Report SAM-TR-78-37

LEVEL (2)

JET ENGINE EXHAUST ANALYSIS BY SUBTRACTIVE CHROMATOGRAPHY

AD A067898

Joseph J. Brooks
Diana S. West
John E. Strobel
Leonard Stamper
Monsanto Research Corporation
Dayton Laboratory
Station B, Box 8
Dayton, Ohio 45407

DDC
RECEIVED
APR 24 1979
C

December 1978

Final Report for Period 1 March 1977 - 24 July 1978

Approved for public release; distribution unlimited.

DDC FILE COPY

Prepared for

USAF SCHOOL OF AEROSPACE MEDICINE
Aerospace Medical Division (AFSC)
Brooks Air Force Base, Texas 78235

79 04 23 [illegible]

NOTICES

This final report was submitted by Monsanto Research Corporation, Dayton Laboratory, Station B, Box 8, Dayton, Ohio 45407, under contract F33615-77-C-0616, job order number 7930-11-38, with the USAF School of Aerospace Medicine, Aerospace Medical Division, AFSC, Brooks Air Force Base, Texas. Lieutenant Colonel Harry J. Suggs and Dr. James P. Conkle (SAM/VNL) were the Laboratory Project Scientists-in-Charge.

This technical report has been reviewed and is approved for publication.

James P. Conkle

JAMES P. CONKLE, Ph.D.
Project Scientist

R. Miller

RICHARD L. MILLER, Ph.D.
Supervisor

L J Enders

LAWRENCE J. ENDERS
Colonel, USAF, MC
Commander

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

(12) **REPORT DOCUMENTATION PAGE**	READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER SAM TR-78-37 · 2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER (9)
4. TITLE (and Subtitle) JET ENGINE EXHAUST ANALYSIS BY SUBTRACTIVE CHROMATOGRAPHY	5. TYPE OF REPORT & PERIOD COVERED Final rept. 1 Mar [redacted]77-24 Jul [redacted]78
	6. PERFORMING ORG. REPORT NUMBER (14) MRC-DA-839
7. AUTHOR(s) (10) Joseph J. Brooks, Diana S. West, John E. Strobel [redacted] Leonard Stamper	8. CONTRACT OR GRANT NUMBER(s) (15) F33615-77-C-0616
9. PERFORMING ORGANIZATION NAME AND ADDRESS Monsanto Research Corporation Dayton Laboratory, Station B, Box 8 Dayton, Ohio 45407	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 62202F (17) (16) 7930 11 38
11. CONTROLLING OFFICE NAME AND ADDRESS USAF School of Aerospace Medicine (VNT) Aerospace Medical Division (AFSC) Brooks Air Force Base, Texas 78235	12. REPORT DATE (11) Dec [redacted]78
	13. NUMBER OF PAGES 73
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office) (12) 77p.	15. SECURITY CLASS. (of this report) Unclassified
	15a. DECLASSIFICATION DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Subtractive chromatography	Jet engine exhaust	Alternate fuel
Sorbent sampling	Tenax-GC	
Hydrocarbon analysis	Ambersorb XE-340	
Organic analysis	JP-4	
Exhaust analysis	J85-5 Engine	

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This report describes the further refinement of a method for the sampling and analysis of organics in jet engine exhaust by chemical classes. Details for the selection, construction, and evaluation of the combination sorbent (Tenax-GC/Ambersorb XE-340) sampling system are given along with the rationale and operational parameters for the subtractive chromatography system that produces the organic

DD FORM 1473 1 JAN 73 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

401 965

20. ABSTRACT (continued)

class analysis. The significant improvements incorporated into both the sampling and analytical systems compared with previous systems used in a jet engine exhaust study of March 1975 are discussed. The capabilities of the system are illustrated by the analysis of actual jet engine exhaust samples from a J85-5 engine using JP-4 and an alternate fuel blend that simulates the higher aromatic content expected from shale and coal-derived fuels.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF ILLUSTRATIONS (continued)

LIST OF ILLUSTRATIONS (continued)

LIST OF TABLES

LIST OF TABLES (continued)

JET ENGINE EXHAUST ANALYSIS BY SUBTRACTIVE CHROMATOGRAPHY

INTRODUCTION

The incomplete combustion of nonhomogeneous hydrocarbon-based fuels in turbine engines produces an exhaust containing a complex mixture of organic compounds. To properly assess the associated health and environmental effects, it is necessary to analyze this organic exhaust fraction. Such analyses can be performed basically at three levels: (1) gross assessment of the total organic content; (2) determination of quantities of organic compounds according to classes or types; and (3) specific compound-by-compound quantitation.

Since each individual organic compound has an associated degree of toxicity and environmental impact, the ideal analysis is the accurate identification and determination of the quantity of each compound present. The USAF School of Aerospace Medicine has performed this type of analysis using coupled gas chromatography/mass spectrometry (GC/MS) to identify and quantitate several hundred organic compounds in engine exhaust. However, the procedure is extremely complex, time-consuming, and costly.

