CHEMICAL CHARACTERIZATION OF AUTOMOBILE FUELS AND EXHAUST EMISSIONS AND EXAMINATION OF THE COMPOSITIONAL CHANGES IN EXHAUST INTRODUCED BY FUEL AND ENGINE DESIGN VARIATIONS

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The hydrocarbons in three modern gasolines and in the exhaust products produced by burning one of the fuels in a laboratory engine were analyzed using gas chromatography - mass spectroscopy techniques. The gasolines were found to be mixtures of straight-chain, branched chain and cyclic aliphatic hydrocarbons, mono- and bi-cyclic aromatics and, at lower concentrations, aliphatic olefins. The carbon number distribution is predominantly between C₃ and C₁₂. High concentrations of aromatic hydrocarbons were found to be present in all of the gasolines examined. Results of preliminary analysis of the exhaust gases are presented and discussed.
Terminal Report of Project Clean Air #133

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MARCH 1973
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The statements and conclusions in this report are those of the contractor and not necessarily those of the California Air Resources Board. The mention of commercial products, their source or their use in connection with material reported herein is not to be construed as either an actual or implied endorsement of such products.
SUMMARY

In this report an account is given of the chemical characterization of gasolines and exhaust. It is apparent that there are major quantitave differences in gasolines. Emphasis has been made that gas chromatography provides excellent separation of components present in complex mixtures but that high resolution gas chromatography must be coupled with mass spectrometry before structural assignments can be made unambiguously.

Several approaches were used to analyse exhaust gases. The method which was technically most straightforward involved bubbling exhaust through cyclohexane. Material so obtained was rich in the higher molecular weight (almost exclusively aromatic) components of gasoline exhaust. This portion of exhaust contains polycyclic aromatics which are of significant toxicological importance. The cyclohexane trapping procedure seems to offer great potential for obtaining large samples sufficient for chemical characterization and toxicity studies.
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Introduction

A complete knowledge of the chemical structure of the individual components of gasolines and automobile-generated exhaust is essential to the solution of today's air pollution problems. It would appear that far too much research is now being carried out using vague or incorrect assumptions on the composition of both gasoline and exhaust. We feel that the only satisfactory approach to the analysis of these extremely complicated mixtures requires rigorous application of combination gas chromatography-mass spectrometry (GC-MS) using high efficiency capillary columns (1 - 4). Over the past 1½ years we have used this technique to make analytical comparisons of gasolines and their exhaust products from an internal combustion engine.

During our analyses of gasolines we have been very surprised at the extremely high concentration of aromatic hydrocarbons which are present. Removal of lead from gasoline would appear to be beneficial to health. However, a severely detrimental effect on air quality could result when such removal is accompanied by an increase in aromatic content. Such an approach is apparently being used to retain the original octane rating in modern gasolines following reduction or removal of lead. Many of the aromatic compounds in gasoline, if not in themselves toxic or carcinogenic, might readily be converted during combustion to harmful polycyclic aromatic compounds (5).

Control of automobile exhaust emissions has been aimed at reducing levels of compounds which can be easily measured (e.g., total hydrocarbons, carbon monoxide and nitrogen oxides) (6, 7).
devices which alter the levels of such compounds are currently being fitted to automobiles. However, the development of such devices and their mandatory installation appear to have outstripped research on detailed analysis of the alteration on exhaust composition that they bring about. For example, a reduction of total hydrocarbons would not be beneficial to health or to air quality if it were accompanied by production of a greater proportion of more highly reactive or toxic hydrocarbons at lower concentrations.

Many analyses of gasoline (8, 9) and exhaust (10 - 12) recorded in the literature rely on "identification" by gas chromatography (GC). Unfortunately, while GC affords excellent separations, even tentative identification of compounds by this method alone is ambiguous and should always be used with extreme caution. On the other hand, when the excellent resolution of GC is combined with mass spectrometric identification of separated compounds, one then has an analytical system with unique capabilities. The fundamental advantage of the dynamic coupling of gas chromatography with mass spectrometry is that the effluent can be monitored continuously, and mass spectra recorded in relation to defined retention times. Additionally, such a combination-instrument can provide resolution and structural information on microgram and even nanogram samples (4), making it a very powerful tool for projects and applications such as the one described here.

The chromatographic liquid phases used in this project were evaluated using gasoline. The gasolines we have studied have been found to be mixtures of aliphatic hydrocarbons (straight-chain, branched-chain and cyclic), mono- and bi-cyclic aromatics and, at lower concentrations, aliphatic olefins. The carbon distribution is between C_3 and C_12.
and for each carbon number a certain number of isomeric compounds exist. If one considers the saturated aliphatic hydrocarbons of the molecular formula \( \text{C}_6\text{H}_{14} \) (the hexanes are major components of gasolines), five isomers are possible as shown in Table 1.

<table>
<thead>
<tr>
<th>Hexanes ( \text{C}<em>6\text{H}</em>{14} )</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 )</td>
<td>n-hexane</td>
</tr>
<tr>
<td>( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 )</td>
<td>2-methylpentane</td>
</tr>
<tr>
<td>( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 )</td>
<td>3-methylpentane</td>
</tr>
<tr>
<td>( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 )</td>
<td>2,2-dimethylbutane</td>
</tr>
<tr>
<td>( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 )</td>
<td>2,3-dimethylbutane</td>
</tr>
</tbody>
</table>

\( \text{C}_7\text{H}_{16} \) Heptanes - 9 isomers
\( \text{C}_8\text{H}_{18} \) Octanes - 18 isomers

Also shown in Table I are the number of possible isomers with the general formula \( \text{C}_7\text{H}_{16} \) and \( \text{C}_8\text{H}_{18} \). Introduction of one degree of unsaturation (double bond or ring) into a \( \text{C}_6 \) molecule results in
19 compounds, while one olefinic bond in a C₆-acyclic molecule furnishes 36 isomers. A parallel situation exists in the case of aromatic compounds. There are four isomers with the general formula PhC₅H₅, namely ethylbenzene, o, m and p xylene, eight compounds of the formula PhC₅H₅, and twenty-two PhC₄H₉ compounds. Thus, in both the aliphatic and aromatic series, increasing molecular weight results in a dramatic increase in the number of possible isomers and an increasingly difficult separation problem. Since compounds in gasolines lie in the C₃ to C₁₂ range, it is imperative to use high efficiency capillary GC columns so that these isomers can be separated.

Many of the silicone liquid phases commonly used in gas chromatography, while performing well in the range of 50 - 250°C, become highly viscous and/or semi-solid at ambient and sub-ambient temperatures. It was found that efficient separation of the lower molecular weight components of gasoline required use of a squalane (an isoprenoid hydrocarbon of formula C₃₀H₆₂) column.

Although squalane has an unparalleled ability to function at low temperatures, columns prepared using it as a liquid phase have an upper temperature limit of 90°C. Unfortunately for convenient analysis times an upper limit of 90°C is too restrictive for compounds higher in molecular weight than heptane or toluene. Accordingly a different GC column, OV-101, had to be used for the higher molecular weight compounds. This silicone liquid phase, although unable to match the separating power of squalane for low molecular weight compounds,

* Ph = phenyl : C₆H₅
can be programmed to 250°C without serious deterioration and gives excellent separation of C₁₀ to C₃₀ hydrocarbons.

