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Gas Chromatographic Determination of C_1 to C_{12} Hydrocarbons in Automotive Exhaust*

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Abstract

A gas chromatographic method is presented for the determination of C_1 to C_{12} hydrocarbons in automotive exhaust. The minimum detectable concentration of each hydrocarbon is one part per billion (v/v). The method has detected about 200 individual peaks in chromatograms of automotive exhaust which represent well over 200 paraffinic, olefinic, and aromatic hydrocarbons. The total analysis time is 25 to 30 minutes. Because of its high sensitivity and excellent resolution, the method should have a wide range of application for automotive exhaust including exhaust from vehicles equipped with emission control devices and in air pollution work; e.g., fuel analysis, atmospheric analysis, and smog chamber reaction studies.

Introduction

Automotive exhaust has been reported to be a significant contributor to air pollution, especially in urban areas, and intensive studies are in progress to minimize pollution from this source. These studies have necessitated the development of analytical techniques capable of obtaining definitive information on the composition of exhaust. A knowledge of the hydrocarbon composition in exhaust is needed because hydrocarbons are known to take part in the formation of photochemical smog (1,2). Individual hydrocarbons can have widely varying reaction rates of the type generally associated with smog formation (1-8). Hence it is important to have analytical capabilities for determining as many of the individual hydrocarbons as possible. Several reactivity scales have been proposed for calculating a "reactivity index" of exhaust which is indicative of the potential of the exhaust to form smog. All of these reactivity scales require an analytical technique which can determine individual hydrocarbons.

Many gas chromatographic methods for determining hydrocarbons in automotive exhaust have been reported in the literature (9-16). Only the methods of Jacobs (13) and McEwen (16) provide sufficiently complete analysis to be considered. The former (13) gives excellent resolution of components but is lacking in sensitivity and reproducibility. The latter (16) has sufficient sensitivity but exhibits less resolution than that reported here, especially in the C_7-C_{12} region.

The method described in this paper is a much improved version of that previously reported by Jacobs (13). The sensitivity of Jacobs' original method was increased five-hundred-fold (to one part per billion) and the precision four-fold (to ±1.5% relative) by several modifications. These are:

1. Replaced the 0.01 in, i.d., capillary column with a 0.02 in capillary column.
2. Lowered the initial temperature to −70°C to effect a cold-trapping of the injected sample at the column inlet and hence keep the injection profile as a narrow band (for best resolution).
3 Removed sample splitter (gives increased sensitivity and precision).

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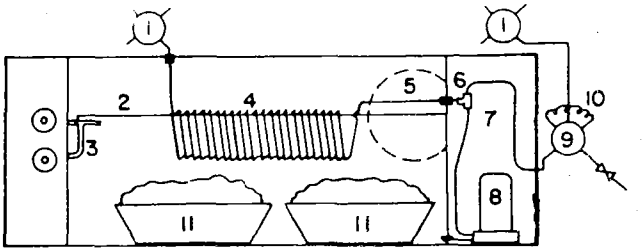
*Research and Development Division Contribution No. 414.

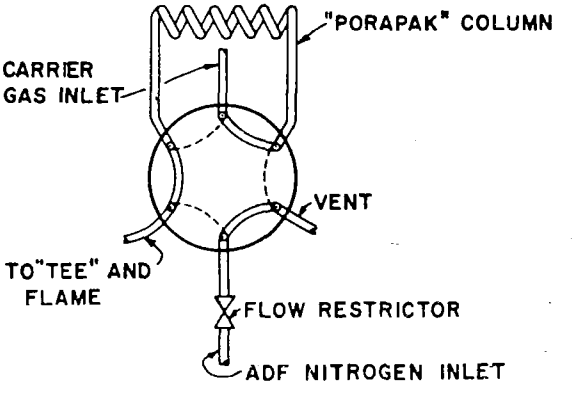
4. Incorporated an auxiliary detector flow (ADF) of nitrogen at the column exit to increase the flame sensitivity and simultaneously increase the resolution by acting as a "sweep gas."
5. Changed to on-column injection.

The modifications mentioned above provided the desired increase in sensitivity without a loss in resolution except for the C_1 and C_2 hydrocarbons which are unresolved. Therefore, it was necessary to determine these compounds on a separate column. This was accomplished on a packed column. The two columns (capillary and packed) were valved together (sharing a common flame detector) via a six-port valve in such a manner as to allow the C_1-C_2 determination to be performed either while the capillary column was being cooled or after the C_3-C_{12} determination was completed. Alternatively, the two columns can be and have been used with two separate instruments or with two flame detectors in a differential or dual unit.



1. GAS SAMPLE VALVES
2. COLUMN SUPPORT
3. SAMPLE SPLITTER
4. CAPILLARY COLUMN
5. OVEN FAN
6. "SWAGELOK" "TEE" (FOR ADF)
7. INSULATED DETECTOR OVEN
8. FLAME IONIZATION DETECTOR
9. SIX-PORT VALVE ASSEMBLY (SEE FIG 3)
10. PACKED COLUMN
11. TRAYS (ALUMINUM) OF DRY ICE

Figure 1. Gas Chromatograph



$=$ C_1-C_2 DETERMINATION POSITION
$--$ BACKFLUSH POSITION

Figure 2. Six-Port Valve Assembly For C_1-C_{12} Determination

Experimental

Apparatus

A Perkin-Elmer Model 800 gas chromatograph was used with several modifications (Figure 1). These are:

1. Two gas sampling valves were mounted on the top of the column oven.
2. The inlet end of the capillary column was run through the top of the column oven (¼ in hole drilled in the top) and attached to one of the gas sample valves. A slotted cork was used to seal the hole.
3. The second gas sample valve was piped with a six-port flow switching valve and the Porapak column (Figure 2).
4. An auxiliary detector flow (ADF) of nitrogen was added at the column outlet by passing the gas through an appropriate restrictor (packed column, valve, etc.) to the six-port valve mentioned above (Figure 2) and then into the detector oven.
5. The detector oven was insulated from the column oven with fiber packing and asbestos sheeting.
6. The instrument pyrometer was replaced with one (−60° to +250°C) obtained from Assembly Products, Inc., Model No. 429-8396.