At the other extreme, total organic analyses are of little value for studies requiring health and environmental information since one must make the erroneous assumption that all of the organic constituents have the same toxicities and propensities for affecting the environment. It is known that part of the hydrocarbons emitted are, in fact, nonreactive and have little or no effect on health.

The second alternative (i.e., organic class analysis) may well represent the most workable compromise between the detailed, yet very costly, compound-by-compound evaluation and the non-definitive total organic analysis. In this case, the assumption of similar toxicities and environmental reactivities within a particular class of compounds may be a reasonable approximation. Such a technique is of value for more routine analyses, particularly where previous detailed studies have established general profiles for the organic emissions.

This report details the refinement of an analytical scheme based on solid sorbent sampling of the exhaust stream followed by organic class analysis using subtractive chromatographic techniques.

In March 1975 MRC, under contract with the USAF Aerospace Research Laboratories (ARL), participated in a joint program with the USAF Aero-Propulsion Laboratory (APL), the USAF School of

Aerospace Medicine (SAM), and A. D. Little, Inc., aimed at characterizing organic emissions in the exhaust from a T56 combustor rig located at APL. The goal of this program was to obtain a profile of the organic exhaust constituents so that a more accurate assessment could be made of the potential environmental and toxicological effects of jet engine exhaust.

The assembling of expertise from five organizations provided a multi-faceted analytical program made up of varying approaches reflecting specialized talent or analytical capabilities of each organization. It was hoped that the data obtained by the different organizations would be corroborative as well as supplemental so that the results could be established with some degree of confidence. Unfortunately, the results obtained in this joint effort showed only qualitative agreement. The lack of quantitative agreement emphasized the need for further refinement of the techniques used.

The approach used by Monsanto Research Corporation (MRC) for these studies was organic class analysis by subtractive chromatography. The details of the sampling and analytical systems used by MRC in these studies are available in the literature (1). The sampling system (Fig. 1) consisted of a combination sorbent trap containing sections of Tenax GC and Carbosieve B. This trap was cooled to -78°C with crushed solid CO_2 during sampling. The heart of the analytical system was the column arrangement shown in Figure 2. The collected exhaust samples were thermally desorbed from the sorbent traps into the analytical system and passed through a column containing 1,2,3-tris(2-cyanoethoxy)propane (TCEP) as the stationary phase. This column retained water and oxygenated and aromatic compounds and allowed the paraffinic and olefinic compounds to elute rapidly. The switching valve was positioned to direct the flow from the TCEP column into a removable subtractor column and subsequently into a flame ionization detector (FID A). The two sections of the subtractor column removed olefinic (Ag_2SO_4/H_2SO_4) and oxygenated ($PdSO_4/H_2SO_4$) compounds. At a predetermined time corresponding to the elution of n-decane from the TCEP column, the valve was switched to direct the water, aromatics, and oxygenates into the Chromosorb 105 column, which was exterior to the GC oven and maintained at ambient temperature. Due to the hydrophobic nature of Chromosorb 105, the water passed through quickly. After the water was eluted, the Chromosorb 105 column temperature was raised to facilitate the elution of the aromatic and oxygenated portion of the sample, which was detected at FID B.

In order to obtain the complete analysis, it was necessary to have two samples of known sample volumes taken under identical conditions. The first sample was analyzed without the subtractor in the system and yielded the following data: (a) FID A response = paraffins + olefins (+ light oxygenates), and (b) FID B response = oxygenates + aromatics. Oxygenated compounds with

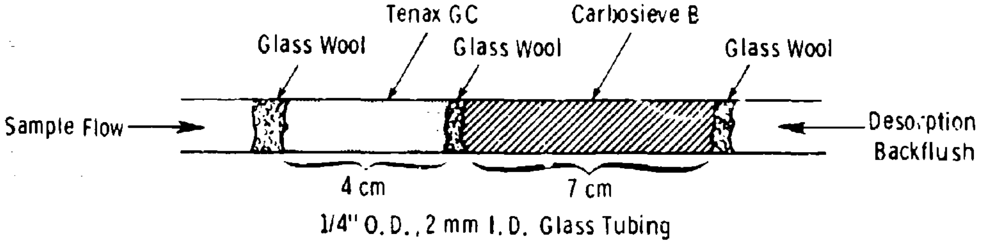


Figure 1. Sampling tube used for March 1975 jet engine exhaust studies.