There is an easily recognizable overlap of the chromatograms produced from these two liquid phases (viz., squalane and OV-101) when they are used in sequence for analysis of the same gasoline. Toluene, the most abundant single component in all of the gasolines analyzed, has proved to be an excellent marker compound in the overlap area.

Once separated by GC the individual hydrocarbons are subjected to mass spectrometry. While differentiation between a hexane and a heptane, for example, is readily achieved it is not always possible to distinguish one isomer from another since their fragmentation patterns are frequently similar. However, in this project where the GC retention time of particular isomers was known from reference compounds, structural assignments could be made without ambiguity. To date we have retention data on C₃, C₄, C₅, C₆, and C₇ acyclic alkanes, C₄, C₅ and C₆ olefins, as well as cyclopentane, cyclohexane, methylcyclopentane, the five dimethylcyclopentanes and toluene.

EXPERIMENTAL

A. Chromatography

High efficiency capillary columns are prepared by coating a liquid phase on the internal wall of a long tube (100 ft to 1 mile) of narrow bore (0.005 to 0.02 in). The columns are generally constructed from copper, glass, stainless steel or nylon. Although copper tubing has been used by many investigators, oxidation at high temperatures
limits its usefulness. Stainless steel tubing was chosen for the present investigation because of its high mechanical and thermal stability, features not enjoyed by glass and nylon respectively. The columns used were 600 ft x 0.01 in. coated with squalane and 100 ft. x 0.01 in. coated with OV-101.

(i) Preparation of columns for coating. Uniform bore stainless steel tubing (0.01 in. internal diameter) was obtained commercially (Hondy and Harman Tube Co., P.O. Box 549, Norristown, Penn., 19404). Uniform coating, which is essential in the preparation of high efficiency capillary columns, can only be obtained if the column has been thoroughly cleaned internally to free it from the extrusion lubricants used in the course of tube manufacture.

Cleaning solutions were passed, under pressure from a stainless steel reservoir, through 100 ft. lengths of the tubing. For squalane columns the following cleaning sequence was used: 10 ml each of: 50% aqueous nitric acid, distilled water, aqueous ammonium hydroxide, distilled water, acetone and heptane. Columns for use with OV-101 liquid phase were cleaned with 10 ml of toluene:chloroform (1:1 v/v).

(ii) Coating of capillary columns. Squalane (Robeco Chemicals, Inc., 51 Madison Avenue, New York, N.Y. 10010) in heptane solution (10% w/v) was forced through the tubing using 5-10 psi nitrogen pressure. The gas pressure was applied to the column overnight, this usually being sufficient to force the liquid through the column and to evaporate the remaining solvent.

Silicone liquid phases are extremely difficult to coat uniformly on stainless steel. However, treatment of the metal surface with a long-chain quaternary ammonium compound or a compound such as benzyl-
triphenylphosphonium chloride results in the formation of an organic monolayer to which the silicone liquid phase adheres.

Benzyltriphenylphosphonium chloride (0.02g; Aldrich Chemical Co., Milwaukee, Wisconsin) and OV-101 (0.5g; Pierce Chemical Co., Rockford, Illinois) were dissolved in 6 ml of xylene:chloroform (1:1 v/v). The solution was allowed to stand for 15 min. and filtered through a plug of glass wool to remove any solid material. 4.5 ml of the filtrate then being used to coat the tubing by transfer from a stainless steel reservoir operating under a head pressure of 20 psi. The solution eluting from the column was collected in a measuring cylinder. Coating normally took 1 - 2 hours and afterwards nitrogen was allowed to flow through the column at the same pressure for 12 hours to evaporate the residual solvent.

(iii) Column conditioning. Squalane columns were conditioned by programming the temperature from ambient to 90°C at 0.5°C/min. using a flow rate of 2 ml/min carrier gas (set at ambient). The maximum temperature was maintained for two days before the column was ready for use.

Using a carrier gas flow rate of 2 ml/min (set at ambient temperature) the following conditioning sequence was used for OV-101 columns:

- Ambient to 100°C (at 0.5°C/min), maintained at 100°C for 12 hours
- 100°C - 200°C (at 0.5°C/min), maintained at 200°C for 12 hours
- 200°C - 270°C (at 0.5°C/min), maintained at 270°C for 4 hours
(iv) Column resolution.

Figure 1.

![Diagram of column resolution](image)

The efficiency of columns was calculated using the following equation:

\[ n = 16 \left( \frac{R_t}{W} \right)^2 \]

where \( n \) is the total number of theoretical plates, \( R_t \) is the retention time of the peak and \( W \) is the width of the base of the peak measured in the same units as \( R_t \). (See Figure 1.)

The squalane column used in the present work was 600 ft. x 0.01 in. with an efficiency of 120,000 theoretical plates optimized and determined using n-pentane at 30°C with a helium flow rate of 0.25 ml/min. The column consisted of four 100 ft. x 0.01 in. and one 200 ft. x 0.01 in. lengths of tubing (joined by minimum dead-volume connectors) each of which was chosen for its optimized total number of theoretical plates.

(v) Gas chromatography instrumentation. Analytical GC was carried out on a Varian Aerograph 2740 gas chromatograph specifically purchased for the project. This instrument, designed for dual column, dual flame ionization detector operation, was not employed in a dual
column mode in this investigation. Instead, one injector was modified to reduce its internal volume rendering it compatible with high efficiency capillary columns while a variable injection splitter was added to the other injector to allow transfer of sub-microliter quantities of gasoline to capillary columns. Additionally capillary lines were installed between the column outlets and the detectors to reduce dead-volume and preserve column efficiency. A six-port gas sampling valve was installed to permit injection of measured amounts of exhaust gas. To prevent leaks in GC-MS operation Cajon ultra-high vacuum couplings (Cajon Company, Solon, Ohio 44139, Model No. IVCR with 1/16 in. tubes) were attached to the ends of all capillary columns: in this respect these couplings were found to be far superior to the more conventional Swagelock fittings.

(vi) Sub-ambient operation of gas chromatograph. At a late stage in the course of the project it became apparent that sub-ambient GC operation was absolutely essential for the separation of the low molecular weight components of gasoline. Commercial attachments utilizing liquid nitrogen are available but insufficient time and lack of funds precluded the installation of such a device on our chromatograph. Placement of dry ice in the oven of the chromatograph (making sure that the pieces did not touch the column causing "cold spots") enabled programming to be conducted in a reasonably controlled manner from 0°C. However, linear programming from sub-zero temperatures was not possible without installation of a new pyrometer and alteration of the electronics of the temperature programming device. As a result reproducibility of sub-zero operation was difficult if not impossible to achieve.
B. Gas Chromatography-Mass Spectrometry (GC-MS)

Most commercial GC-MS combination instruments utilize a so-called "molecular separator" at the interface of the gas chromatograph and the mass spectrometer. Such a device is necessary to remove the bulk of the GC carrier gas before delivery of the separated components to the high vacuum source of the mass spectrometer. Most molecular separators suffer from the disadvantage of having a very large internal volume and they are not, therefore, altogether suitable for use with high efficiency capillary columns. In our GC-MS instrument, however, the addition of an extra large source diffusion pump enables the total effluent of the chromatograph to be taken directly into the ion source of the mass spectrometer. In this way the high chromatographic resolution is maintained. A schematic diagram of the GC-MS instrument is shown in Figure 2. The gas chromatograph described in A(v) above was used in the GC-MS operation, the GC effluent being diverted, with the GC vent valve closed, through the mass spectrometer isolation valve $V_1$ into the mass spectrometer. Both valves were located in a heated box thermostatically maintained at 250°C.