Gas samples were injected with Perkin-Elmer gas sample valves (part No. 154-0067).

A 3½ ft by ⅛ in, o.d., column packed with a 1:1 intimate mixture of Porapak Q and Porapak T (80/100 mesh) obtained from Waters Associates was used for C_1-C_2 determinations. The columns were packed, precoiled with an automatic pressure type packer. A 150 ft by 0.02 in, i.d., capillary column coated with Dow-Corning DC-200 silicone oil was used for the C_3-C_{12} determinations. This column was purchased from the Perkin-Elmer Corporation.

A Leeds and Northrup Type G Speedomax recorder with a 2 mv range, ¼ second full-scale pen response was used to record all chromatograms. The recorder was also equipped with an Insco multispeed chart drive which provides variable speeds from 1 to 1/60 of the basic chart speed of 12 in/min.

An Infotronics Model CRS-11HSB extended range digital integrator with heavy duty printer and automatic electronic base line drift corrector was used for all quantitative peak area measurements.

Reagents

Gaseous hydrocarbons (pure and diluted with nitrogen) were obtained from Scott Research Laboratories, Matheson Company, and Phillips Petroleum Company. Liquid hydrocarbons (pure and in mixtures) were obtained from Phillips Petroleum Company, PolyScience Corporation, Chemical Samples Company, and Microtek (Distanal Inc.). In doubtful cases, time-of-flight mass spectrometry, gas chromatography, and nuclear magnetic resonance techniques were used to check the identities of pure components and mixtures of hydrocarbons.

Seaford grade nitrogen (Airco) was used for preparing gaseous standards, for the auxiliary detector

flow, and for the packed column carrier gas. Extra dry electrolytic hydrogen (Matheson) was used as the detector fuel along with compressed breathing air (Linde or Airco). Helium (Airco) was used as the carrier gas for the capillary column. All of these gases were passed through Gas-Dry filter traps (Chemical Research Services, Inc.), which consist of Molecular Sieve 5A and indicator Drierite, for a final purification.

Procedure

The gas chromatographic conditions for the determination of the C_1 to C_{12} hydrocarbons are listed in Table I. The capillary column oven is cooled with powdered dry ice contained in two aluminum trays (8 x 1.5 x 1.25 in) placed inside the column oven (Figure 1). More than one tray filling is generally necessary to reach −70°C. The last filling should be made when the oven reaches −55° to −60°C to insure that the temperature will hold at −70°C for 5 min. When this time has elapsed, a gas sample is injected into the capillary column. Forty-five seconds after the sample is injected, the trays of ice are removed, the column oven temperature is set at +30°C, and full heat is applied to the oven. Five minutes after the sample is injected, the column oven temperature is programmed from +30°C to +120°C at 10°C/min. When all of the hydrocarbons have eluted, a second sample is injected into the Porapak column with the six-port valve positioned to allow the column effluent to reach the detector (in this position the ADF goes to vent). The C_1 and C_2 hydrocarbons are now allowed to elute through the column to the detector. After acetylene has completely eluted (~5 min), the six-port valve is rotated to backflush the Porapak column (ADF is now routed to the flame), and the analysis is completed. Alternatively, the C_1-C_2 determination can be performed during the 5-minute cooling period (see Discussion for details).

Calibration

The flame conditions were deliberately selected to provide a similar response (area/ppm carbon) for every hydrocarbon determined in the method. This was verified by quantitatively preparing gaseous standards (in nitrogen) and liquid standards (see Tables II and III for sample results). The liquid standards were prepared by weight on an analytical balance. The gaseous standards were prepared by:

1. Volumetric techniques which involved the use of a wet test meter to measure the nitrogen and a gas-tight syringe to measure the hydrocarbon gases. The standards were prepared in Saran bags (30 in square). This technique was used only for C_1-C_3 hydrocarbons.
2. Partial pressure techniques in which the hydrocarbon(s) and diluent (dry nitrogen) were placed in evacuated stainless steel cylinders at known pressures.

When the linearity of response was verified, a primary calibration was made by preparing many standards of propane and later the C_1-C_2 components using the above techniques. After this primary calibration was

Table I. Chromatographic Conditions

	C_1-C_2 Detn.	C_3-C_{12} Detn.
Column Substrate	Porapak T and Q	DC-200
Column Length	3½ ft	150 ft
Column Diameter	⅛ in, o.d.	0.02 in, i.d.
Column Material	Stainless Steel	Stainless Steel
Column Temp.		
Start	Room Temp.	−65° to −70°C
End	Room Temp.	+120°C
Program Rate	0	10°C/min
Detector Temp.	150°C	150°C
Carrier Gas	Nitrogen	Helium
Carrier Gas Flow	35 ml/min	12 ml/min
Air Flow (Detector)	~400 ml/min	~400 ml/min
H_2 Flow (Detector)	60 ml/min	60 ml/min
N_2 (ADF) Flow	5 ml	35 ml/min
Sample Size	—	5 ml

