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GAS CHROMATOGRAPHIC TECHNIQUE FOR COMPOUND CLASS ANALYSIS OF JET ENGINE EXHAUST

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SUMMARY

A simple gas chromatographic (GC) technique utilizing two analytical columns and efficient olefin and oxygenate scrubbers has been developed for the determination of saturated, olefinic, and combined oxygenated–aromatic fractions of jet engine exhaust. The exhaust sample is collected on a dual-adsorbent trap containing Tenax GC and Carbosieve B at dry ice temperature and is desorbed directly into the GC system by use of a high-temperature oven. Experimental results have been obtained with synthetic exhaust hydrocarbon mixtures and actual jet combustor exhaust samples.

INTRODUCTION

Exhaust emissions from jet engines contain a complex mixture of unburned fuel hydrocarbons and partially oxidized derivatives. These compounds include environmentally "reactive" species, such as oxygenates, olefins, and aromatics, as well as "non-reactive" species, which consist essentially of saturated paraffins. The reactive compounds are environmentally significant because of their detrimental photochemical and olfactory reactivity. Olefins are known to be active in smog-producing reactions, and oxygenates and aromatics are recognized as odorous and toxic compounds. The saturates, in contrast, are relatively unreactive and innocuous.

Since the different classes of hydrocarbons have varying pollution potentials, total hydrocarbon analysis does not provide sufficient information to permit adequate assessment of the environmental consequences. A detailed identification and analysis of each compound in the emissions would require a considerable amount of time, money, and sophisticated instrumentation. The present study was designed to develop

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a simple and efficient approach to collecting the exhaust emissions and analyzing them according to compound class.

The analytical approach in this study is to use a dual-column gas chromatographic (GC)–subtractive technique for determining the saturated, olefinic, and combined oxygenated–aromatic fractions of jet engine exhaust. Similar subtractive techniques have been successfully used in other applications[1–10]. The exhaust sample is collected in a dual-adsorbent trap containing Tenax GC and Carbosieve B. The adsorbent technique will allow effective preconcentration of the gaseous samples while maintaining chemical integrity of the samples. Porous polymers[11–29] and activated carbon adsorbents[30–35] have been used for collecting gaseous samples. The dual-adsorbent trap in this present study is efficient in collecting low- and high-molecular-weight compounds, yet readily permits desorption for analysis.

A gas chromatograph with two flame ionization detectors (FIDs) is required for the method developed. The exhaust sample is collected in a dual-adsorbent trap and subsequently desorbed directly onto a 1,2,3-tris(2-cyanoethoxy)propane (TCEP) column which efficiently separates oxygenates and aromatics from saturates and olefins. The saturates and olefins are eluted rapidly from TCEP, but aromatics and oxygenates are appreciably retained and eluted at later times. The saturate and olefin fraction, after being eluted from TCEP, passes through an efficient Ag_2SO_4 scrubber which traps olefins and allows only saturates to be detected at the first flame ionization detector.

After the saturate–olefin fraction is eluted from TCEP, a switching valve is used to re-direct the TCEP column effluent to a short column of Chromosorb 105 maintained at ambient temperature. Chromosorb 105, a hydrophobic porous polymer, retains oxygenates and aromatics of the TCEP effluent while allowing water to pass through quickly. The Chromosorb bed is heated rapidly and the collected aromatics and oxygenates are eluted and detected at the second FID. There is a possibility that very light oxygenates (e.g., acetaldehyde) may pass through TCEP prior to the switching time and thus be detected along with the saturates. This possibility is eliminated by placing a column containing an oxygenate scrubber ($PdSO_4$), in line with the column of Ag_2SO_4, the olefin scrubber. Any light oxygenated compound eluted with the olefin–saturate fraction is then adsorbed and appears as a fraction of the olefinic fraction.

Two identically collected exhaust samples of known volume are run through the GC system, one with the subtractors in line and one without them. Results can be obtained for the following fractions: (1) saturates, (2) olefins and light oxygenates (by difference), and (3) oxygenates and aromatics. Peak areas resulting from each signal are noted, and, by comparison with areas from standard hexane solutions, concentrations are determined.

