, there were approximately 100 low-intensity peaks at Allegheny that remain unidentified and are excluded from Table I, and there are approximately 165 compounds in Table I that are only partially identified, among which are undoubtedly a great many of the compounds listed in Table III. Second, some of the lightest compounds in Table III would have been ineffectively retained on the Tenax adsorbent during sampling, because of their volatility. Third, there are many

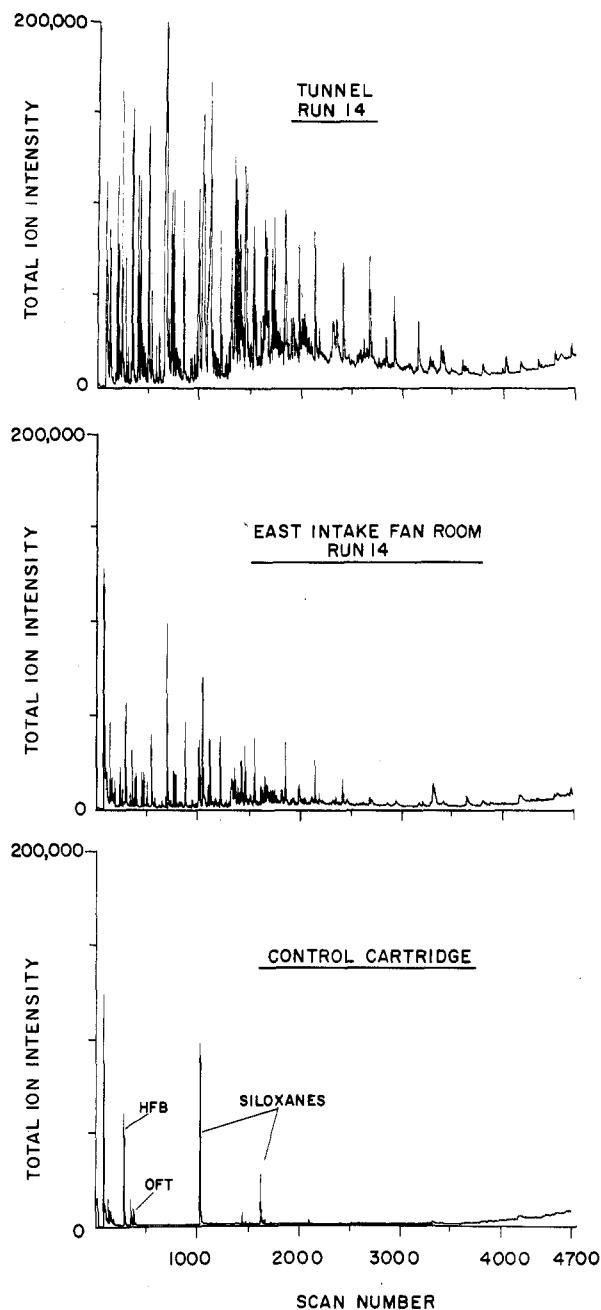


Figure 6. GC/MS RIC chromatograms of tunnel air sample, intake ventilation air sample, and control cartridge from the Allegheny Tunnel August/September 1979 experiment. Tunnel and east intake samples are 66-L samples collected at 300 mL/min for 220 min beginning 1125 EST Tuesday September 4, 1979 (Run 14). The tunnel sample is filtered. The sample volumes and all three intensity scales are the same; therefore, the intake and blank contributions to the tunnel sample are directly apparent.

classes of compounds for which the SF-96 GC column is unsuitable—for example, condensed-ring aromatic hydrocarbons (beyond fluorene) or highly polar compounds such as carboxylic acids, cresols, xlenols, or nitro compounds. It should be noted that polar species comprise nearly half of Table III. Fourth, cruise conditions (as would be represented in the Allegheny Tunnel) are said (11) to give especially low oxygenate emissions relative to cyclic driving such as was used in most cases in Table III.