Table II. Relative Responses for Gaseous Diluted Hydrocarbons

	Relative Response (Area/ppm Carbon)	
Hydrocarbons	Instr. No. 1	Instr. No. 2
Methane	1.01	1.01
Ethane	1.01	1.00
Ethylene	1.01	1.01
Acetylene	1.04	1.03
Propane	1.00	0.99
Propylene	0.99	0.98
Cyclopropane	1.01	0.98
n-Pentane	0.97	0.98
n-Heptane	1.00	1.00
Benzene	1.00	0.99
Toluene	1.01	0.98
Ethylbenzene	0.97	0.97

Table III. Relative Responses for Liquid Hydrocarbons

	Relative Response (Area/m Mole Carbon)	
Hydrocarbons	Instr. No. 1	Instr. No. 2
n-Pentane	0.96	0.97
n-Heptane	1.00	1.00
Isooctane	1.02	1.00
2-Methyl-1-Pentene	0.96	0.97
Octene-1	1.03	0.97
Decene-1	1.00	1.05
Toluene	1.00	0.96
Ethylbenzene	1.00	0.98
o-Xylene	1.00	0.99
Benzene	0.97	1.00

established, two cylinders of dilute hydrocarbon mixtures were purchased from Scott Research Laboratories. One of the cylinders contained a mixture of cyclopropane, n-pentane, benzene, n-heptane, toluene, and ethylbenzene (25-50 ppm) and the other contained a mixture of methane, ethane, ethylene, and acetylene (~1000 ppm). These cylinders were then calibrated from the primary calibration and are used as daily standards. These standards are run twice daily (morning and afternoon) to insure that the operation is functioning properly.

Discussion

As mentioned previously, the original method developed by Jacobs (13) does not have sufficient sensitivity to determine hydrocarbon concentrations in diluted exhaust samples and in exhaust from engines equipped with emission control devices. Another drawback to the original method is that several 0.01 in, i.d., capillary columns (DC-200) subsequently purchased from Perkin-Elmer (and made in this laboratory) could not reproduce the necessary separation of the C_1 and C_2 hydrocarbons. Therefore, it became necessary to modify the method to give increased sensitivity without the loss of resolution. This was accomplished by increasing the sensitivity of the detection system, using a purge gas at the column outlet, changing column diameter, increasing the sample size by removal of the splitter, injecting directly on-column, and changing the temperature program.

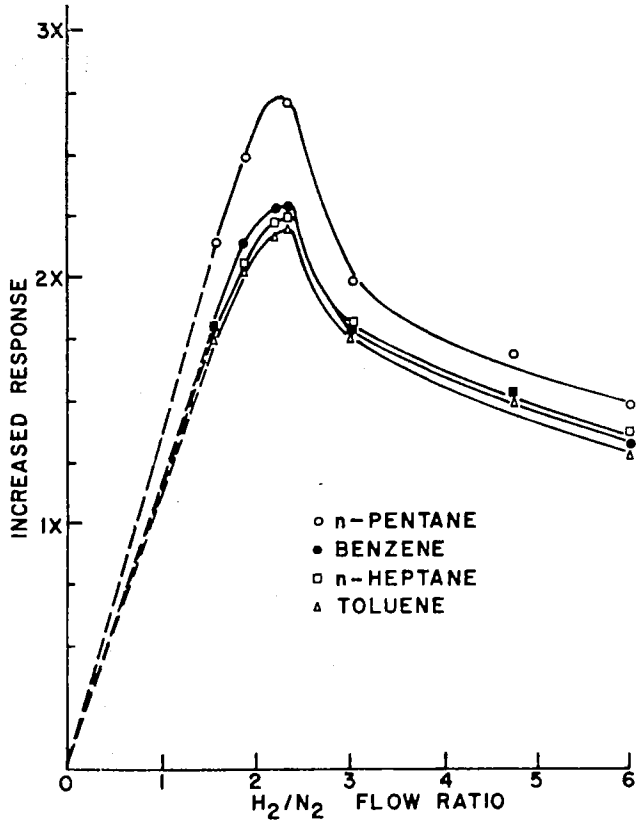


Figure 3. Effect of Auxiliary Detector Flow on Response

Detection System

The sensitivity of the detector supplied by Perkin-Elmer (ceramic jet type) was increased by the addition of nitrogen as an auxiliary detector flow (ADF) to the air-fuel mixture. The precise mechanism for the increased sensitivity is not known although it is related to the thermal conductivity of the added gas (17). Figure 3 is a plot of response vs. the ratio of hydrogen to nitrogen and demonstrates the change in sensitivity due to the added nitrogen. The actual gas flows (Table I) were selected to give the maximum response per carbon while maintaining a linear response per carbon for all of the hydrocarbons regardless of class. The relative responses for several representative hydrocarbons are listed in Table II.

The ADF was added at the column outlet with a tee rather than directly into the hydrogen line to serve as a purge gas and hence to increase the resolution by reducing tailing and minimizing band spreading. When this addition was made in the column oven, excessive noise resulted. This noise could be eliminated by wrapping the tee with asbestos tape or inserting the tee in the detector oven. The latter approach was preferred.

The detector should be well insulated to minimize temperature changes during the course of the determination. Detector temperature changes lead to response changes (at least for this instrument) for some of the hydrocarbons; acetylene appears to be the worst offender in this respect. The detector oven of this instrument was created by insulating the detector section of the column oven with asbestos sheeting and fiberglass insulation. The insulation helps to stabilize the temperature but the detector oven still changes during the initial 5-minute cooling period. Because of this initial detector temperature change, the C_1-C_2 determination is best performed after the C_3-C_{12} determination is completed. At this point, the detector temperature is stable. When the determination was performed during the 5-minute cooling period, 5 per cent variations were experienced with acetylene. A better-insulated detector or a different instrument with a separate detector oven would eliminate this effect and allow the C_1-C_2 determination to be performed during the 5-minute cooling period without a response variation. This would result in a 5-minute time savings. An alternative approach would be the use of two separate instruments. Both of these approaches have been tried with success.