EXPERIMENTAL

Instrumentation

Analyses were conducted on a Hewlett-Packard Model 5750B research gas chromatograph equipped with two FIDs and interfaced with an Autolab System IV computing integrator. A flow system schematic of the GC is shown in Fig. 1. A 4-port switching valve (Circle Seal, Pasadena, Calif., U.S.A.) was used to control the flow
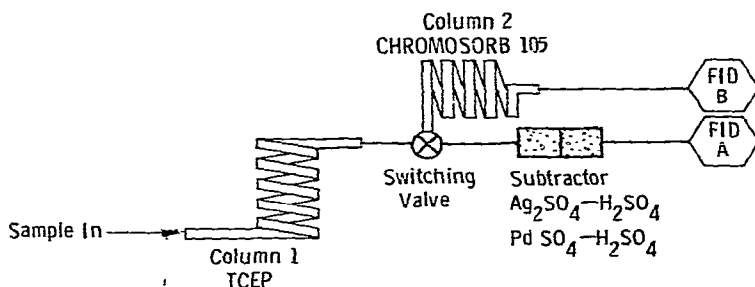
Fig. 1. Flow schematic of GC–subtractive system.

direction of the column effluent. Exhaust samples were introduced via a modified Hewlett-Packard Model 19021A heated gas sample valve.

Desorption of the sample from the sorbent was accomplished by surrounding the tube with two heated halves of an aluminum block furnace. Two cartridge heaters from a Hewlett-Packard Model 810 GC injection port were used to heat the furnace. Maximum operating temperature of the homemade furnace was 400°. Temperature measurements were made with a Sargent-Welch Chromel-Alumel thermocouple connected to a potentiometer.

Adsorption tubes

Exhaust samples were collected in tubes prepared by packing 7 cm of 60–80-mesh Carbosieve B (Supelco, Bellefonte, Pa., U.S.A.) and 4–5 cm of 60–80-mesh Tenax GC (Applied Science Labs., State College, Pa., U.S.A.) in 16–17-cm lengths of $\frac{1}{4}$ in. O.D. × 2 mm I.D. glass tubing. Fig. 2 is a diagram of the adsorption tube. The Tenax GC was used to trap high-molecular-weight organic compounds while the Carbosieve B retained the low-molecular-weight compounds not trapped by Tenax GC. All connections between traps, drying tubes, and sample lines were made with $\frac{1}{4}$-in. Swagelok fittings. The tubes were conditioned by heating them at 350° for 12 h with helium carrier gas. Also, within 24 h prior to sample collection, the tubes were finally cleaned by flushing with nitrogen for 5–10 min at the temperature used to desorb samples. Standard $\frac{1}{4}$-in. Swagelok caps were used to seal the tubes during storage. During sampling the traps were cooled to −78° with crushed dry ice.
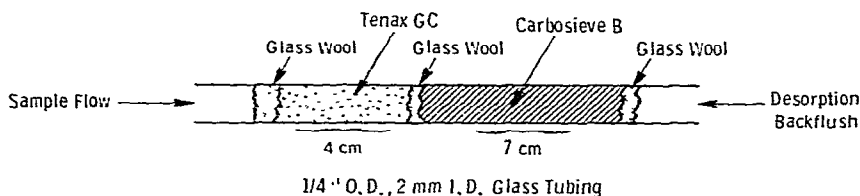

Fig. 2. Adsorption tube.

During sample collection, gas flow was directed through the Tenax GC portion of the tube first. The sorbed samples were sealed and then stored in dry ice until analysis. During the desorption process, the sample was backflushed into the GC.

Desorption consisted of connecting the cold tube to the GC via the modified heated sampling valve, enclosing it within the furnace, preheating it for 5 sec and flushing the sample onto the GC column with helium carrier gas. Heating was continued for *ca.* 100 sec with carrier gas flowing through the tube. The sampling valve was then switched so that the carrier flow bypassed the adsorption tube.