The mass spectrometer that was used is a DuPont Model 21-492-1 (DuPont Instrument Division, Monrovia, California), designed specifically for high resolution, high sensitivity GC-MS analysis. It has a double focusing analyzer (95° electric sector and 90° magnetic sector geometry), with a conventional electron bombardment source. Differential pumping of the source and analyzer is achieved using two all stainless steel diffusion pumps. A 4 in. diffusion pump is connected to the source via a 4 in. pumping line while the analyzer section is pumped using
FIGURE 2
SCHEMATIC DIAGRAM OF A "TOTAL EFFLUENT" GC-MS

source diffusion pump

$V_2$

$V_1$

gas chromatograph

electric sector

ion source

electron multiplier

magnetic sector

$V_1$ mass spectrometer isolation valve
$V_2$ GC vent valve
a conventional 2 in. diffusion pump. The pumping speeds for helium of these two diffusion pumps are 1500 l./sec and 250 l./sec respectively.

C. Reference Compounds (list of available compounds in appendix)

GC retention data were obtained on the 600' squalane column for the compounds in Tables II and IV. Since, to avoid ambiguity, only one compound at a time can be injected into the column some 60 consecutive GC runs were required to obtain the chromatograms of reference compounds shown in Figures 4 and 5.

D. Gasoline Sampling

The gasolines used in the investigation were as follows:

* Shell of the Future
  Shell Super Regular
  Shell Premium
  Chevron Unleaded
  Chevron Supreme

Since gasolines supplied by gas stations vary from day to day, purchase of small quantities, only when required would have been inappropriate. Consequently gasolines were sampled from 55 gallon drums (obtained directly from the oil companies). Aliquots (250 ml) were siphoned from the center of the drum to obtain representative samples and, once removed, were stored in a refrigerator in tightly stoppered glass bottles to avoid the loss of "light-ends".

E. Engines

Although three engines, viz., a CFR (Cooperative Fuel Research),

* Marketing of Shell of the Future stopped on August 27th, 1972; it was immediately replaced by Shell Super Regular.
an Oldsmobile V-8 and a Mazda-Wankel rotary engine were available to the project, time permitted only exhaust samples from the CFR engine to be examined. The CFR engine is a single-cylinder engine with a variable compression ratio achieved by adjustment of the cylinder. The engine is coupled to a dynamometer which is used to control the engine speed. The engine was operated with the parameters shown:

- Bore: 3.25 in. diameter
- Stroke: 4.5 in.
- Displacement: 37.33 cu. in.
- Compression ratio: 7.5/1 *
- Fuel/Air ratio (by weight): 0.0795/9.8
- Ignition timing: 30° before top dead center
- Horsepower output: 7.9
- Coolant temperature: 210°F
- Air inlet temperature: 125°F
- Oil temperature: 165°F
- Inlet manifold air pressure: 30" Hg
- Engine speed: 1800 rpm

**E  Exhaust Gas Sampling**

Several methods were used to obtain samples of exhaust gases emitted by the CFR engine running on Shell of the Future gasoline under the conditions given in E above. The CFR engine, located in the Engine Laboratory of the Mechanical Engineering Department at U.C. Berkeley, is fitted with an exhaust sampling port which allows a portion of the gas flowing through the exhaust manifold to be diverted.

* The compression ratio of 7.5/1 was chosen for use with Shell of the Future, which is an unleaded fuel, to stay away from a ratio at which incipient knock would occur.
through a 1/8 in. tube. This 1/8 in. tube is positioned at the center of the exhaust manifold and is downstream from a series of mixing baffles. The exhaust under normal operation on the CFR engine is removed by a slight "vacuum" into the effluent stack of the Engine Laboratory. Therefore during trapping of exhaust it was necessary to reduce the flow of gas to the effluent stack using a valve especially installed for this purpose. Closing this valve to an appropriate extent forced exhaust gas to flow through the 1/8 in. sampling line. Exhaust gas flowing through this sample line was collected in the following ways:

(i) Evacuated glass bulb. A cylindrical glass bulb (approximate volume - 100 ml) was attached to 1/8 in. stainless steel tubing by a Kovar glass to metal seal. An all steel Nupro valve (Nupro Co., Cleveland, Ohio, Model No. SS-4BW-SW) was located in the stainless steel tubing. Prior to use the glass bulb was rigorously cleaned with appropriate chemicals and solvents and in the final stage alternately filled with nitrogen and evacuated. In the evacuated condition the bulb was immersed in liquid nitrogen and connected to the 1/8 in. exhaust sampling line through which exhaust had previously been passed until an equilibrium temperature was judged to have been attained. The Nupro valve was opened allowing the previously evacuated bulb to fill with exhaust gas. The bulb was then carried to the Chemistry Department for analysis of the exhaust.

It soon became apparent however that cooling the bulb in liquid nitrogen had serious disadvantages. The original idea of using a liquid nitrogen-cooled bulb was to reduce the interaction of exhaust components. However it is likely that this approach resulted in
an increase rather than in a reduction of such interactions. This is believed to be the case since the exhaust components condensed on the glass surface of the bulb (in which situation they would be more proximate to one another than in the gas phase) will react extensively during the extended period which elapses while the vessel is allowed to warm up to, or is heated to, room temperature. After the vessel had reached room temperature the contained gases were withdrawn with a syringe, through a septum fitted to the stainless steel tubing, and injected onto a GC column.

(ii) Aluminized Mylar bag. A sample of exhaust was collected from the CFR engine in an aluminized Mylar bag which when deflated measured 12 in. x 17 in. The bag had previously been alternately filled with nitrogen and evacuated. The bag was attached to the exhaust sampling line in the evacuated state and after filling was brought to the Chemistry Department. The bag was then connected to a Valco six-port gas sampling valve and the exhaust transferred, by deflecting the bag, into a 0.5 ml gas loop. The contents of the 0.5 ml gas loop were then injected into the GC-MS system but all organic components in the exhaust were completely masked by carbon dioxide and water. The carbon dioxide and water were derived from the exhaust since a previous run in which the Mylar bag was filled with high purity helium produced no response in the mass spectrometer.