Carrier Gas

Helium and nitrogen were evaluated as the carrier gases for the capillary column (C_3-C_{12} determination). Helium was selected because it gave better resolution of some of the individual hydrocarbons and smaller response differences per change in the carrier gas flow rate. This is important because the flow rate of the carrier gas does vary due to the wide range of temperature in the method. Nitrogen was selected for the

17. Hoffman, R. L., and Evans, C. D., Science 153, 173 (1966).

C_1-C_2 determination because it gave adequate resolution and an increased sensitivity over that obtained with helium. The flow rate was set to match that used for the ADF in the C_3-C_{12} determination. In this manner, the flame conditions, i.e., the hydrogen, air, helium, and nitrogen flows, are the same for both determinations, and the same response factors (area/ppm carbon) are obtained for all of the hydrocarbons.

Columns

The choice of the capillary column was discussed previously (13). The column diameter was changed to 0.02 in, i.d., to better accommodate a larger sample size by reducing the possibility of overloading. Also, the large diameter column has a longer lifetime.

The best column found for the C_1-C_2 separation was a mixed column of Porapak T and Q. This column was much superior to adsorption columns because it provided symmetrical peaks, excellent reproducibility, did not require activation, and could be used at ambient temperatures for this separation. A mixture was necessary because "Q" did not separate ethylene and acetylene at all, and "T" gave incomplete separation of ethylene and ethane. The actual column selected consisted of the two Porapaks intimately mixed in a 1:1 proportion. However, two separate columns in series, one containing "Q" and the other "T," can be used. If so, either column may be placed first. The column order is not important for this separation although Hildebrand and Reilly (18) have shown that it can be very important for many separations.

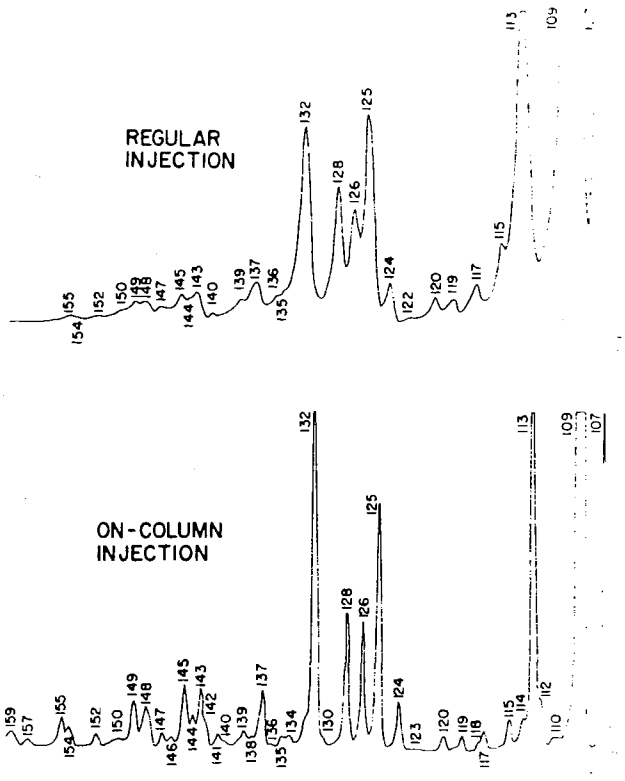


Figure 4. Effect of On-Column Injection

Temperature Program

The temperature program begins with a 5-minute hold period at −70°C before sample injection. This period assures that the column attains a low enough temperature to perform the desired separation. Furthermore, the column attains a sufficiently low temperature to act as a "cold trap" on the injected sample. This cold-trapping allows a relatively large sample (5-15 cc) to be condensed into a rather narrow band at the head of the column. Thus good resolution can be achieved for large sample volumes without the need for a sample splitter. The removal of the sample splitter greatly increased the sensitivity (150-fold) and precision (3-4-fold) of the method. With the sample splitter gone, the sample is now injected directly onto the head of the column by attaching the column directly to the gas sample valve, external to the column oven (Figure 1) rather than passing the sample through the entire inlet system provided with the chromatograph. When the sample is injected in this manner, the resolution of components is markedly increased especially in the C_8-C_{12} region. This increased resolution is illustrated in Figure 4 which shows the back section of two chromatograms obtained with and without on-column injections. It can be seen that in the on-column injection case the peaks are much sharper, exhibit a marked decrease in tailing and are much better resolved. This contributes to the increased sensitivity and precision. All of the improvements mentioned above are a direct result of the initial cold period. It is perhaps noteworthy that if a small section of the column inlet (about 1 foot) is immersed in a low temperature coolant (external to the column oven) such as liquid nitrogen, a much more efficient trapping will result which will permit larger samples to be injected and hence give a further increase in sensitivity. This technique has allowed us to inject samples as large as 50 ml, thus giving another tenfold sensitivity increase. This technique can be very useful in atmospheric analysis and smog chamber work where the hydrocarbons are present in very small quantities. Further increases in sensitivity can probably be obtained by injecting still larger samples. The upper limit on sample size has not yet been determined. Cold trapping in this manner also separates methane from the C_2 hydrocarbons.

The sample is injected after the initial hold period at −70°C. The temperature is then brought up to 120°C in three steps as described in the procedure. This mode of programming was selected to give the desired separations in the simplest manner possible. The upper temperature was limited to +120°C to help prolong column life.