GC columns

Initial studies were performed with 1-m and 0.76-m columns containing 30% TCEP (Applied Science Labs.) coated on Chromosorb P, 60–80-mesh (Fisher Scientific, Pittsburgh, Pa., U.S.A.). The column was conditioned at 80° for 72 h with the carrier gas. No apparent bleed or loss of activity was noted over a 2-month period. It was operated at 80° with a helium carrier flow of *ca.* 60 ml/min.

A 30.5-cm Tenax GC column was used in preliminary studies for oxygenate and aromatic analysis. Tenax GC (60–80-mesh) was packed in heavy walled 6 mm O.D. × 3 mm I.D. PTFE tubing and conditioned with helium carrier flow at 200° for 24 h.

Actual combustor exhaust samples were later analyzed for the oxygenate–aromatic fraction using a Chromosorb 105 column. It was prepared by packing a U-shaped glass tube, 13 cm × 2 mm I.D. with Chromosorb 105 (Alltech, Arlington Heights, Ill., U.S.A.). The column was connected to the switching valve and placed exterior to the GC oven so that it could be operated at ambient temperature. Heating tape with Variac control was wrapped around the column so that it could be quickly heated to *ca.* 150° to facilitate the elution of the oxygenates and aromatics. The column was maintained at ambient temperature until water had been eluted.

Subtractors

Ag_2SO_4–H_2SO_4 was chosen to evaluate for olefin subtraction and $PdSO_4$–H_2SO_4 for oxygenate subtraction. The subtractors were prepared similarly to those described by Klosterman and Sigsby[8]. The subtractor materials were stored in tightly sealed glass bottles protected from the sunlight. A subtractor tube for analysis was prepared by placing 0.5 g of each subtractor packing, separated by a plug of glass wool, in 12 cm of 6 mm O.D. × 4 mm I.D. glass tubing. The subtractor tube was re-packed when 50% of either or both subtractors had turned black.

Sampling system

Real exhaust samples were collected from a T-56 combustor rig at the Air Force Aero Propulsion Laboratory (AFAPL), Wright-Patterson AFB, Ohio, U.S.A. The on-line sampling arrangement is shown in Fig. 3. Two adsorption tubes were placed in line. One served as a dummy for regulating the exhaust flow-rate between 50–100 ml/min. The flow-rate was continually monitored during sample collection so that the total volume was precisely known. Sampling time was 5 min. The exhaust sample line to the tubes was heated to *ca.* 150°. Samples were collected from the combustor rig when it was operated with JP-4, JP-5, JP-8, isooctane, and DEL-5 fuels at various inlet pressures. JP-4, JP-5, and JP-8 are standard fuel blends used by military aircraft. Isooctane was used to compare combustion products of a pure compound fuel with those from the mixed compound fuels. DEL-5 is a specially blended fuel
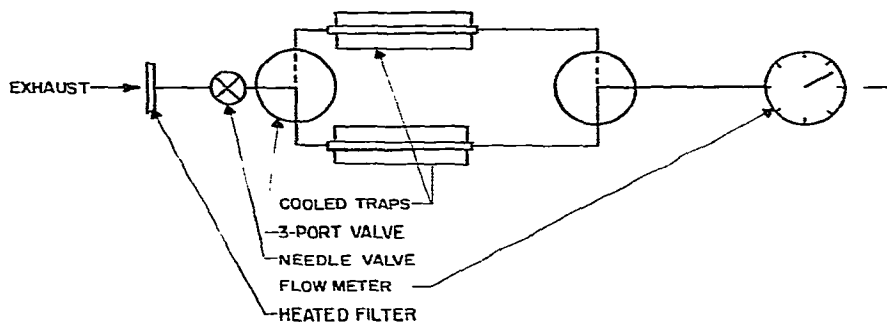
Fig. 3. Exhaust sampling line.

made by adding 1.6% (w/w) pyridine to the stock JP-4 fuel and additionally increasing the aromatic content of the fuel from *ca.* 12 to 25%. DEL-5 was prepared to simulate fuels which may be obtained from alternative sources such as Colorado oil shale.