(iii) Gas sampling loop attached directly to CFR engine.
To ascertain what changes in exhaust composition take place by interaction of exhaust components after emission from the CFR engine the GC instrument was taken to the Engine Laboratory in the Mechanical Engineering Department. The CFR engine exhaust line was connected to the six-port
gas sampling valve through a minimum length of stainless steel tubing. Emitted exhaust was then allowed to pass through the gas sampling valve (while set in the "road" position) until an equilibrium condition was judged to have been attained. At this point the 0.5 ml of exhaust gas was immediately injected onto the GC column. In a subsequent experiment exhaust gas was allowed to remain in the sampling loop for 10 minutes and was then injected onto the GC column. The GC traces obtained in these two experiments were substantially different.

(iv) Use of a GC column for trapping exhaust. A possible method for trapping exhaust involves the use of a short length of GC column. Gases flowing directly from the exhaust manifold into a short GC column would be expected to be subjected to chromatography and after a certain time, assuming the exhaust composition is constant, a steady state condition would be attained. Attachment of this trapping column to an analytical column should then furnish a chromatogram that is representative of the emitted exhaust from the standpoint of components present. It is unlikely of course that the relative amounts of components will be the same as exists in the exhaust as initially emitted since, for example, there would be a bias in favor of strongly absorbed components over those that are weakly absorbed.

Initial experiments were carried out using various lengths of 0.01 in. Apiezon L capillary column which was mounted between two toggle valves. This system was found to have very poor trapping efficiency and also had a tendency to be plugged by particulate matter from the exhaust. In subsequent experiments the very narrow capillary column was replaced by a chromatographic column consisting of a 3 in. x 1/8 in. stainless steel tube packed with 3% JXR on Gas Chrom Q
(60 - 80 mesh). The tube was wrapped with heating wire so that it
could be rapidly heated to 200°C, enabling the trapped components
to be eluted as quickly as possible

During trapping, the exhaust gas from the CFR engine was
allowed to pass through the JXR column for a period of 10 minutes.
After this both valves were simultaneously closed, the tube brought
to the Chemistry Department and placed in series with the column
selected for chromatography. Analysis was initiated by heating the
trap to 200°C and opening the inlet valve to allow helium into the
system. The outlet valve was then opened allowing the carrier gas
to flush the exhaust sample onto the analysis column in a discrete
plug.

(v) Cyclohexane trapping. Since we were interested in examining
the higher molecular weight fraction of the exhaust, the next trapping
procedure involved bubbling the CFR engine effluent for 15 min. through
spectroscopic grade cyclohexane (0.5 l) contained in a gas washing
bottle. The cyclohexane, which became cloudy due to the presence
of water and which it was observed contained suspended particulate
matter (c.f. F(iv) above), was transferred to a round bottom flask
and concentrated to 10 ml on a rotary evaporator. (Since the azeotopic
composition of cyclohexane:water is 9:1.5:8.5 concentration of the
cyclohexane resulted in complete removal of water.) The 10 ml cyclohexane
was filtered: an ultraviolet spectrum of the filtrate indicated the
presence of a substantial amount of aromatic material. Complete
removal of the cyclohexane furnished 5 mg of material which was dissolved
in heptane. A "solvent blank" was obtained by evaporating 500 ml
of spectroscopic cyclohexane and dissolving the residue in the same
volume of heptane as the material obtained from the exhaust.

RESULTS AND DISCUSSION

A. Gasoline Analysis

As noted in the introduction to this report it was found
necessary to use a dual column approach to analyse gasolines because
it was not possible to achieve high GC resolution over a carbon range
of 3 to 12 with only one GC column. Frequently dual column analysis
can be performed by injecting a sample onto a column which is eluted
until the low-boiling components have been detected. The flow in the
column is then reversed and the high boiling components contained in
the column are backflushed onto a further column which is suitable for
their separation. Backflushing requires auxiliary equipment which is
not necessarily easy to install and to render operable in a short
space of time. However, we were precluded from using such a technique
in this project for a further reason. Since the analysis of the low
boiling components of gasoline was carried out with temperature programming,
backflushing of the column did not elute the high boiling components
as a single peak. Instead the high boiling compounds, on backflushing
(by manually reversing the column), were spread out over an extended
period of time (often in excess of an hour). To effect even reasonable
resolution, mixtures need to be injected onto a GC column over a short
time span so clearly backflushing was not applicable in this instance.

Analytical GC traces were obtained on the low molecular weight
components of five gasolines using a 600 in. x 0.01 in. squalane column.
For each gasoline, namely, Chevron Unleaded and Chevron Supreme (marketed
by Standard Oil of California, and Shell Oil Company's Shell Premium, Shell of the Future and Shell Super Regular, the column was linearly programmed and maintained at 80°C until the elution of toluene. Figure 3 shows the five chromatograms obtained from the squalane column. Peak 51 corresponds to toluene in each of the five traces and was found to be the major single component in all of the gasolines studied. Ideally one would quantitate peaks such as peak 51 since, as may be observed from examination of Figure 3, the gasolines have many peaks in common but the relative concentrations are quite different. Clearly quantitation of individual peaks is necessary for describing and comparing these gasolines exactly, but manual triangulation is certainly not applicable and a commercial integrator would be required.

Nonetheless it is possible to make some general comments on the apparent differences between the "low ends" of the gasolines studied. For example using an en-scale peak such as 6 (Figure 3), and bearing in mind the attenuation changes in the GC traces, it is evident that the two Chevron gasolines contain substantially more of the components in peaks 2, 2a, 4 and 5 than do the Shell gasolines. [Since GC-MS runs were only obtained on Shell of the Future, positive structural assignments have not been made to peaks 2a, 4, 5 and 6. However, on the basis of exact GC retention data obtained on reference compounds they would appear to be isobutene/butene-1, trans-butene-2, cis-butene-2 and 3-methylbutene-1 respectively.]

For the five gasolines, comparison of the relative intensities of peaks 12 and 13 (GC-MS identification in Shell of the Future: 2-methylbutene-2 and 2,2-dimethylbutane respectively) indicates that Shell of
Figure 3. Gas chromatograms of low molecular weight components of:

Shell of the Future
Shell Super Regular
Shell Premium
Chevron Unleaded
Chevron Supreme

Column: 600’ x 0.01 in. squalane
Conditions: 0 - 80°C programmed at 0.5°C/min
Flow rate (helium) - 0.25 ml/min (set at ambient temperature)
Injection temperature 180°C
Detector temperature 195°C
the Future has a much lower concentration of 2-methylbutene-2 than the other gasolines. Of the lower molecular weight olefins, 2-methylbutene-2 has been determined to be one of the most photochemically reactive compounds and is considered a major contributor to smog formation (13). Unfortunately, at least from this one particular standpoint, marketing of Shell of the Future was terminated August 27, 1972, when it was immediately replaced by Shell Super Regular. Clearly this replacement will have an effect on smog formation since the concentration of 2-methylbutene-2 in the air will be increased by evaporative emissions and by its presence in automobile exhaust, 14% of which, we estimate, based on data presented by Starkman (14), is fuel derived. In a general way it appears that this replacement of Shell of the Future by Shell Super Regular will have resulted in increasing concentrations of photochemically active compounds since there are higher concentrations of olefins in Shell Super Regular than in Shell of the Future, viz., peak 9 (2-methylbutene-1), peak 12 (2-methylbutene-2) -- both identified by GC-MS, peak 14 (4-methylpentene-1), peak 15 (3-methylpentene-1), peak 16 (4-methyl-cis-pentene-2), peak 17 (2,3-dimethylbutene-1), peak 21 (2-methylpentene-1), peak 23 (trans-3-hexene and/or cis-3-hexene and/or 2-ethylbutene-1), peak 25 (trans-3-methylpentene-2)* -- all tentatively assigned on the basis of GC retention times.