Chromatographic Sampling

Liquid samples, such as prepared standards and gasolines, were injected (~0.2 μl) with a Hamilton microliter syringe using a different chromatographic setup than was shown for the gaseous determinations

18. Hildebrand, G. P., and Reilley, C. N., Anal. Chem. 36, 47 (1964).

(Figure 1). In this case the column was reattached to the injection port (heated to 160°C) and a 16:1 sample splitter was used. All other conditions (temperature program, detection system, etc.) were the same as reported above. The results were calculated as area per cent which is directly related to mole per cent because of the linearity in responses for the various hydrocarbons (see Tables I and II). Thus, the injected volume is not critical as long as the column is not overloaded and all of the components elute.

Gaseous samples are injected with a gas sample valve using the modified apparatus previously described (Figure 1). The sample is introduced into the loop from a plastic bag in either of two methods: flow-through or evacuation. The first method is performed by squeezing the bag and purging the loop. The gas is vented through an exit line which is immersed in water to provide pressure equilibration and to prevent air from backing up into the loop. The second is accomplished by evacuating the loop (via appropriate hardware) and then opening it to the sample bag to allow the loop to fill to atmospheric pressure. When a valve is in good operating condition, i.e., clean and leak-free, these methods are equivalent. The former is preferred because of its simplicity. However, when valves are in constant use, they tend to become "dirty" (although not visible to the eye), and adsorption occurs in the valve body. This leads to response factors (area/ppm carbon) which decrease with increasing molecular weight when the evacuation technique is used and increase with increasing molecular weight when the flow-through technique is used. The increases and decreases are most marked with the aromatic hydrocarbons. It is believed that a contaminant film, perhaps of high molecular weight hydrocarbon(s), accumulates in the valve body to cause these effects. Thus, in the evacuation technique, hydrocarbons are lost by adsorption into the contaminant film leading to a response decrease. On the other hand, the flow-through technique leads to a build-up of hydrocarbons in the film. Injecting the sample causes the valve to be purged by the carrier gas which now sweeps the excess hydrocarbons out of the film and into the column thus causing the increasing response factors. Verifications for this belief are:

1. The longer the loop is purged (on a dirty valve) during the flow-through technique, the larger are the increases in the response factors.
2. The valves can sometimes be restored to their original operating condition by heating at 100°C while under vacuum.
3. Thus far the valves have *always* been restored to their original operating condition by cleaning in an ultrasonic bath containing "Freon-113" Trichlorotrifluoroethane (one to two hours in each valve position).

It is noteworthy that not all new valves were found to operate properly without prior cleaning. The adsorption effect must, of course, be watched closely if accurate determinations are to be made (see Standardization section).

Calibration gases are transferred from pressurized cylinder to plastic bags using a needle valve as an expansion apparatus to prevent fractionation. In principle, this is similar to the apparatus described by McEwen (16). The gas is introduced into the needle valve at cylinder pressure, and the cylinder valve is closed. The entire gas sample in the needle valve is then discharged into the plastic bag. This process is repeated until the bag is filled.

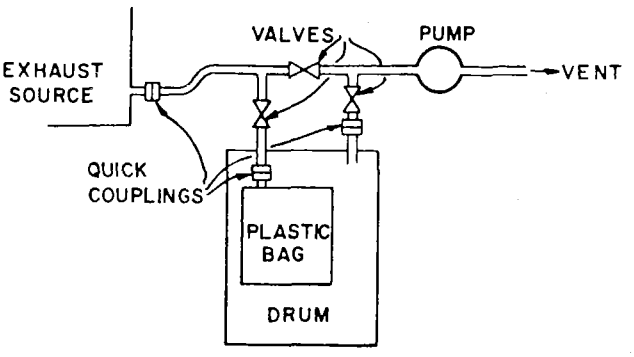


Figure 5. Exhaust Sample Collection Apparatus

Exhaust Sampling

Exhaust samples are collected by the California cycle bag procedure described by Zelson (19). The chromatographic sample is then transferred as quickly as possible to a smaller bag (18 in square) in the diluted form by partially prefilling the smaller bag with nitrogen and then admitting the raw exhaust. This is accomplished by placing the prefilled bag into a suitable container (a Fibrepak drum was used in this work) and making a short, direct connection from the bag to the exhaust source through the lid of the container (see Figure 5). Air is then drawn from the container (around the outside of the bag) via a pump, and exhaust enters the bag to equalize the pressure. In this manner, raw exhaust enters the bag having only passed through a small amount of tubing (stainless steel and/or "Teflon" TFE Fluorocarbon Resin). The exhaust is diluted, thereby preventing water condensation and minimizing hydrocarbon losses which can occur by reaction, adsorption, etc. Simultaneously, an empty bag is filled with raw exhaust which has passed through two ice-cooled traps in series. The carbon dioxide content is determined for each of these bags by another gas chromatographic procedure. These carbon dioxide values are then used to calculate the dilution ratio in the sample bag. A dilution ratio of 3-4:1 is used for exhaust from normal vehicles and of 2-3:1 for exhaust from vehicles equipped with air-injection emission control devices.

Bag Materials

The material of which the chromatographic sample bag is constructed is very important. These small

19. Zelson, J., California Cycle Bag Technique For Vehicle Emissions Testing, Du Pont Technical Memorandum 10,006, March 1, 1966.