RESULTS AND DISCUSSION

Desorption efficiency
        The efficiency of sample desorption from the Tenax GC–Carbosieve B sorption tube was evaluated. Desorption efficiencies for various compounds are presented in Table I. Samples consisting of either aqueous or carbon tetrachloride solutions of the compound of interest were collected at dry ice temperature. The furnace temperature, as illustrated in Table I, is critical for efficient compound desorption. Desorption efficiency is illustrated in Fig. 4, in which chromatograms of desorbed samples are compared with those of samples injected directly into the GC column.

TABLE I

DESORPTION EFFICIENCIES OF VARIOUS COMPOUNDS FROM COMBINATION CARBOSIEVE–TENAX TRAPS USING A FURNACE

Only 0–10-sec preheat times were used prior to opening the valve for injection of the desorbed sample into the column. The temperature at which the sample was collected was −78°. This temperature was not radically changed prior to desorption. Exact temperature control was not maintained: −78° implies cooling with crushed dry ice. All compounds were in aqueous solutions except *p*-xylene and 2-octanol.

Compound	Mass (ng)	Furnace temp. (°C)*	Average % desorbed (n = 3–6)
Methanol	320	345	104
Propanal	32,320	345	86
	88	355	95
Ethyl ether	28,028	345	80
	270	355	95.5
p-Xylene	104	365	90
2-Octanol	82	365	112

*The equilibrium furnace temperature, to the nearest 5°.
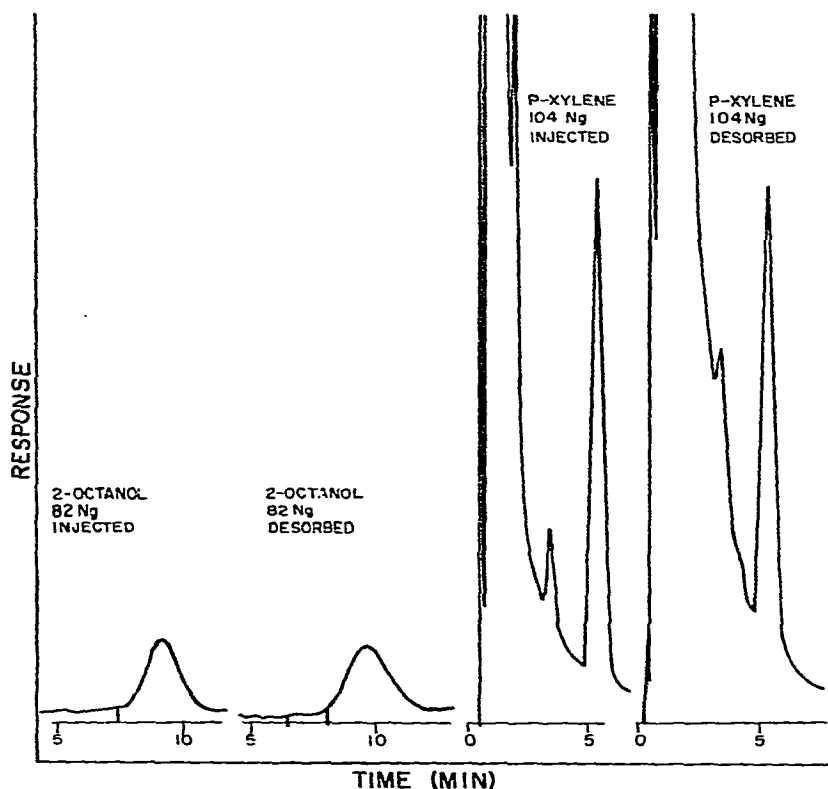
Fig. 4. Comparison between some injected and desorbed solutes from combination traps with furnace.