In addition, however, Table III probably contains some misidentified compounds since there are some inconsistencies within the literature. In constructing this table no attempt was made to resolve these inconsistencies; all entries were duly recorded. Some of the species un-

Table III. Exhaust Gases (D = Diesel, G = Gasoline Engine) Reported in the Literature but Not Identified at Allegheny Tunnel 1979^a

	vehicle type	ref
2,2-dimethylbutane	G	21, 25, 27, 40, 48, 53, 55
2,3-dimethylbutane ^b	G	20, 21, 25, 34, 42, 53
2,2,3-trimethylbutane	G	25, 27
3,3-dimethylpentane	G	21, 25
2,2,3-trimethylpentane ^b	G	20, 25, 27, 53
2,2,4-trimethylpentane (isooctane) ^b	G	12, 13, 20, 21, 25, 31, 33, 34, 40, 42, 50, 53, 55
2,2-dimethylhexane	G	48
2,2,3-trimethylhexane	G	53
2,2,4-trimethylhexane ^b	G	53
2-methyl-3-ethylhexane	G	40
3,5-dimethylheptane	G	48, 53, 55
2,3,5-trimethylheptane	G	53
2,4,5-trimethylheptane	G	53
3,3,4-trimethylheptane	G	53
3,4,4-trimethylheptane	G	53
3,4,5-trimethylheptane	G	53
4-methylnonane	G	53
cyclopentane	G	12, 13, 21, 25, 27, 40, 53, 55
methylcyclopentane	G	10, 12, 13, 17, 20, 25, 34, 40, 48, 53
2-methyl-1-butene	G, D	2, 12-14, 17, 20, 21, 25, 27, 34, 53
2-methyl-2-butene	G, D	2, 12-14, 20, 21, 25, 27, 31, 34, 40, 42, 53
3-methyl-1-butene	G, D	2, 12, 20, 21, 25, 27, 40, 42, 53
2-methyl-1,3-butadiene	G	21, 25, 27, 34, 53
3-methyl-1,2-butadiene	G	48
1-pentene ^b	G, D	2, 12-14, 17, 21, 25, 27, 39, 42, 53, 55
2-pentene, cis	G, D	2, 12-14, 17, 21, 25, 27, 39, 42, 53, 55
2-pentene, trans	G, D	2, 14, 17, 21, 25, 27, 39, 42, 53, 55
1,3-pentadiene	G	21, 27
2,3-dimethyl-1-butene	G	21, 27, 53
2,3-dimethyl-2-butene	G	21, 27, 33, 53
3,3-dimethyl-1-butene	G	21, 27
2-ethyl-1-butene	G	25, 27, 53
2-methyl-1-pentene	G	27, 53
2-methyl-2-pentene	G	21, 25, 27, 42, 53
3-methyl-1-pentene	G	53
3-methyl-2-pentene, cis	G	27, 53
3-methyl-2-pentene, trans	G	21, 25, 27, 48, 53, 55
4-methyl-1-pentene	G, D	2, 10, 12, 13, 27, 53
and/or 3-methyl-1-pentene	G	25
4-methyl-2-pentene, cis	G	25, 27, 40, 53
4-methyl-2-pentene, trans	G	25, 27, 40
2- and 3-hexenes, cis and trans (two more than in Table I)	G	25, 27, 31, 53
2,3,3-trimethyl-1-butene	G	21, 27
3,4-dimethyl-1-pentene	G	25, 27
3,4-dimethyl-2-pentene, cis and trans	G	21, 27
4,4-dimethyl-2-pentene, cis	G	25
3-ethyl-1-pentene	G	25
3-ethyl-2-pentene	G	25, 27
2-methyl-1-hexene	G	27
3-methyl-1-hexene	G	40
4-methyl-1-hexene	G	25, 53
5-methyl-1-hexene	G	25, 27
5-methyl-2-hexene, cis and trans	G	21, 27
2-heptene, cis or trans (one more than in Table I) ^b	G	27
3-heptene, cis and trans	G	25, 27
2,4,4-trimethyl-1-pentene	G	25, 27, 55
2,4,4-trimethyl-2-pentene	G	20, 21, 25, 27
2,3-dimethyl-2-hexene	G	27, 53
2,5-dimethyl-2-hexene, trans	G	25
2,5-dimethyl-3-hexene, trans	G	25
2-ethyl-1-hexene	G	27
2-octene, cis	G	25
2-octene, trans	G	25, 27, 53
2,6-dimethyl-3-heptene	G	27
2-methyl-1-octene	G	48
1-decene	D	39
1-dodecene	G	25
tridecene	D	36
tetradecene	D	36
pentadecene	D	36