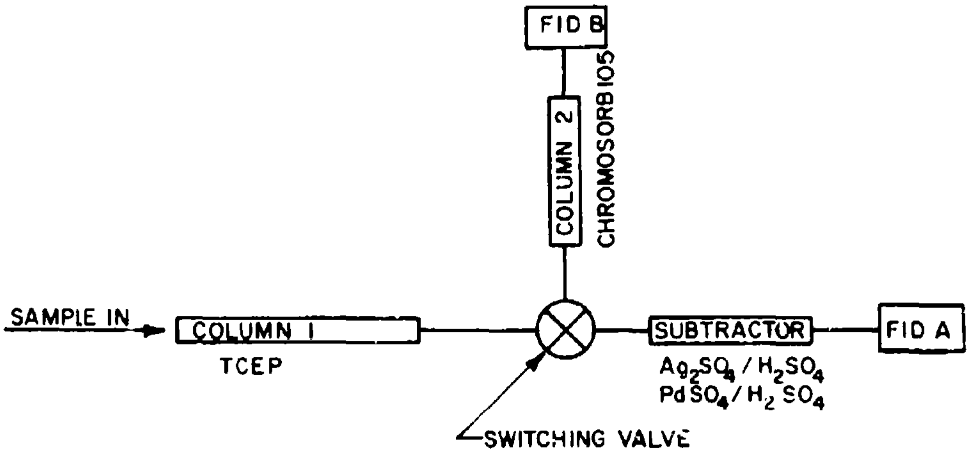


Figure 2. Schematic for organic class analysis system used in March 1975 jet engine exhaust studies.

retention times on TCEP shorter than that of propionaldehyde eluted with the paraffins and olefins before the valve was switched. Thus, they were included in the FID A response and grouped with the olefins since they were also removed by the subtractor. The second sample was analyzed with the subtractor in the system and yielded the following data: (a) FID A response = paraffins (total unreactive), and (b) FID B response = oxygenates + aromatics.

Olefins were obtained by difference by subtracting the FID A response of the second sample from the FID A response of the first sample. The total reactive hydrocarbon value was obtained by summing the values for olefins and oxygenates + aromatics. A total hydrocarbon (THC) value was obtained by combining the total reactive and total unreactive hydrocarbon values.

The data obtained from these analyses are summarized in Table 1. At the same time that these samples were being collected, on-line total hydrocarbon (THC) measurements were being made by Aero-Propulsion Laboratory (APL) personnel. A comparison of the THC values obtained by MRC and APL is given in Table 2. At best only about 70% of the total hydrocarbons were recovered by the MRC sampling system.

TABLE 1. HYDROCARBON ANALYSES SUMMARY (ppmC/%) FOR MARCH 1975 JET ENGINE EXHAUST STUDIES

Fuel (inlet pressure)	Olefins + light oxygenates	Oxygenates + aromatics	Total reactive	Total unreactive	THC
JP-4 (15 psig)	54.6/12.7	257/59.8	312/72.6	118/27.4	430
JP-4 (33 psig)	22.8/25.6	52.5/59.0	75.4/84.7	13.6/15.3	89.0
JP-4 (50 psig)	10.2/34.9	17.0/58.2	27.3/93.5	1.88/6.4	29.2
JP-5 (33 psig)	-	77.7/66.4	-	-	117
JP-8 (33 psig)	-	81.7/74.3	-	-	110
Alternate fuel blend (33 psig)	16.7/22.6	50.8/68.6	67.5/91.2	6.48/8.8	74.0
Alternate fuel blend (33 psig)	18.2/19.8	62.4/67.8	80.8/87.6	11.4/12.4	92.0
Isooctane	6.82/29.9	7.33/32.1	14.1/61.8	8.70/38.2	22.8

TABLE 2. COMPARISON OF MRC AND APL TOTAL HYDROCARBON (THC) RESULTS FOR THE MARCH 1975 JET ENGINE EXHAUST STUDIES

Fuel (inlet pressure)	MRC THC (ppmC)	APL THC (ppmC)	MRC THC/ APL THC
JP-4 (15 psig)	430	636	68
JP-5 (33 psig)	117	337	35
JP-8 (33 psig)	110	203	54
Alternate fuel blend (33 psig)	92.0	154	60
JP-4 (33 psig)	89.0	165	54
Alternate fuel blend (33 psig)	74.0	113	66
JP-4 (50 psig)	29.2	57	51
Isooctane (33 psig)	22.8	32	71

Because of the low recoveries and several desirable refinements of the system that became obvious during the course of these studies, a new study was initiated to improve the quality of the data obtainable from this analytical approach.

This study contained three areas of investigation:

1. Develop improved solid sorbent sampling devices for use with subtractive chromatography analysis techniques.

2. Develop improved capability in subtractive chromatography analysis techniques, and

3. Conduct a field demonstration of the solid sorbent sampling/subtractive chromatography analysis system.

This report contains the results of these investigations.

EXPERIMENTAL PROCEDURE AND DISCUSSION

Development of the Sampling System

Choice of Sorbent Materials

The poor recoveries obtained by the previous sampling system as compared with the on-line THC values for the March 1975 studies indicated a need for improvement in the solid sorbent sampling technique. In an attempt to explain these low recoveries, samples were collected from the APL combustor rig under similar conditions to those used in the March 1975 studies. The sampling system was modified by placing an evacuated bulb after the sorbent trap to collect the effluent that passed through the trap. Although the experiment was qualitative, the results showed that the sample collected in the bulb contained organic compounds which were of the same general composition as those collected in the sorbent trap. These results confirmed that the trap capacities had been exceeded in the March 1975 studies with subsequent low THC recoveries.