Many other interesting differences are apparent between the gasolines although the significance, if any, might not be as worrisome as that just discussed. For example, peak 51 (cyclohexane, GC-MS identification) is considerably larger with respect to peak 30 (3,3-dimethylpentane -- GC-MS) in Shell of the Future than it is in Chevron Supreme and Shell Premium. These and other differences, and less obvious

* tentative assignment since confirmed by GC-MS
ones, would be readily discerned with appropriate integration.

The mass spectral data from GC-MS analysis of gasoline and the GC retention data obtained for reference compounds were not compared until all experimental work had been completed. In this way mass spectral structural assignments were not influenced by the GC data and were made solely on the basis of comparison to the reference mass spectral compilation of Cornu and Massot (15). Subsequently the GC and GC-MS data were correlated allowing the identifications to be confirmed.

The mass spectral data obtained from the low molecular weight end of Shell of the Future gasoline during GC-MS analysis are shown in Table II. Structures were usually assigned by comparing the relative intensities of the six principal ions in the mass spectrum of each GC peak with corresponding data from the literature. However, in some instances it proved necessary to use the ten most abundant ions. It was found that such a comparison was sufficient to make unambiguous structural assignments for the compounds listed in Table II. For each chromatographic peak shown in this table we have listed the molecular ion obtained in our GC-MS studies and the six most abundant ions in the mass spectrum with their relative abundance in parenthesis. Directly below is a similar tabulation for the corresponding reference compound published by Cornu and Massot.

Mass spectra obtained for a given compound vary from one mass spectrometer to another and also vary depending upon the mode of sample introduction, e.g., GC-MS, batch inlet. Using GC-MS the sample concentration in the ion source alters continuously during the scan time of approximately five seconds. As a result the spectra represent the average composition of the chromatographic peak during the scan time. On the other hand
Table II. GC-MS ANALYSIS OF SHELL OF THE FUTURE GASOLINE (squalane column)

(Tabulation includes comparison with literature spectra)

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<th>Principal Ions</th>
<th>Identity</th>
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<td>42 (86)</td>
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<td>36</td>
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**GC-MS Analysis of Shell of the Future Gasoline (cont'd.)**

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<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
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<td>56 (49)</td>
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<td>29 (31)</td>
<td>27 (17)</td>
<td>C_{7}H_{16} and C_{7}H_{14}</td>
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<td>43 (100)</td>
<td>29 (48)</td>
<td>57 (42)</td>
<td>41 (42)</td>
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<td>71 (28)</td>
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<tr>
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<td>98</td>
<td>56 (100)</td>
<td>70 (83)</td>
<td>41 (70)</td>
<td>57 (65)</td>
<td>55 (57)</td>
<td>69 (30)</td>
<td>1-cis-2-dimethyl-cyclopentane</td>
</tr>
<tr>
<td>51</td>
<td>92</td>
<td>91 (100)</td>
<td>92 (85)</td>
<td>39 (35)</td>
<td>51 (19)</td>
<td>65 (17)</td>
<td>63 (13)</td>
<td>toluene</td>
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</table>

Mass spectra were recorded at 70eV.
the Cornu and Massot spectra were obtained by introduction techniques where the sample concentration remained constant during scanning. Nevertheless, for the compounds given in Table II, the agreement is excellent between spectra obtained in our GC-MS runs and those recorded in the literature compilation even though these data were obtained from a number of different laboratories and instruments.

Furthermore when the mass spectra, structural assignments (Table II) were subsequently compared with assignments made on the basis of GC reference compound studies, agreement was complete. Figure 4 shows the GC trace obtained on a reference mixture of C3, C4, C5, C6 and C7 alkanes, cyclopentane, cyclohexane, methylcyclopentane, the five isomeric dimethylcyclopentanes and toluene. Table III lists the compounds given in Figure 4. Those compounds assigned numbers in Figure 4 coincide in retention time with the corresponding peaks in the GC traces of the gasolines shown in Figure 3.

Peak 26 in Figure 4 consists of 2,2-dimethylpentane and methylcyclopentane while peak 36 is composed of 3-ethylpentane and 1-trans-3-dimethylcyclopentane. Since these peaks are completely symmetrical it points out quite clearly the danger of assigning structures by GC alone. (An example is given below of a symmetrical peak which contains three components.) GC-MS data obtained on both of the potentially two-component peaks in Shell of the Future show that peak 26 is principally methylcyclopentane and peak 36 is predominantly 1-trans-3-dimethylcyclopentane.

In Figure 4 there are four components indicated by name. On the basis of comparable retention time, peaks 28, 33 and 37 (in Figure 3) were tentatively assigned the structures 2,2,3-trimethylbutane, 2,3-dimethylpentane/1,1-dimethylcyclopentane and 1-trans-2-dimethylcyclopentane
Figure 4. Gas chromatogram of reference compounds listed in Table III. Conditions as for Figure 3.

<table>
<thead>
<tr>
<th>Number of Peak</th>
<th>Reference Compound</th>
<th>Number of Peak</th>
<th>Reference Compound</th>
<th>Number of Peak</th>
<th>Reference Compound</th>
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<td>propane</td>
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<td>2,3-dimethylbutane</td>
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<td>2</td>
<td>2-methylpropane</td>
<td>22</td>
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<td>3-methylhexane</td>
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<tr>
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<td>n-butane</td>
<td>24</td>
<td>n-hexane</td>
<td>35</td>
<td>1-cis-3-dimethylcyclopentane</td>
</tr>
<tr>
<td>7</td>
<td>2-methylbutane</td>
<td>26</td>
<td>2,2-dimethylpentane and methylcyclopentane</td>
<td>36</td>
<td>3-ethylpentane and 1-trans-3-dimethylcyclopentane</td>
</tr>
<tr>
<td>10</td>
<td>n-pentane</td>
<td>27</td>
<td>2,4-dimethylpentane</td>
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<td>n-heptane</td>
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<tr>
<td>13</td>
<td>2,2,2-trimethylbutane</td>
<td>30</td>
<td>3,3-dimethylpentane</td>
<td>43</td>
<td>1-cis-2-dimethylcyclopentane</td>
</tr>
<tr>
<td>18</td>
<td>cyclopentane</td>
<td>31</td>
<td>cyclohexane</td>
<td>51</td>
<td>toluene</td>
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<tr>
<td>19</td>
<td>2,3-dimethylbutane</td>
<td>32</td>
<td>2-methylhexane</td>
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</table>
respectively. However GC-MS analysis showed in fact that peak 28 in Figure 3 was benzene, peak 33 was 2,3-dimethylpentane, with little if any 1,1-dimethylcyclopentane, and peak 37 was not 1-trans-2-dimethylcyclopentane but more likely a heptene for which there are 36 isomers.