Table III (Continued)

	vehicle type	ref
hexadecene	D	36
heptadecene	D	36
(octadecene?)	D	36
nonadecene	D	36
eicosene	D	36
heneicosene	D	36
cyclopentadiene	G	37
cyclopentene	G	12, 13, 21, 25, 27, 53, 55
1-methylcyclopentene	G	53
3-methylcyclopentene ^b	G	53
cyclohexene	G, D	21, 25, 27, 39, 53
3-methylcyclohexene	G	21, 27
4-methylcyclohexene	G	20, 21, 25, 27
(1,7-octadiyne?)	D	32
allyltoluene	D	32
<i>tert</i> -butylbenzene	G	15, 25, 27, 40
C ₂ alkylcumene	D	32
methyltetralins (two isomers)	D	32
dimethyltetralins (two isomers more than in Table I)	D	32
trimethyltetralin	D	32
alkyltetralins (seven additional isomers)	D	32
alkylindenes (two isomers)	D	32
trimethylindans (four isomers)	D	32
acenaphthene	D	32
trimethylthiophene	D	32
dimethylbenzothiophenes (two isomers)	D	32
ethyl sulfide	G	44
methyl disulfide	G	44
diethylamine	G	49
<i>sec</i> -butanol	G	11
allyl alcohol	G	37
2-buten-1-ol	G	37
hexanol	D	36
heptanol	D	36
octanol	D	36
α -hydroxytoluene	G, D	36, 37
other alcohols	D	26
methoxybenzene	G, D	37, 51
<i>o</i> -cresol	G, D	6, 18, 28
<i>m</i> -cresol	G	18, 28
<i>p</i> -cresol	G, D	6, 7, 18, 28
2,3-xylene	G, D	6, 7, 18
2,4-xylene	G, D	6, 7, 18
2,5-xylene	G, D	6, 7, 18
3,4-xylene	G	18
3,5-xylene	G, D	6, 7, 18
hydroxybiphenyl	D	36
2-methoxyphenol	D	36
other phenols	D	26, 51
methacrolein	G	37
<i>n</i> -butanal	G, D	11, 19, 23, 29, 32, 34, 38, 41, 50
2-methylpropanal	G, D	3, 4, 7, 11, 19, 29, 41, 44, 45
2-butenal	G, D ^d	3, 4, 7, 11, 16, 23, 34, 37, 41, 44, 45
2-methyl-2-butenal	G	37
<i>n</i> -pentanal ^b	G, D	32, 34, 41
3-methylbutanal	G	11
<i>n</i> -hexanal	G, D ^d	3, 4, 7, 32, 41, 44, 45, 50
<i>n</i> -heptanal	D	32
<i>n</i> -octanal	D	32
cinnamaldehyde	D	26, 36
<i>n</i> -decanal	G	23
salicylaldehyde	G	37
tolualdehyde (<i>o</i> and <i>p</i> , possibly also <i>m</i>)	G, D	30, 32, 34, 37, 38, 50
4-methoxybenzoic aldehyde	D	36
ethylbenzaldehyde	G, D	32, 37
dimethylbenzaldehyde	D	32
naphthaldehydes	D	51
other aldehydes	D	26
furan ^e	G, D	11, 51
tetrahydrofuran	G	13
methylfuran	G	37
2-methyltetrahydrofuran	G	11