At least three factors could singly or in combination be responsible for exceeding the trap capacities:

1. Inefficient sorbent material
2. Insufficient quantity of sorbent
3. Improper sample volume (i.e., flow rate and/or time)

It was decided to examine the proper relationship between these factors to develop a sorbent trapping system that would be efficient for recovering jet engine exhaust samples.

Under an internally funded program MRC has been actively pursuing the study of solid sorbent materials as sampling media for organic compounds. One of the major products to come out of these efforts is a detailed compilation of information from the major sources of expertise in the area of solid sorbent sampling. During the process of compiling this information a new series of sorbent materials that show promising sorbent characteristics was identified. These are the Ambersorb resins (XE-340, XE-347, XE-348) produced by Rohm and Haas Company. The unique feature about these sorbent materials is that they possess sorbent characteristics that are intermediate between the porous polymer type materials and the activated charcoal. They are produced by a process which "carbonizes" a porous polymer material. The product is a hard, shiny, black-beaded material. The promotional literature suggests that these materials can be tailored to be more porous polymer-like or more charcoal-like depending upon the degree of carbonization. The promising forecast for these materials is that they will combine the best qualities of porous polymers and activated charcoal to "bridge the gap" between these types of materials. For example, one would hope that they would have the ability to trap highly volatile compounds but not be adversely affected by water, a highly attractive feature for exhaust sampling.

Some preliminary evaluations have been made of the sorbent characteristics of Ambersorb XE-340 (the most polymer-like of the series). Holzer et al. (6) determined the specific retention volumes for a group of normal alkanes on Ambersorb XE-340 at 25°C. The results of this work are given in Table 3.

TABLE 3. SPECIFIC RETENTION VOLUMES (Vg) FOR SELECTED ALKANES ON AMBERSORB XE-340

Compound	Vg at 25°C (liters/g)
Ethane	0.8
n-Propane	8.5
n-Butane	81.0
n-Pentane	880.0
n-Hexane	7600.0
n-Heptane	74000.0

We have evaluated Ambersorb XE-340 for an EPA research program (EPA Contract No. 68-02-2774) and have obtained similar results (3). Our studies involved the determination of retention volumes at several temperatures for various hydrocarbons on a column containing a known quantity of Ambersorb XE-340. Figure 3 is a plot of the log of the $^{FET}V_g$ (retention volume corresponding to the first detectable elution of a compound) versus 1/T (°K) for the studies conducted with Ambersorb XE-340 at MRC. The time associated with each of the curves for the various compounds represents the maximum sampling time before compound breakthrough for a sample collected at 20°C using 1 gram of XE-340 and a flow rate of 30 ml/min. Based on the indicated effectiveness of XE-340 for highly volatile compounds and the anticipated sampling parameters, we decided to pursue the use of this material for collecting the very volatile components in jet engine exhaust.

Tenax-GC is probably the most widely used and most thoroughly characterized sorbent material for sampling volatile organic compounds in air. It has very desirable characteristics including high temperature limit (350°C) and low background bleed. It is generally considered to be an effective sampling material for compounds C_6-C_7 and above. This, of course, is very dependent on the sampling parameters. We have conducted extensive studies of Tenax-GC as a sorbent material using a selection of organic compounds representing a wide range of volatilities and polarities (4). Table 4 contains the capacity data and theoretical sampling times for these test compounds.