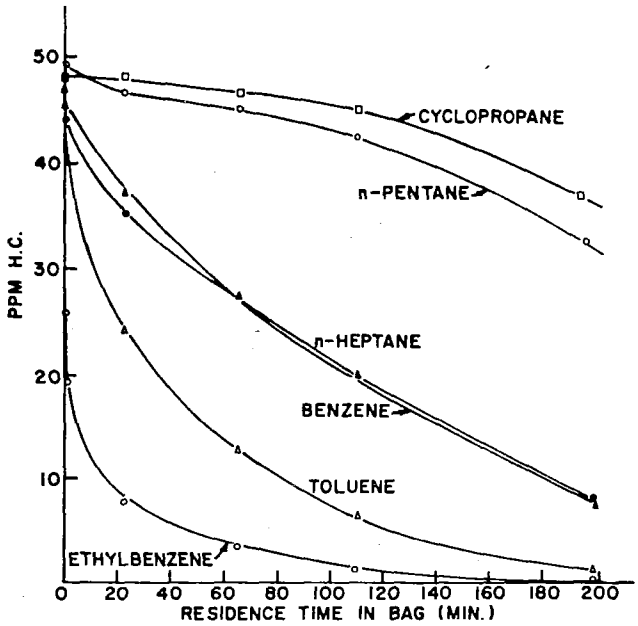


Figure 6. Hydrocarbon Losses In Polyethylene Bag

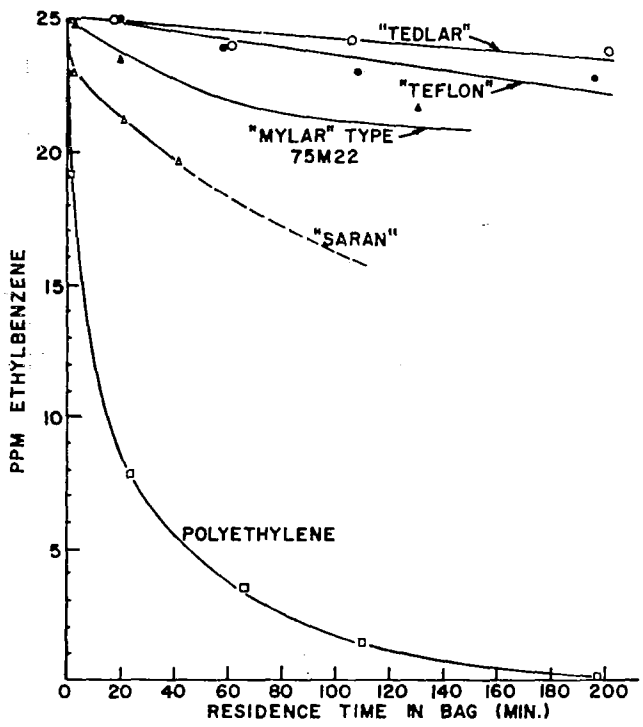


Figure 7. Ethylbenzene Losses In Several Plastic Bags

bags, unlike the large bag used for the total exhaust collection, have a high surface to volume ratio ($\sim$10 ft^2/ft^3), unconditioned walls, and no water film. Therefore, hydrocarbons are much more likely to be lost by adsorption, permeation, etc. Several bag materials were studied in an effort to select one for the exhaust collection. Decay curves were constructed for several hydrocarbons in various plastic bags. A typical example is shown in Figure 6 for six hydrocarbons in a polyethylene bag. Ethylbenzene exhibited the most rapid disappearance in the polyethylene bag as well as in the other bags tested ["Tedlar" PVF Polyvinylfluoride Film, "Teflon" FEP Fluorocarbon Resin, "Mylar" type 75M22 (coated "Mylar")]. A plot of ethylbenzene concentration vs. residence time, for all of the bags tested, is shown in Figure 7. "Teflon" and "Tedlar" had essentially no effect on the composition of the sample over a 3-hour period. On the basis of these tests, it is recommended that "Teflon" or "Tedlar" bags be used for exhaust sampling.

Studies conducted on sampling line materials yielded similar results. Nylon is better than polyethylene, but neither is considered satisfactory. Sampling lines of "Teflon" and/or stainless steel are recommended. Needless to say, it is necessary for all materials that contact the sample to be clean.

Standardization

As mentioned previously, it is desirable to calibrate twice daily to be sure that everything is functioning properly. The C_1-C_2 method is calibrated with a mixture composed of methane, ethane, ethylene, and acetylene. The C_3-C_{12} method is calibrated with a mixture composed of cyclopropane, n-pentane, benzene, n-heptane, toluene, and ethylbenzene. These compounds were selected for three reasons:

1. They cover most of the retention time range of normal exhaust chromatograms.
2. It is desirable to have more than one hydrocarbon class present to insure that the detector response has not changed for a given class. That is, if the flame conditions are changed, the response of one class, aromatics for example, might change significantly while the response of paraffins does not.
3. If any of the sample handling equipment, such as the gas sampling valve, becomes dirty, adsorption of hydrocarbons can occur causing erroneous results. When this occurs, the aromatics are generally affected to the greatest extent. Significant changes in the response factors for toluene and ethylbenzene will pinpoint this effect.

Data Handling

The chromatographic signal is fed to an Infotronics Model CRS-11HSB extended range digital integrator to integrate each of the peak areas as the peaks emerge from the column. The peaks are simultaneously displayed on a strip chart recorder. The electrical connections to both the strip chart recorder and the integrator are made from the 0-5 mv taps located behind the gas chromatograph. This setup allows peaks with 8 mv heights (4 times larger than full scale) to be accurately integrated before a nonlinear condition is reached due to saturation of the amplifier. Thus the attenuation must be selected to satisfy this requirement. When it is desired to accurately integrate the large peaks and also detect and integrate the very small peaks, the attenuation should be adjusted during the course of the determination. The peaks are then

identified by peak number from a "standard" chromatogram and these peak numbers, peak areas, and attenuation levels of the signal are keypunched onto IBM cards along with the response factor (integrator counts per ppm carbon). The cards are then fed into a computer which is programmed to print out concentrations and reactivity indices.