Table III (Continued)

	vehicle type	ref
2,2,4,4-tetramethyltetrahydrofuran	G	37
benzofuran	G, D	37, 51
furfural	D	51
2-butanone	G	11, 16, 19, 23, 29, 37, 44
3-buten-2-one	G	11, 37
(acetoin and methyl allyl ketone?)	D	32
3-methyl-2-butanone	G	11, 41, 53
methyl isobutyl ketone	G	41
methyl <i>sec</i> -butyl ketone	G	41
3-methyl-2-pentanone	G	41, 53
acetophenone	G, D	28, 32, 36, 37
methylacetophenone	D	32
dienones	D	51
indenones	D	51
indanones	D	51
methoxyindanones	D	51
hydroxyindanones	D	51
other ketones	D	26, 51
hydroxy cyclocarbonyls	D	51
propanoic acid	D	36
butanoic acid	D	36
2-butenic acid	D	36
pentanoic acid	D	36
benzoic acid	D	36
other carboxylic acids	D	26
esters	G	27
nitrophenols	D	26
other nitro compounds	D	26
benzonitrile	G	37

^a Excluded from the tabulation are hydrocarbons that would not have been collected by Tenax adsorbent at Allegheny (generally hydrocarbons lighter than C₈) and nonhydrocarbons below the same molecular weight cutoff (i.e., mol wt ≤ 60). Examples in the latter category were methyl sulfide, methyl- and dimethylamine, methanol, ethanol, propanol, acetaldehyde, propionaldehyde, acrolein, acetone, acetic acid, and nitromethane; see ref 2-4, 7, 11, 16, 19, 22, 23, 28, 29, 32, 34, 36-38, 41, 44, 45, 49, 50). ^b Found in fuel but not in Allegheny Tunnel; see text. ^c Also detected in crankcase or "blowby" emissions; see ref 50. ^d Also detected in diesel blowby; see ref 59. ^e May have been detected at Allegheny (scan 380, Table II).

doubtedly were only provisionally assigned but this is generally impossible to ascertain by studying the published papers. Finally, many of the species in Table III we were able to detect in a gasoline/diesel fuel mixture (as indicated by a footnote) and should have been able to detect at Allegheny had they been present in appreciable amounts.

Of the missing species (Table III), over one-fourth are alkenes, possibly reflecting artifacts (53) stemming from the subtractive column techniques employed in some of the published work. Among the missing alkanes, isooctane (2,2,4-trimethylpentane) deserves comment since it has been reported consistently in gasoline-engine exhaust. It is also one of the more abundant constituents of gasoline (34) and is, as expected, a substantial component of evaporative emissions (55). Two of the other three trimethylpentane isomers, both of them less abundant in gasoline than is isooctane (34), were detected at Allegheny whereas isooctane was not. As to the validity of the GC/MS analytical technique, isooctane was readily detected in the mixed-fuel sample. Ciccioli (75) reports poor retention of alkanes up to and including isooctane on Tenax adsorbent even with small sampling volumes (5 L of air, drawn through 0.28 g of Tenax), and it is true that breakthrough was considerable at Allegheny for alkanes C₈ and below. However, the fact remains that breakthrough cannot be expected to be more favored for isooctane than for these other alkanes—which were detected.

There is a remote chance that isooctane is the unidentified alkane at scan no. 614 in Table I. If so, the amount is extremely small. Pending further analysis which lies

beyond our present means, it remains a puzzle why isooctane was not detected at Allegheny (or, for that matter, at Tuscarora).

The only exhaust-gas aromatic hydrocarbon commonly reported in the literature and not identified at Allegheny was *tert*-butylbenzene. The rest of the missing species are predominantly polar compounds that would not have been observable under the GC conditions used in this study. Phenol is one of the few polar compounds detected. Its lack of resolution on the chromatographic column indicates, however, that oxygenates of higher molecular weight would not be chromatographable.