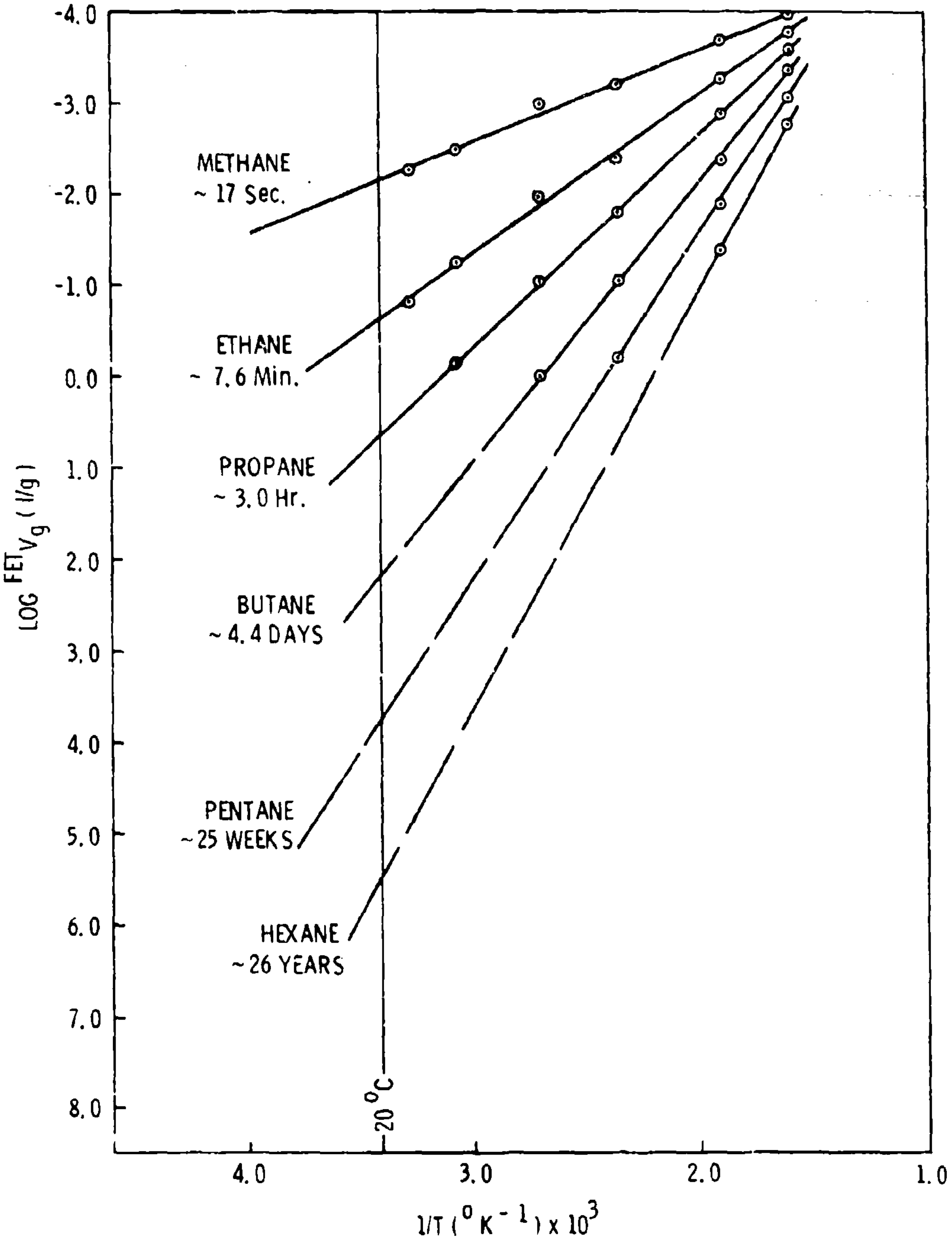


Figure 3. Plot of log ^{FET}Vg versus 1/T for standard gases on Ambersorb XE-340.

TABLE 4. CAPACITIES AND THEORETICAL SAMPLING TIMES FOR TEST COMPOUNDS ON TENAX-GC AT 20°C

No.	Compound name	FETVg (liters/g)	Sampling time[a]
1	n-Hexadecane	1.3×10^5	41 years
2	Hexachloro-1,3-butadiene	1.15×10^4	19 weeks
3	Succinonitrile	1.04×10^4	17 weeks
4	iso-Octane	0.532	9 minutes
5	Bis-(2-chloroethyl)ether	1.06×10^4	17 weeks
6	Ethylene glycol	120	34 hours
7	n-Butane	0.16	2.6 minutes
8	Propylene oxide	3.14	52 minutes
9	Acrylonitrile	9.35	2.6 hours
10	Phenanthrene	1.9×10^6	61 years
11	4-Bromodiphenyl ether	2.4×10^6	75 years
12	o-Nitroaniline	2.9×10^4	48 weeks
13	Naphthalene	3260	5 weeks
14	1,2,4-Trichlorobenzene	1.57×10^4	26 weeks
15	o-Nitroanisole	1.14×10^4	19 weeks
16	Benzene	82	23 hours
17	Benzyl chloride	1.02×10^4	17 weeks
18	Phenol	5460	9 weeks

---

[a] Assuming 0.5 g of sorbent material and 30 ml/min sampling rate.

Based on the capacity data that we had on these two sorbent materials, indicating that a sufficiently broad range of compounds can be collected, it was decided that a sampling system using a combination of these materials should be evaluated. Two attractive features of this combination trap are:

1. Both materials have high temperature limits (>350°C) and can be thermally desorbed under the same conditions making containment in the same tube and single analysis possible.

2. Both materials are hydrophobic and should be minimally affected by the water in exhaust gases.

Once the selection of sorbent materials had been made, a calculation of theoretical trap capacities was made based on expected sampling parameters to see if this combination could be expected to efficiently recover the organics from exhaust samples. The design parameter that was used as a starting point for these calculations was the sample tube size (1/4 in. O.D. x 6 in. long) (0.6 cm O.D. x 15.2 cm long). This was chosen since the tube furnace that was to be used for thermal desorption of the samples accommodated tubes of these dimensions. It was found that a 1/4 in. O.D. x 3/16 in. I.D. x 6 in. long (0.6 cm O.D. x 0.5 cm I.D. x 15.2 cm long) stainless steel tube conveniently contained ∿0.2 g of Tenax-GC (8 cm) and ∿0.4 g of Ambersorb XE-340 (5 cm). Table 5 can be used to illustrate the types of capacities that would be expected for a tube containing these quantities of sorbent materials.