Evaluation of subtractors

A Ag_2SO_4–H_2SO_4 subtractor was chosen for evaluation of the efficiency of olefin removal. Approximately 0.5 g of the subtractor packing material was placed in a glass tube and connected into the GC between the TCEP column and FID. A series of compounds was injected and the results are shown in Table II. The compounds evaluated were typical of those expected in jet engine exhaust, and the amounts injected were comparable to or higher than those expected in actual samples. As can be seen from Table II, the Ag_2SO_4–H_2SO_4 subtractor was very efficient in removing the olefins tested, while allowing the saturates to pass through quantitatively. The optimum operating temperature was found to be 80°. Above this temperature, the efficiency of olefin removal decreased.

Because of the possibility that light oxygenates present in the exhaust (particularly acetaldehyde) might be eluted with some of the saturates and olefins, it was necessary to evaluate the efficiency of $PdSO_4$–H_2SO_4 as an oxygenate subtractor. The results, at 80°, are shown in Table III. The light oxygenates tested were very efficiently removed, while saturated compounds passed unaffected.

A synthetic solution of olefins in carbon tetrachloride was prepared to evaluate the Ag_2SO_4–H_2SO_4 subtractor. The mixture was chromatographed through the 1-m TCEP column with and without the subtractor before the FID. As can be seen in Fig. 5, all of the olefins were efficiently removed by the subtractor.

TABLE II

EFFICIENCY OF Ag_2SO_4–H_2SO_4 ADSORBENT (80°)

Compound	Mass (μg)	Efficiency, % compound removed
Saturates		
n-Pentane	90	0
n-Heptane	19	1.1
n-Decane	2	3.1
Methyl cyclopropane	37	1.4
2,3-Dimethyl butane	56	0.4
Unsaturates		
Acetylene	5780	100
Ethylene	1273	99.4
2-Ethyl-butene-1	123	100
4-Methyl-pentene-1	121	100
Hexene-1	47	100
Octene-1	10	100
Decene-1	2	100
Aromatics		
Benzene	78	100
Ethyl benzene	48	100

TABLE III

EFFICIENCY OF $PdSO_4$–H_2SO_4 ADSORBENT (80°)

Compound	Mass (μg)	Efficiency, % compound removed
Oxygenates		
Acetaldehyde	100	99.1
n-Propionaldehyde	67	100
n-Butyraldehyde	22	100
Allyl ether	98	100
2-Methyl furan	125	100
Methyl acetate	53	100
Acetone	25	100
Methanol	19	100
Saturates		
n-Pentane	90	0
n-Heptane	19	0
n-Decane	2	0.1
Methyl cyclopropane	37	0.2
2,3-Dimethyl butane	56	0.2