Artifact formation should be of concern whenever polymer adsorbent is used for sampling in the tunnel. In the Tuscarora Tunnel experiment (60), the Tenax degraded during sampling. A reddish-brown solid was produced, identified as 2,6-diphenyl-1,4-benzoquinone by infrared spectroscopy and solids-probe mass spectrometry (60). This same degradation product has been reported as forming at room temperature in the presence of nitric acid (76). It was not observed at Allegheny.

Conclusion

Table I serves as the summary statement of this paper. It is evident from Tables I and III together that an enormous number of gas-phase organics are emitted from motor vehicles. Dealing with such a complex mixture brings out the need to employ several identification criteria—retention time, mass fragmentation pattern, and thermodynamic properties—and to list them along with the assignments.

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NOTES

Floc Breakage during HIAC Light-Blocking Analysis

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■ Flocs of kaolinite and natural suspended sediment samples were measured by using an optical microscope before and after analysis with a HIAC light-blocking instrument. Extensive floc breakage was indicated for all samples after they passed through the HIAC sensor. This breakage was dominant in the upper two-thirds of the recommended size range for the HIAC sensing cell.

Introduction

Determining the size of flocs or aggregates is important in studying transportation processes in nature because flocs determine the hydrodynamic behavior of suspended solids. The existence of flocs in the environment has been observed by Berthois (1), Biddle and Miles (2), Edzwald (3), Edzwald and O'Melia (4), Gibbs (5), Kranck (6), Krone (7), Schubel and Kana (8), Sheldon (9), and Zabawa (10).

Because flocs and aggregates are often fragile, utmost care must be taken during the measurement process. While, intuitively, many scientists think flocs are fragile, there are few quantitative studies that test what procedures do and do not break flocs during sampling and analysis. Using any type of pump for sampling was shown by Gibbs (11) to break flocs. Pipetting samples is also a cause of floc disruption (12). Another common sampling technique in oceanography, using Niskin bottles, was shown by Gibbs and Konwar (13) to break flocs. The size analysis of flocs by using the Coulter counter had extensive error due to breakage of flocs (14).

The purpose of the present study is to evaluate the effectiveness of the popular HIAC light-blocking instrument in measuring flocculated material for size.

Procedures

Flocs of known size were passed through the HIAC instrument and then measured again. The materials utilized

to produce the flocs for this study were coating-free, untreated kaolinite (API standard no. 3), size-fractionated to obtain the 2- to 4- μ m material, and an untreated sample of suspended sediment from the Amazon River obtained from the Atlantic Ocean area off the mouth of the Amazon River. Because this 2-6- μ m size fraction from the Amazon River was not treated, its natural organic and iron coatings were retained. This natural sample was composed of 40% kaolinite, 40% illite, and 20% montmorillonite. The flocs were produced in a reaction chamber using stirring blades similar to those utilized in the work of Edzwald (3) and Eppler et al. (15). The turbulence produced in the reaction chamber (a shear rate, G , of 10 s^{-1}) would represent above-average turbulence, that is, greater turbulence than found in most parts of estuaries and oceans. Sediment concentration was 50 mg/L and salinity was 2‰ for all experiments. The flocs were removed from the flocculation chamber by using a pipette having a 3-mm opening, and the sample was carefully diluted to 1/100 with filtered 2‰ salinity solution. This diluted sample was analyzed by using a HIAC instrument. Samples from before and after HIAC analyses were also taken and placed on a special slide having a well for sizing and counting using an optical microscope at 100-450 magnification. The HIAC light-blocking sensor, CMH-60, is recommended by the manufacturer for use with particles having diameters up to 60 μ m, so the flocs were produced to a maximum diameter of 55 μ m. The HIAC instrument was set with its 12 channels ranging from 1.4- to 60- μ m particle diameters. Immediately behind the sensing cell of the HIAC instrument a special large-bore outlet was placed, through which the samples were obtained for microscopic analysis. The particle-size distribution in the beaker from which the HIAC instrument draws its sample was stirred gently to maintain uniform distribution. When monitored, the sample was shown to have no effect on floc-size distribu-