Figure 5 shows a GC trace of selected reference alkanes (peaks 1, 2, 3, 7, 10, 13, 19, 20 and 24) and all the possible C₄, C₅ and C₆ olefins (four, six, and seventeen compounds respectively) together with cyclopentane. These compounds are listed in Table IV. Certain of these olefins in Shell of the Future were identified by GC-MS and in these instances they are listed by numbers in Figure 5, e.g., peak 9 (2-methylbutene-1), peak 12 (2-methylbutene-2) and peak 25 (trans-3-methylpentene-2). Cyclopentane (peak 18) has also been identified by GC-MS. Peak 2a has been tentatively assigned to butene-1 and 2-methylpropene-1 on the basis of GC retention. GC-MS analysis of this peak in Shell of the Future gasoline was not possible in any of the runs conducted because of the peaks' small concentration.

It would be possible to identify peaks such as 2a and others arising from the presence of low concentrations of components, i.e., 4, 5, 6, 8, 11, 14-17, 21, 29 and 38 in Shell of the Future gasoline by conducting GC-MS on larger amounts of sample. There is of course an upper limit to the size of sample that can be used. Too large a sample would adversely effect the separation of peaks that are only marginally resolved. At present we are only able to speculate (on the basis of GC retention data) that peak C (cis-butene-2) for example in Figure 5 corresponds to peak 5 in the gasolines (Figure 3) and so on. The other tentative correspondence of lettered and numbered
Figure 5. Gas chromatogram of reference compounds listed in Table IV. Conditions as for Figure 3.
Table IV. Reference compounds used in obtaining GC trace shown in Figure 5.

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peaks of Figures 5 and 3 respectively are shown in Table V.

Peaks M (trans-hexene-2 and 2-methylpentene-2) and peak N (cis-hexene-2 and cis-3-methylpentene-2) in Figure 5 do not appear in the GC trace of Shell of the Future (see Figure 3) and in the GC-MS the n-hexane (peak 24) is in such high concentration that these unsaturated components were not detected. However in the GC traces of the gasolines other than Shell of the Future, peaks are evident on either side of peak 24, indicating the possible presence of at least two of the four hexenes in peaks M and N.

In a similar way the methylcyclopentane of peak 26 in Shell of the Future is in such high concentration that it is not possible to tell whether any 2,3-dimethylbutene-2 (peak 0 in Figure 5) is present.

It should not be inferred from the above examples that minor components of two component peaks cannot be identified by GC-MS. Such identification is possible using a GC-MS data handling system which has the capability of deducting one mass spectrum from another and which can also increase the speed of scanning so that more scans can be obtained in traversing GC peaks. While not evident from the appearance in Figure 5 of peak L, which is off-scale, a GC run conducted at a higher attenuation setting showed that this three component peak (cis-hexene-3, trans-hexene-3 and 2-ethylbutene-1) is completely symmetrical. This again indicates the ambiguity of assigning structures on the basis of GC alone.

Analytical GC traces were obtained on the high boiling (largely aromatic) components of the gasolines using a 100 ft. x 0.01 in. OV-101 column. The chromatograms are given in Figure 6.
Table V. Correspondence of GC Retention Time of Gasoline Components and Reference Compounds

<table>
<thead>
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<th>Identification Number of peak in gasolines (see Figure 3)</th>
<th>Corresponding peak in reference compounds (see Figure 5)</th>
<th>Reference compound(s) injected</th>
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Figure 6. Gas chromatograms of high molecular weight components of:

Shell of the Future
Shell Super Regular
Shell Premium
Chevron Unleaded
Chevron Supreme

Column: 100 ft. x 0.01 in. OV-101
Conditions: Flow rate 2.3 ml/min (set at ambient temperature)
            Injector temperature 220°C
            Detector temperature 270°C

Program: 0 - 3°C at 0.5°C/min
         3 - 8°C at 1°C/min
         8 - 12°C at 2°C/min
        12 - 76°C at 4°C/min
       76 - 96°C at 6°C/min
      96 - 110°C at 8°C/min
    110 - 170°C at 10°C/min
   170 - 250°C at 20°C/min
As noted previously, toluene, marked as peak 51 in these traces, acted as an indicator of the point at which the low molecular weight (Figure 3) and high molecular weight GC traces (Figure 6) overlap.

Shell of the Future gasoline was examined by GC-MS; the total ion current chromatogram obtained is shown in Figure 7. This total ion current chromatogram is equivalent to a GC trace obtained using a flame ionization detector except in this case the mass spectrometer was used as the detector. The difference between the appearance of Figure 7 and that of Shell of the Future gasoline as given in Figure 6 is a function of different temperature program rates (resulting in changes in resolution) and not of different methods of detection.

In Figure 7 the most prominent peaks have been numbered but in addition there are many other peaks. Bearing in mind that even symmetrical peaks can consist of three components (e.g., peak L in Figure 5) this gives some idea of the enormous complexity of the analytical problem with which we are dealing. Certainly an estimate of 200 components in this, and possibly other gasolines, is not unreasonable.

Table VI lists numbered peaks in Figure 7 which have been assigned structures. Because time did not permit the injection of reference hydrocarbons to obtain retention data on these higher boiling components, and since in many instances reference mass spectra are not available it was not possible to assign definite structures in many cases. By definite in this instance we refer to positions of alkyl substituents on the benzene ring and the detailed structure of alkyl side chains.

Most of the numbered peaks given in Table VI are aromatic and include benzenoid compounds to which alkyl substituents are attached. Thus peaks 63, 64, 65 and 67 in Figure 7 (and Figure 6) are ethylbenzene
Figure 7. Total ion current chromatogram of high molecular weight components of Shell of the Future gasoline.

This chromatogram was obtained using a 100 ft. x 0.01 in. OV-101 capillary column which was programmed between 0° and 55° at 0.5°/min and between 55° and 140° at 2°/min.
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Table VI. GC-MS ANALYSIS OF SHELL OF THE FUTURE GASOLINE (OV-101 column)
Table VI. (cont'd.)

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Mass spectra were recorded at 70eV.
and the three xylenes; peaks 77, 78, 79, 81 and 84 are C₃-substituted benzenes (of which there are eight isomers) and peaks 87, 88, 89, 90 and 93 are C₄-substituted benzenes. Since there are twenty-two compounds with the formula PhC₆H₄ the magnitude of the problem of assigning definite structures to members of this group can be realized. Such definitive identifications can only be arrived at after careful correlation of chromatographic and mass spectral data.

B. Exhaust Gas Analysis (CFR engine, Shell of the Future gasoline)

Examination of the ultraviolet spectrum recorded for an aliquot of the concentrate from the cyclohexane trap showed an intense but broad absorption band at 240 - 280 nm (cyclohexane), characteristic of the presence of aromatic material. However, the broadness of this absorption band suggested that we were dealing with a complicated mixture. This idea was borne out by examination of the concentrate by gas chromatography and, as detailed below, by thin-layer chromatography.