Identification of Hydrocarbons

The hydrocarbons in the exhaust chromatograms were identified by several techniques. Known, pure hydrocarbons were added to previously run exhaust samples so that the peak number could be determined. Also, time-of-flight mass spectrometry and gas chromatography (in combination) were used to positively identify many of the components. Many exhaust samples were run through the chromatographic procedure as described and with a mercuric perchlorate precolumn used to remove olefins and aromatics. This aided in the identifications and pointed out several cases of overlap between paraffins and non-paraffins. Because there are relatively few cases of this type of overlap,

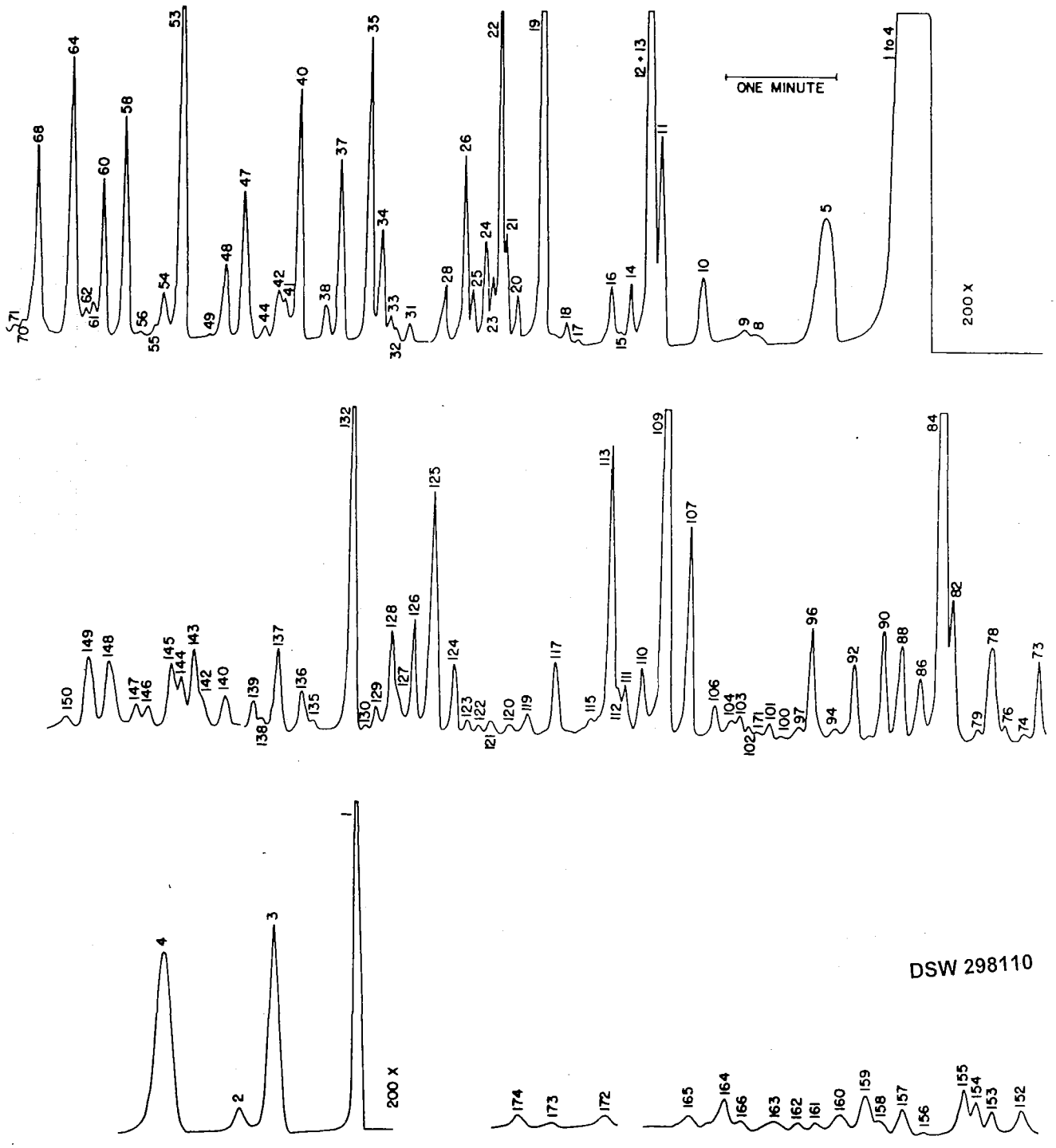


Figure 8. Gas Chromatogram of Typical Exhaust Sample

it was found that using an average reactivity index for the overlapping components did not significantly alter the final reactivity index for the exhaust sample. Thus it was unnecessary to make two runs on each exhaust sample, i.e., one regular and one with a subtractive column.

A gas chromatogram of a typical exhaust sample is shown in Figure 8. This particular sample contained approximately 1200 ppm (mole basis) hydrocarbons. This figure illustrates the high degree of resolution obtained with this method. The sensitivity which can be achieved with this method can be seen from peak No. 48, 2,4-dimethypentane, which is 1.0 ppm in this particular sample (run at 200X attenuation).

A complete list of all of the hydrocarbon peaks that have been detected to date is shown in Table IV. The peaks are listed by peak number. As can be seen, many are still unknown but, in general, these amount to less than 4 per cent of the total moles of hydrocarbon in automotive exhaust.