Evaluation of TCEP column

In this study the use of TCEP for selectively retaining oxygenate and aromatic compounds while allowing the rapid elution of saturates and olefins was investigated. The retention times of a series of compounds were measured on a 1-m 30% TCEP column at 80° with a helium flow-rate of 60 ml/min. Results are shown in Table IV. Compounds tested were representative of those expected to be present in engine exhaust. The saturates and olefins were eluted rapidly, whereas the oxygenates and
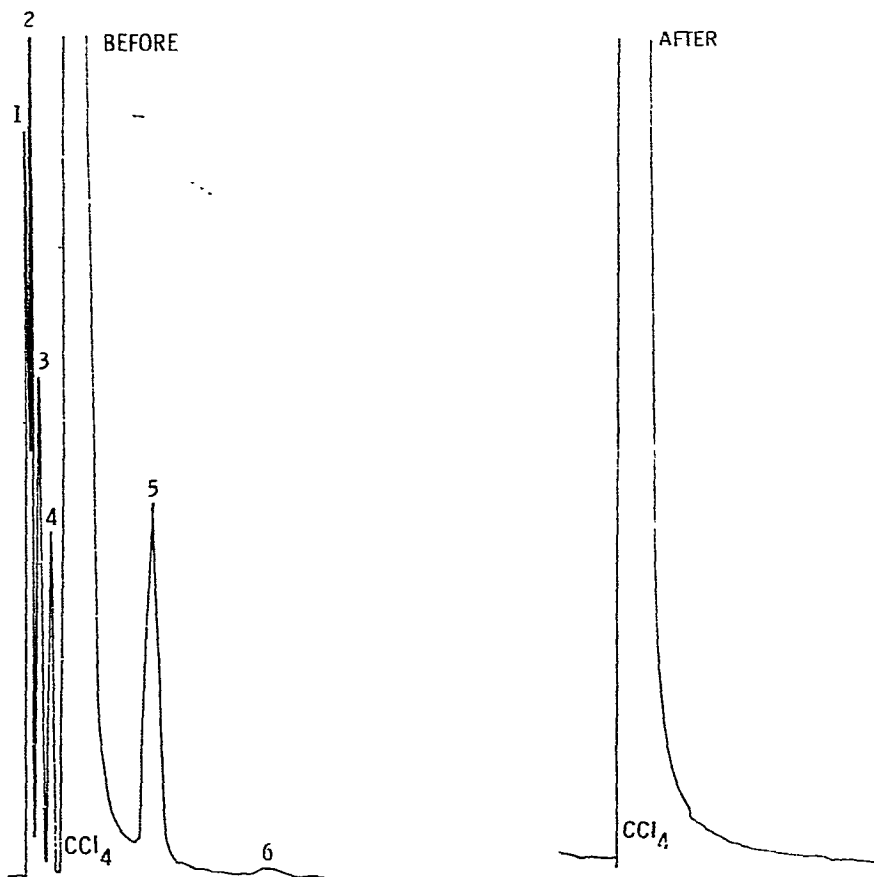
Fig. 5. Chromatograms of a solution of olefins with and without subtractors in line. Peaks: 1 = 4-methyl-pentene-1; 2 = 2-methyl-pentene-1; 3 = hexene-1; 4 = heptene-3; 5 = diisobutylene; 6 = octene-1.

aromatics were retained. Even propionaldehyde was eluted after decane and decene-1, which are the highest molecular weight saturate and olefin expected at appreciable concentrations in the engine exhaust. The column was later shortened to 0.76 m to shorten the retention times and speed up the analyses.

Evaluation of Chromosorb 105

Chromosorb 105 is a hydrophobic porous polymer which allows water to pass quickly through while retaining the oxygenates and aromatics at ambient temperature. Tests indicated that water did not interfere with the determination of oxygenates and aromatics because of its short retention time relative to organic compounds in the Chromosorb 105 column.

Evaluation of class separation

A quantitative synthetic mixture of various saturates, oxygenates, olefins, and aromatics was evaluated on the GC-subtractive system shown in Fig. 1. Fig. 6, ob-

TABLE IV

RETENTION TIMES OF VARIOUS COMPOUNDS ON 30% TCEP COLUMN AT 80°
Helium flow-rate, 60 ml/min.

Compound	Retention time (sec)
Saturates	
Methane	14
Methyl cyclopentane	31
n-Hexane	22
n-Octane	37
n-Decane	81
n-Dodecane	222
Unsaturates	
Acetylene	16
2,2,4-Trimethyl-pentene-1	30
Nonene-1	60
Decene-1	92
Oxygenates	
Propionaldehyde	128
Butyraldehyde	196
Valeraldehyde	323
Benzaldehyde	375
Allyl ether	168
Methyl furan	118
Methanol	258
Acetone	187
Methyl ethyl ketone	273
Aromatics	
Benzene	241

tained from preliminary studies with the 30-cm Tenax GC column operated iso-
thermally at 80° in place of the Chromosorb 105 column, illustrates the principle of
compound class separation. Similar results were obtained with the Chromosorb 105
column having independent temperature control. Chromosorb 105 was later adopted
since it exhibited more reproducible retention characteristics than the Tenax column.
The shift in baseline occurring after peak 2 corresponds to switching of the valve.
Hexane and decane passed through the TCEP column and were detected at FID A
(see Fig. 1). Water, propionaldehyde, acetone, methanol, and benzene passed through
the TCEP and the Tenax GC and were detected at FID B. The hexene-2 present in
the mixture was removed by the Ag_2SO_4–H_2SO_4 scrubber. The switching time chosen
(65 sec in this case) allowed olefins and saturates through C_{10} to be eluted from TCEP
and detected at FID A. To obtain complete analyses, it was necessary to analyze two
identical samples. The first sample was run through the system with the subtractor
in line. The following data were obtained:

FID A response = saturates (total unreactive)
FID B response = oxygenates + aromatics

Fig. 6. Chromatogram of hydrocarbon mixture illustrating class separations. Peaks: 1 = hexane; 2 = decane; 3 = water; 4 = propionaldehyde; 5 = acetone + methanol; 6 = benzene.

The second sample was analyzed without the subtractor in line, and the following data were obtained:

FID A response = saturates + olefins
FID B response = oxygenates + aromatics

The olefin response was obtained by subtracting the FID A response of the first sample from the FID A response of the second sample. A total reactive hydrocarbon content could be obtained by adding the response from olefins to that from oxygenates + aromatics.

Analysis of real exhaust samples

The GC-subtractive system shown in Fig. 1 was used to analyze exhaust samples from the combustion of various fuels in the combustor rig. The manually controlled switching valve was first positioned to direct the flow from the TCEP column into the subtractor tube, if present, or into FID A. At 65 sec, a predetermined time corresponding to the elution of *n*-decane from the TCEP column, the valve was switched to direct the flow to the Chromosorb 105 column at ambient temperature. After water was eluted, the Chromosorb 105 column temperature was raised to 150° to facilitate the elution of aromatics and oxygenates. Samples were collected on site

using the Tenax–Carbosieve adsorption tubes at dry ice temperature and were taken to a nearby laboratory for GC analysis. Two samples of known volumes were collected under identical conditions and were stored under dry ice until analysis.

A chromatogram typical of an actual exhaust sample analysis is shown in Fig. 7. The important events in the analytical sequence are noted on the chromatogram. The first peak is labeled "paraffins", signifying that this particular analysis was performed with the subtractor system. The "column switch" designation corresponds to the time at which effluent from the TCEP column is directed into the Chromosorb 105 column. The area of the chromatogram labeled "reconcentration period" represents the period of time during which the Chromosorb 105 column is maintained at ambient temperature to allow the water to pass through. The point at which heating of the Chromosorb 105 column begins is indicated on the chromatogram. After this, the oxygenates and aromatics are eluted, as shown by the labeled area of the chromatogram. The final peak of the chromatogram labeled "excess area" is an impurity or column bleed that appears reproducibly when the Chromosorb 105 is heated even when no sample is injected.
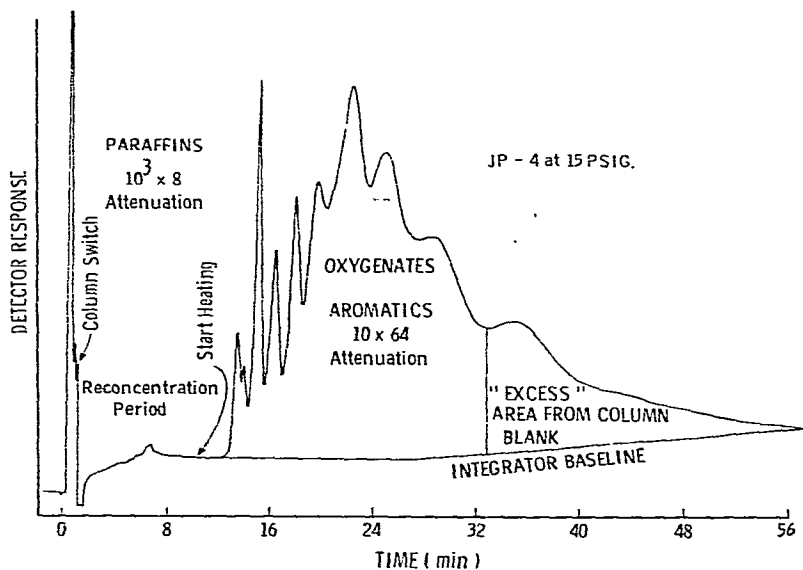

Fig. 7. Chromatogram of an actual combustor exhaust sample showing low resolution separation of classes of organic pollutants.