Figure 8 shows a total ion current chromatogram produced during GC-MS analysis of the concentrate. From this chromatogram it is evident that at least twenty-eight major components are present. The molecular ion and six most abundant ions in the mass spectrum obtained of each chromatographic peak during GC-MS analysis are shown in Table VII together with a tentative structure. The spectra obtained are exclusively from aromatic compounds, ranging from a xylene to a series of dimethylnaphthalenes. We have only given class names (e.g., C₃-substituted benzene) to many of the peaks in Table VII, since accurate retention data will have to be obtained for a large number of aromatic reference compounds before we can arrive at definitive structural identifications. However in some
Figure 8. A total ion current chromatogram of cyclohexane trapped exhaust sample obtained for a CFR engine using Shell of the Future gasoline as fuel. The chromatogram was obtained using a 100 ft. x 0.01 in. OV-101 capillary column which was programmed between 0° and 200° at 2°/min. Identities of the lettered peaks are given in Table VII.
Table VII. GC-MS ANALYSIS OF CFR ENGINE EXHAUST (Cyclohexane Trap, Shell of the Future Gasoline)

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Mass spectra were recorded at 70 eV.
instances (e.g., peak x, n-propylbenzene; peak i, indene; and peak y, an ethynaphthalene) the spectra were sufficiently unique to allow complete identification.

Comparison of the data in Table VII with those in Table VI (high molecular weight components of Shell of the Future gasoline) shows that there are many components in common. It cannot be assumed, however, that this correspondence is due solely to fuel derived materials. It may well be that certain proportions of these exhaust components are combustion derived. There appears to be evidence for combustion derived materials in the exhaust. For example in Figure 8 peak i is indene, a compound that we have not detected in the gasoline. There is a possibility however that indene was present in the gasoline (since it does occur in crude oil) but the concentration may have been too low for the compound to have been shown as a discrete GC peak. Additionally high concentrations of methylidihydroidenones and/or dimethylstyrenes (molecular weight - 132) are evident in the cyclohexane trapped exhaust material whereas compounds having similar structure were at a considerably lower relative concentration in the gasoline. It would however be necessary to assign definite structures to the exhaust and gasoline components of molecular weight 132 before a positive statement can be made on whether it was combustion or our trapping method that increased the concentration of certain compounds. Moreover exhaust components in addition to being fuel and/or combustion derived can also arise from crank-case lubricating oil decomposition.

The concentrate obtained from the cyclohexane trap was
also examined by thin-layer chromatography using silica gel G as adsorbent and heptane as mobile phase. The bulk of the material moved in this solvent suggesting that it was hydrocarbon in nature but a significant proportion remained at the origin of the chromatogram. This polar fraction gave an intense yellow coloration when sprayed with an acidic solution of 2:4 dinitrophenylhydrazine indicating the presence of compounds with carbonyl functionality. These compounds could be either aldehydes or ketones or a mixture of both and could readily be separated from the hydrocarbons by preparative thin-layer chromatography and characterized by GC-MS.

In practice the JXR trap proved to be difficult to use. The fact that the trap had to be installed in series to the column caused leaks which were often difficult to remove. In addition the necessarily large volume of the trap severely increased the dead-volume causing a marked drop in the efficiency of the column. We were constantly plagued with large volumes of trapped water, which while not appreciably affecting analytical GC, totally masked the organic components in GC-MS analysis. This problem of water was partially overcome by placing a 3 in. x 1/8 in. potassium carbonate tube between the JXR trap and the capillary column. Potassium carbonate has been shown to trap water very effectively while not removing significant quantities of hydrocarbons or aldehydes [16]. The material collected by the JXR trap was largely aromatic and very similar in composition to that obtained using the cyclohexane trap. However, the JXR trapping procedure was technically much more difficult to carry out.
Exhaust samples collected in a Mylar bag and introduced into the GC-MS via the gas sampling loop were found to be very rich in carbon dioxide and water which resulted in dilution of the organic components to such an extent that they could not be identified. Water severely reduces ion source filament life and results in a very high background in the mass spectrometer. As a result this method was abandoned in favor of the approach described above using cyclohexane.

CONCLUSIONS

An account has been given of the way in which combined gas chromatography-mass spectrometry can be used unambiguously to assign structures to the individual components of gasoline and exhaust gases. Defects in "identification" by gas chromatography have been pointed out.

Contrary to popular belief, gasolines are not identical although they do have many components in common. A knowledge of the composition of various gasolines would be of value to the Air Resources Board for use in discussions with oil companies and organizations concerned with pollution control. In the event that gasoline rationing is introduced by the Environmental Protection Agency, it would certainly be more appropriate to limit the sale of specific gasolines proven to be major contributors to pollution, rather than restricting sales on an "across-the-board" basis. Additionally, if the possibility of selective rationing on the basis of gasoline composition were to be made known, it might well force oil companies to reduce the
concentration of certain gasoline components that are judged to be especially detrimental to the environment.

We have commented on the high aromatic contents of those gasolines which we have analyzed. The presence of high concentrations of these materials would appear to be harmful in themselves from an evaporative emission standpoint. Also many aromatic compounds appeared in exhaust samples that we examined. Based on published data [14] we have estimated that 11% of exhaust is fuel derived so the contribution to atmospheric pollution of aromatic compounds in gasoline is substantial. Additionally, aromatics can be regarded as potential precursors of even more harmful pollutants. We have noticed the presence of indene in exhaust from Shell of the Future gasoline which indicates that cyclization reactions occur during combustion. In a parallel sense it has been shown that the origin of benzo(a) pyrene in exhaust is only 36% fuel derived [5] so clearly such cyclization reactions during combustion can be inferred from other studies.

Another compositional feature of gasolines that has been of concern to previous workers and ourselves is the concentration of low molecular weight olefins. In this report we have noted the substantial increase that must have occurred in the concentration of low molecular weight olefins in the atmosphere when Shell of the Future was replaced by Shell Super Regular. Similar significant data, which is directly correlatable with photochemical reactivity and hence smog formation, could be obtained from examination of other gasolines.
Previous GC analyses on hydrocarbons in exhaust samples seem to have placed little emphasis on the higher molecular weight components. This fraction of exhaust contains the polycyclic aromatics which we believe have considerable significance from a toxicological standpoint. We were therefore particularly pleased with the effectiveness of cyclohexane for trapping this portion of the exhaust. Suitable separation techniques such as preparative thin-layer chromatography (TLC) would undoubtedly furnish fractions of cyclohexane trapped exhaust components that are rich in polycyclic aromatics. We have found that analytical TLC and visualization with 2,4-dinitrophenylhydrazine gave a strong reaction corresponding to the presence of aldehydes and/or ketones. It would be fairly straightforward to isolate such materials in quantity for complete characterization by GC-MS. We feel that a cyclohexane trap could provide samples of aromatic components whose composition could be studied and related to type of fuel (e.g., leaded vs unleaded) and type of engine (viz., CFR, Oldsmobile V-8 and Mazda-Wankel rotary).

Another significant fraction of exhaust components could be obtained by solvent washing exhaust particulates. In all probability our cyclohexane trapped exhaust components already contain the materials which could be washed off the particulate matter using solvent. It would however be interesting to examine particle adsorbed components as a discrete fraction.