TABLE 5. THEORETICAL CAPACITIES FOR REPRESENTATIVE COMPOUNDS AT 20°C ON COMBINATION SORBENT TRAPS

Sorbent	Compound	Capacity
Tenax-GC:	Benzene	16.4 (liters/0.2g)
	Propylene oxide	0.6 (liters/0.2g)
	n-Butane	0.03 (liters/0.2g)
Ambersorb XE-340:	n-Butane	42.4 (liters/0.4g)
	Ethane	0.09 (liters/0.4g)
	Methane	0.004 (liters/0.4g)

The quantity of exhaust sampled in the March 1975 studies was normally ∿0.8 liter. This amount proved to be more than sufficient to carry out the class analysis, and the signal had to be attenuated to keep the recorder trace on scale. For this reason a smaller sample size (100 ml) should provide sufficient sample to complete the analysis. It was decided that a sample flow rate of 10 ml/min for 10 minutes, providing a total of 100 ml of sample, would be a convenient size for this program. From the capacity data using the described tube design (0.2 g Tenax-GC and 0.4 g Ambersorb XE-340) and sampling parameters (10 ml/min for 10 minutes) one could expect to retain essentially all of the organics except methane.

Conditioning of Sorbent Materials

It is usually the case that commercially available sorbent materials are not suitable for use as sampling media in the condition received because of interfering background impurities that are desorbed under the conditions used for sample desorption. The degree to which this is a problem depends largely upon the individual sampling problem, particularly the comparative level of the sample to be collected with that of the background impurities. In any case it is essential to do at least a minimum preconditioning of the sorbent material which corresponds to cycling it through the desorption procedure and evaluating the background level.

As an extra precaution we used a more stringent "clean-up" procedure for the sorbents used in the jet exhaust studies. This procedure involved both solvent clean-up and thermal preconditioning. The details for each of the sorbents are as follows:

Ambersorb XE-340--The Ambersorb XE-340 resin was conditioned by a series of solvent extractions using methylene chloride, methanol, and distilled water. Each extraction was for 24 hours in a Soxhlet extractor. After the final extraction, the XE-340 was dried in a vacuum oven at ∿100°C overnight and stored in a vacuum desiccator until being packed into sampling tubes.

Tenax-GC--The Tenax-GC was preconditioned using a series of Soxhlet extractions involving pentane (24 hours), ethyl acetate (24 hours), and methanol (72 hours). Following the final extraction, the Tenax was dried in a vacuum oven at ∿100°C overnight and stored in a vacuum desiccator until being packed into the sampling tubes.

Preparation of Sorbent Sampling Tubes

The sorbent sampling tubes to be used in the jet engine exhaust studies were made of 1/4 in. O.D. x 3/16 in. I.D. x 6 in. long (0.6 cm O.D. x 0.5 cm I.D. x 15.2 cm long) stainless steel tubing. The choice of stainless steel was made to provide ruggedness to the sampling tubes and prevent breakage that was experienced in earlier tests due to extremes of heat and stresses during sampling. The problems with compound reactivity on metal surfaces and higher backgrounds are not so critical at the high concentrations that are anticipated in exhaust samples.

The stainless steel tubes were filled with ∿0.2 g Tenax-GC and ∿0.4 g Ambersorb XE-340 separated by a plug of silanized glass wool and contained by similar plugs at each end. Figure 4 is a schematic of the sampling tube.

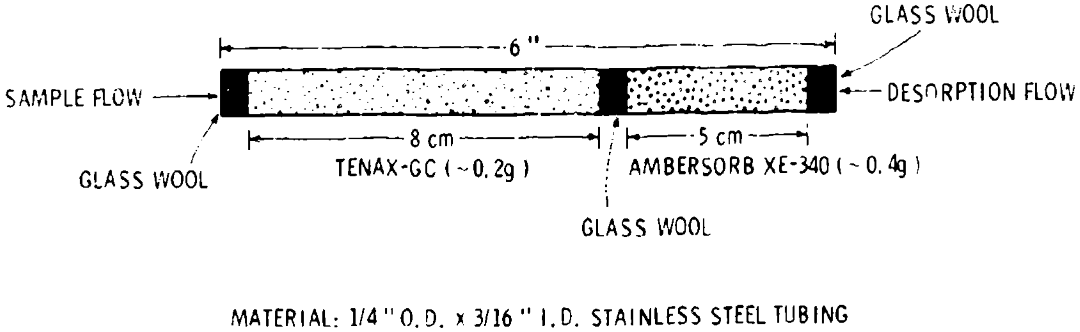


Figure 4. Combination sorbent sampling tube for jet engine exhaust studies.

After packing, the tubes were thermally conditioned at 300°C under a flow of He for 16 hours. As indicated in Figure 4, the sample flow direction is through the Tenax first, then through the Ambersorb. This allows the higher molecular weight compounds to be collected on the Tenax while the more volatile compounds are collected on the Ambersorb. Desorption is in the opposite direction (backflush) so that the less volatile compounds never come in contact with the Ambersorb.