Table IV. Identification of Hydrocarbon Peaks

Peak Number	Hydrocarbons
1	Methane
2	Ethane
3	Ethylene
4	Acetylene
5	Propylene
6	Propane
7	Cyclopropane
8	Propadiene
9	Methylacetylene
10	Isobutane
11	Isobutylene and/or 1-Butene
12	1,3-Butadiene
13	n-Butane
14	trans-2-Butene
15	Unknown 15
16	cis-2-Butene
17	Unknown 17
18	3-Methyl-1-butene
19	Isopentane
20	1-Pentene
21	2-Methyl-1-butene
22	n-Pentane
23	2-Methyl-1-3-butadiene
24	trans-2-Pentene
25	cis-2-Pentene
26	2-Methyl-2-butene
27	Unknown 27
28	2,2-Dimethylbutane
29	Unknown 29
30	Unknown 30
31	Cyclopentene
32	4-Methyl-1-pentene and/or 3-Methyl-1-pentene
33	Cyclopentane
34	2,3-Dimethylbutane
35	2-Methylpentane
36	4-Methyl-cis-2-pentene
37	3-Methylpentane
38	2-Methyl-1-pentene and/or 1-Hexene
39	2-Ethyl-1-butene
40	n-Hexane
41	trans-3-Hexene
42	trans-2-Hexene
43	2-Methyl-2-pentene
44	cis-3-Hexene
45	cis-2-Hexene
46	3-Methyl-trans-2-pentene and/or 3-Methyl-cis-2-pentene
47	Methylcyclopentane
48	2,4-Dimethylpentane
49	2,2,3-Trimethylbutane
50	3,4-Dimethyl-1-pentene
51	4,4-Dimethyl-cis-2-pentene
52	3,3-Dimethylpentane
53	Benzene
54	Cyclohexane
55	3-Ethyl-1-pentene
56	5-Methyl-1-hexene
57	4-Methyl-1-hexene
58	2-Methylhexane and/or 2,3-Dimethylpentane
59	Cyclohexene
60	3-Methylhexane
61	Unknown 61
62	Unknown 62
63	Unknown 63
64	2,2,4-Trimethylpentane
65	1-Heptene
66	Unknown 66
67	trans-3-Heptene
68	n-Heptane
69	cis-3-Heptene and/or 3-Ethyl-trans-2-pentene
70	2,4,4-Trimethyl-1-pentene and/or trans-2-Heptene
71	cis-2-Heptene
72	2,5-Dimethyl-trans-3-hexene
73	Methylcyclohexane
74	Unknown 74
75	Unknown 75
76	2,4,4-Trimethyl-2-pentene
77	4-Methyl-1-cyclohexene
78	2,4-Dimethylhexane and/or 2,5-Dimethylhexane
79	2,2,3-Trimethylpentane
80	Unknown 80
81	4-Methylheptane
82	2,3,4-Trimethylpentane
83	Unknown 83
84	Toluene
85	Unknown 85

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Table IV. (continued)

Peak Number	Hydrocarbons
86	2,3,3-Trimethylpentane
87	2,5-Dimethyl-trans-2-hexene
88	2-Methyl-3-ethylpentane and/or 2,3-Dimethylhexane
89	Unknown 89
90	3,4-Dimethylhexane and/or 3-Methylheptane
91	Unknown 91
92	2,2,5-Trimethylhexane
93	1-Octene
94	trans-1,2-Dimethylcyclohexane
95	Unknown 95
96	n-Octane
97	trans-2-Octene
98	Unknown 98
99	Dimethylheptane
100	cis-2-Octene
101	cis-1,2-Dimethylcyclohexane
102	Unknown 102
103	Ethylcyclohexane
104	Unknown 104
105	Unknown 105
106	Unknown 106
107	Ethylbenzene
108	Unknown 108
109	m + p-Xylene
110	Unknown 110
111	Unknown 111
112	Unknown 112
113	o-Xylene
114	2-Methyloctane
115	Unknown 115
116	Unknown 116
117	n-Nonane
118	Unknown 118
119	Isopropylbenzene
120	Unknown 120
121	Unknown 121
122	Unknown 122
123	Unknown 123
124	n-Propylbenzene
125	1-Methyl-4-ethylbenzene and/or 1-Methyl-3-ethylbenzene
126	1,3,5-Trimethylbenzene
127	Unknown 127
128	1-Methyl-2-ethylbenzene
129	Unknown 129
130	Unknown 130
131	t-Butylbenzene
132	1,2,4-Trimethylbenzene
133	Unknown 133
134	Isobutylbenzene
135	Unknown 135
136	Unknown 136
137	sec-Butylbenzene
138	1-Methyl-3-isopropylbenzene
139	n-Decane
140	1,2,3-Trimethylbenzene
141	1-Methyl-4-isopropylbenzene
142	1,3-Diethylbenzene
143	Unknown 143
144	n-Butylbenzene and/or 1-Methyl-4-n-propylbenzene
145	1,3-Dimethyl-5-ethylbenzene and/or 1,2-Diethylbenzene
146	1-Methyl-2-n-propylbenzene
147-153	Unknown
154	Durene
155-172	Unknown
173	1-Dodecene
174-200	Unknown

Applications

The method presented has been successfully applied to automotive exhaust analysis for some time. Applications have already been reported in which the effect of gasoline antiknock additives (20) and gasoline composition (21) on exhaust emissions has been determined. The technique also finds utility in the study of emission control devices. In studies of this type, it is desirable to determine the concentration of individual components rather than a simple total hydrocarbon level. The more definitive data offer a better method of evaluating and designing a device because effects such as selective oxidation can be uncovered. For similar reasons, the technique is desirable for studying the effects of fuel additives and engine variables on the composition and reactivity of exhaust.

The applications of the method are not restricted to exhaust and fuel analysis. Due to its high sensitivity and excellent resolution, the method should have a wide range of application in air pollution work, e.g., atmospheric analysis, smog chamber reaction studies, and evaporative emissions. ■

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