The data that have been presented in this report were obtained without the help of a computerized data handling system. If such a system had been available it would have been possible to carry out complete analyses on a much larger number of samples. The necessity
for data handling capabilities when dealing with the GC-MS analysis
of complex mixtures has been accurately and succinctly expressed
by Karasek [16] as follows:

"An operating GC-MS system generates an incredible
amount of data. For a complex mixture yielding 100
GC peaks during an hour's run, 5 mass scans of 500
mass units for each GC peak result in 250,000 data
points of mass position and ion intensity to be recorded
and measured. Normalization of each spectrum for
interpretation, correlation of the data with points
on the chromatogram, and extraction of other interpretive
data increase the effort required. This situation
clearly points to the need for use of the data handling
and computational capabilities of a digital computer.
Without its use, only a small amount of this valuable
information is acquired, and even then at considerable
expense of time and manpower."

Further instrumental requirements are indicated for rapid
and accurate analyses of gasoline and exhaust. An appropriate sub-ambient
attachment for the GC instrument would allow reproducible temperature
programmed runs to be made from -70°C. Additionally it is necessary
to quantitative GC peaks so that exact compositional data are available
on individual components of gasolines and exhaust. Suitable commercial
integrators for GC instruments are readily available.

In conclusion we feel that accurate analytical data of the
type that have been presented in this report are essential before
meaningful air pollution abatement regulations are enacted. We believe
that we have demonstrated how readily these data could be obtained.
Literature References


Literature References (cont'd.)

12. L.J. Papa, D.L. Dinsel and W.C. Harris, "Gas Chromatographic Determination of \( C_1 \) to \( C_{12} \) Hydrocarbons in Automotive Exhaust." J. Gas Chromatog. 1968, 6, 270.


## REFERENCE HYDROCARBONS

### PARAFFINS C₅-C₇
- Pentane
- 2-Methylbutane
- 2,2-Dimethylpropane
- Hexane
- 2-Methylpentane
- 3-Methylpentane
- 2,2-Dimethylbutane
- 2,3-Dimethylbutane
- Heptane
- 2-Methylhexane
- 3-Methylhexane
- 3-Ethylpentane
- 2,2-Dimethylpentane
- 2,3-Dimethylpentane
- 2,4-Dimethylpentane
- 3,3-Dimethylpentane
- 2,2,3-Trimethylbutane

### OLEFINS C₅-C₆
- 1-Pentene
- cis-2-Pentene
- trans-2-Pentene
- 2-Methyl-1-butene
- 3-Methyl-1-butene
- 2-Methyl-2-butene
- 1-Hexene
- cis-2-Hexene
- trans-2-Hexene
- cis-3-Hexene
- trans-3-Hexene
- 2-Methyl-1-pentene
- 3-Methyl-1-pentene
- 4-Methyl-1-pentene
- 2-Methyl-2-pentene
- cis-3-Methyl-2-pentene
- trans-3-Methyl-2-pentene
- cis-4-Methyl-2-pentene
- trans-4-Methyl-2-pentene
- 2-Ethyl-1-butene
- 2,3-Dimethyl-1-butene
- 3,3-Dimethyl-1-butene
- 2,3-Dimethyl-2-butene

### PARAFFINS C₈
- Octane
- 2-Methylheptane
- 3-Methylheptane
- 4-Methylheptane
- 3-Ethylhexane
- 2,2-Dimethylhexane
- 2,3-Dimethylhexane
- 2,4-Dimethylhexane
- 2,5-Dimethylhexane
- 3,3-Dimethylhexane
- 3,4-Dimethylhexane
- 3-Ethyl-2-methylpentane
- 3-Ethyl-3-methylpentane
- 2,2,3-Trimethylpentane
- 2,2,4-Trimethylpentane
- 2,3,3-Trimethylpentane
- 2,2,3,3-Tetramethylbutane

### C₃ - C₄ COMPOUNDS
- Propane
- Butane
- Isobutane
- 1-Butene
- cis-2-Butene
- trans-2-Butene
- 2-Methyl-1-Propene

### ALICYCLIC COMPOUNDS
- Cyclopentane
- Methylcyclopentane
- Cyclohexane
- 1,1-Dimethylcyclopentane
- 1-cis-2-Dimethylcyclopentane
- 1-trans-2-Dimethylcyclopentane
- 1-cis-3-Dimethylcyclopentane
- 1-trans-3-Dimethylcyclopentane

* Manufacturer's nomenclature used in this table.
OLEFINS C$_{7}$

1-Heptene
cis-2-Heptene
trans-2-Heptene
cis-3-Heptene
trans-3-Heptene
2-Methyl-1-hexene
3-Methyl-hexene
4-Methyl-1-hexene
5-Methyl-1-hexene
2-Methyl-2-hexene
cis-3-Methyl-2-hexene
trans-3-Methyl-2-hexene
cis-4-Methyl-2-hexene
trans-4-Methyl-2-hexene
cis-5-Methyl-2-hexene
trans-5-Methyl-2-hexene
cis-2-Methyl-3-hexene
trans-2-Methyl-3-hexene
cis-3-Methyl-3-hexene
trans-3-Methyl-3-hexene
2-Ethyl-1-pentene
3-Ethyl-1-pentene
3-Ethyl-2-pentene
2,3-Dimethyl-1-pentene
2,4-Dimethyl-1-pentene
3,3-Dimethyl-1-pentene
3,4-Dimethyl-1-pentene
4,4-Dimethyl-1-pentene
2,5-Dimethyl-2-pentene
2,4-Dimethyl-2-pentene
cis-3,4-Dimethyl-2-pentene
trans-3,4-Dimethyl-2-pentene
cis-4,4-Dimethyl-2-pentene
trans-4,4-Dimethyl-2-pentene
2-Ethyl-3-methyl-1-butene
2,3,3-Trimethyl-1-butene

ALKYLBENZENES C$_{6}$-C$_{9}$

Benzene
Methylbenzene
Ethylbenzene
1,2-Dimethylbenzene
1,3-Dimethylbenzene
1,4-Dimethylbenzene
Propylbenzene
iso-Propylbenzene
1-Ethyl-2-methylbenzene
1-Ethyl-3-methylbenzene
1-Ethyl-4-methylbenzene
1,2,3-Trimethylbenzene
1,2,4-Trimethylbenzene
1,3,5-Trimethylbenzene

mono-ALKYLBENZENES C$_{6}$-C$_{11}$

Benzene
Methylbenzene
Ethylbenzene
Propylbenzene
iso-Propylbenzene
Butylbenzene
iso-Butylbenzene
sec-Butylbenzene
tert-Butylbenzene
Pentylbenzene
(1-Methylbutyl)benzene
(2-Methylbutyl)benzene
(3-Methylbutyl)benzene
(1-Ethylpropyl)benzene
(1,2-Dimethylpropyl)benzene
tert-Pentylbenzene
neo-Pentylbenzene

POLYNUCLEAR AROMATICS

benzo[a]pyrene
fluoranthene
crysene
pyrene
anthracene
perylene