All samples were subjected to the analytical sequence described above, and the areas corresponding to the different portions of the chromatogram were automatically recorded by the Autolab System IV integrator.

Results of exhaust analyses

Table V presents a summary of the real exhaust samples analyzed in terms of ppm carbon and Table VI shows the composition as a percent of the organic constituents of the exhaust. Hexane was used as a standard. "Reactive compounds" include

TABLE V

SUMMARY OF HYDROCARBON ANALYSES (ppm C)

Fuel	Inlet pressure (p.s.i.g.)	Olefins + light oxygenates	Oxygenates + aromatics	Total reactive compounds	Total unreactive compounds	THC
JP-4	15	54.6	257	312	118	430
JP-4	33	22.8	52.5	75.4	13.6	89.0
JP-4	50	10.2	17.0	27.3	1.88	29.2
JP-5	33	—	77.7	—	—	117
JP-8	33	—	81.7	—	=. .	110
DEL-5*	33	16.7	50.8	67.5	6.48	74.0
DEL-5	33	18.2	62.4	80.6	11.4	92.0
Isooctane	33	6.82	7.33	14.1	8.70	22.8

* Samples were taken on two different days with the same nominal combustor operating conditions; an on-line total hydrocarbon analyzer showed that the emission levels were somewhat different.

TABLE VI

PERCENT COMPOSITION OF REAL COMBUSTOR EXHAUST

Fuel	Inlet pressure (p.s.i.g.)	Olefins + light oxygenates (%)	Oxygenates + aromatics (%)	Reactive compounds (%)	Unreactive compounds (%)
JP-4	15	12.7	59.8	72.6	27.4
JP-4	33	25.6	59.0	84.7	15.3
JP-4	50	34.9	58.2	93.5	6.4
JP-5	33		66.4		
JP-8	33		74.3		
DEL-5	33	22.6	68.6	91.2	8.8
DEL-5	33	19.8	67.8	87.6	12.4
Isooctane	33	29.9	32.1	61.8	38.2

olefins, oxygenates, and aromatics, and "non-reactive compounds" consist of saturates. The data obtained from these real samples are valuable in assessing the pollution potential of jet engine exhaust. The following tentative conclusions can be reached by consideration of the results obtained:

(1) The major portion of the organic jet exhaust products from all fuels tested is environmentally reactive in nature.

(2) For a given fuel, the percentage composition of reactive compounds in the exhaust increases as the power is increased.

(3) There is a general decrease in absolute concentration of all classes of organic compounds as the power is increased.

(4) The distribution of species in the various classifications does not differ appreciably for JP-4 compared to DEL-5 even though DEL-5 is JP-4 with added aromatics.

(5) Greater than 55% of the total hydrocarbons sampled from actual jet fuel exhausts was classified as either aromatic or oxygenated.

(6) The exhaust from pure isooctane showed marked reduction in total hydrocarbons compared with actual jet fuels and had the highest percentage of unreactive compounds.

The GC-subtractive system developed in this study has effectively been used to analyze jet combustor exhaust samples with respect to hydrocarbons emitted. The analysis procedure allows one to distinguish between and measure the reactive hydrocarbons, those possessing greater pollution potential, and non-reactive hydrocarbons, those considered comparatively innocuous in the environment. The relatively simple, yet very efficient, method is capable of providing data that will permit more accurate and realistic assessment of the environmental quality degradation caused by emission of unburned or partially oxidized or degraded hydrocarbon fuels.

ACKNOWLEDGEMENTS

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