Evaluation of Sampling Characteristics of Sorbent Tubes

The combination Tenax-GC/Ambersorb XE-340 sorbent sampling tubes were evaluated using known concentrations of test compounds generated on the standard sample generation system described in Appendix A. The first compound to be evaluated was heptane. It was decided to generate these samples at relatively high levels to test the capacities of the traps in single compound concentration ranges that would be similar to the total hydrocarbon concentrations anticipated for exhaust samples. Such conditions would represent the "worst case" for any single compound. Heptane vapors were generated at a level of ~400 ppm (~2800 ppmC) in nitrogen using the dynamic generation system. Samples were collected for 2, 4, 5, 6, 8, and 10 minutes at 10 ml/min using the combination sorbent traps. These samples were subsequently thermally desorbed at 300°C using a modified Chromalytics Concentrator and analyzed with FID. A plot of sampling time versus integrator counts is shown in Figure 5. The linear plot indicates a quantitative recovery of the heptane. In addition, a backup tube collected in series with the 10-minute sample showed no breakthrough of heptane.

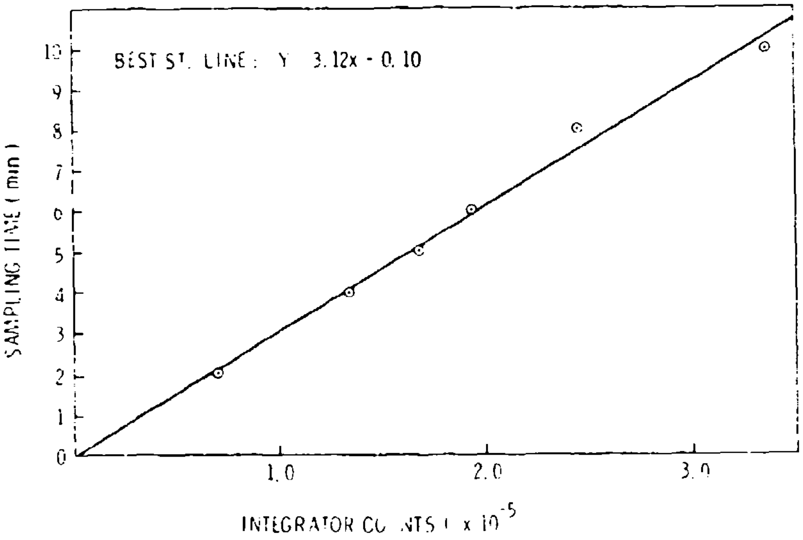


Figure 5. Sampling time versus integrator counts for 400 ppm heptane at 10 ml/min.

The second compound to be evaluated was pentane. There was some concern about our ability to recover pentane quantitatively since Holzer (6) had cited an inability to quantitatively desorb pentane from Ambersorb XE-340 at 300°C (the desorption temperature we used). Pentane was generated at ∿520 ppm (∿2600 ppmC). Samples were collected for 2, 4, 5, 6, 8, and 10 minutes. As in the case of heptane, the linear plot of sample time versus integrator counts (Fig. 6) indicates quantitative recovery. No breakthrough was observed in the backup tube for the 10-minute sample.

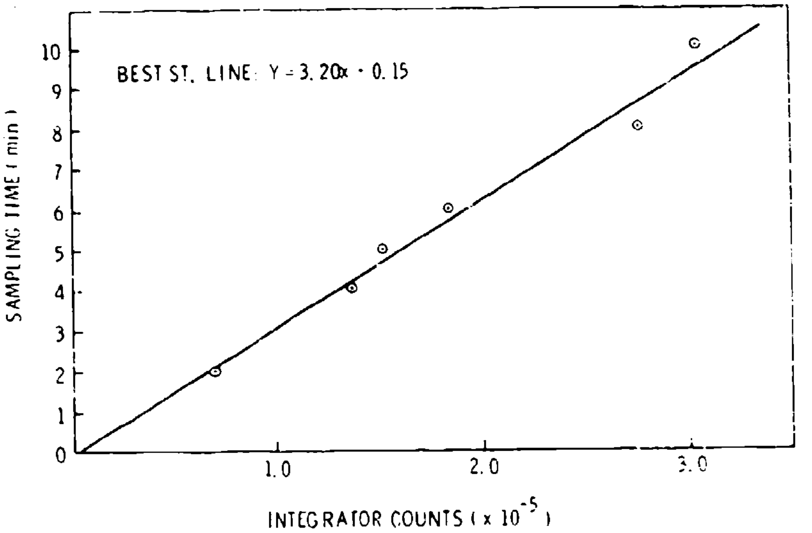


Figure 6. Sampling time versus integrator counts for 520 ppm pentane at 10 ml/min.

The combination sampling tube was also evaluated using methanol as a representative volatile oxygenate. These types of polar compounds are the ones that have traditionally given problems with activated charcoal sampling due to reactivity and/or irreversible adsorption. Methanol was generated at ∿1080 ppm using the sample generation system and samples of 1, 2, 4, 5, 6, 8, and 10 minutes were collected at 10 ml/min. The plot of sampling time versus integrator counts is shown in Figure 7. Although not as linear as the plots for pentane and heptane, there appears to be satisfactorily consistent recovery of methanol using this technique. Two of the points (4 and 10 minutes) seem to deviate appreciably from the line. If these two points are excluded, an excellent straight line relationship is obtained for the remaining points as indicated by a correlation coefficient of 0.9997. Unfortunately, each of these points represents a single sample, and due to time restrictions it was not possible to repeat the experiments.

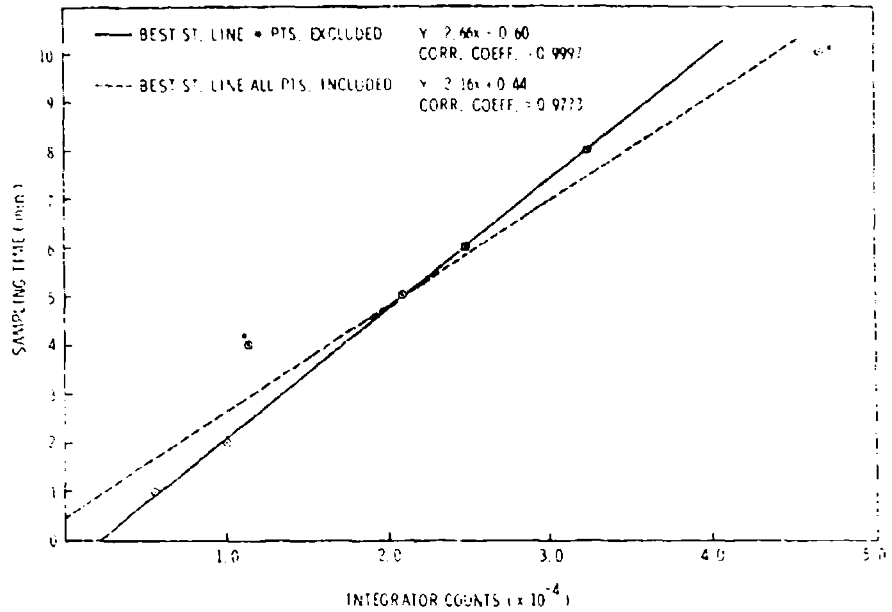


Figure 7. Sampling time versus integrator counts for 1080 ppm methanol at 10 ml/min.

The combination trap was also evaluated using a mixture of compounds to be used as calibration standards for the jet engine exhaust studies. The mixture consisted of 1 ml each of pentane, heptane, decane, benzene, toluene, m-xylene, and p-xylene. This was introduced into the sample generation system at the rate of 0.0121 µl/min and a diluent carrier flow of 1000 ml/min. No further dilution was made. The concentrations of the various components in the effluent from the sample generation system are given in Table 6.

TABLE 6. CONCENTRATION OF TEST MIXTURE COMPONENTS IN SAMPLE GENERATION SYSTEM EFFLUENT

Compound	ppm	ppmC
Pentane	0.37	1.84
Heptane	0.33	2.28
Decane	0.22	2.20
Benzene	0.48	2.88
Toluene	0.40	2.80
m-Xylene	0.35	2.76
p-Xylene	0.35	2.76

A sample was collected for 17 minutes at 10 ml/min using the combination Tenax/Ambersorb trap. The chromatogram for this sample is shown in Figure 8. The "subtracted" and "unsubtracted" traces refer to the splitting of the sample to achieve analysis with and without the olefin/oxygenate subtractor respectively (see section on "Development of the Analytical System," p. 25). Also included is the chromatogram for the backup tube (bottom two traces) used in series with the sampling tube during sample collection. The recovery of these compounds was excellent, and no significant breakthrough above tube background was detected.

A similar experiment was run with the addition of 4 times the volume of water (compared to the volume of sample added). This produced a concentration of ~65 ppm water. There was no detectable change in the recovery efficiency, and no sample breakthrough occurred as the result of the addition of water.

In order to evaluate the effectiveness of the combination trap for collecting gaseous compounds, the sample generation system was modified to accommodate gas cylinders containing standard gas concentrations. This series of studies involved the use of two sorbent tubes in series to check for sample breakthrough. A 1060 ppm methane standard was collected at 10 ml/min for 10 minutes. Analysis of the two tubes showed definite breakthrough with as much or more of the CH_4 collected on the second tube as the first. Figure 9 contains the chromatograms for the analysis of the two tubes from a similar experiment using 1025 ppm ethane. Only a very small amount (<2%) of the ethane was detected on the second tube. Ethylene (1010 ppm) showed no detectable breakthrough when sampled at 10 ml/min for 10 minutes. These data indicate that the combination Tenax/Ambersorb trap should efficiently collect all volatile organic compounds except methane at room temperature under the anticipated sampling conditions (i.e., 10 ml/min for 10 minutes).

The evaluation of the sorbent traps was much less extensive than had originally been planned because of limitations of time and funding. Nevertheless, the preliminary data indicated that this selection of sorbent materials should be effective in collecting the organic compounds from jet engine exhaust.

Differences From Previously Used Sampling System

One of the main thrusts of the current program was to improve the sampling system used in the March 1975 studies so that samples could be collected more efficiently and conveniently. It is worthwhile to enumerate the differences in this sampling system compared to that used in the 1975 studies. The following areas differ significantly in the two systems:

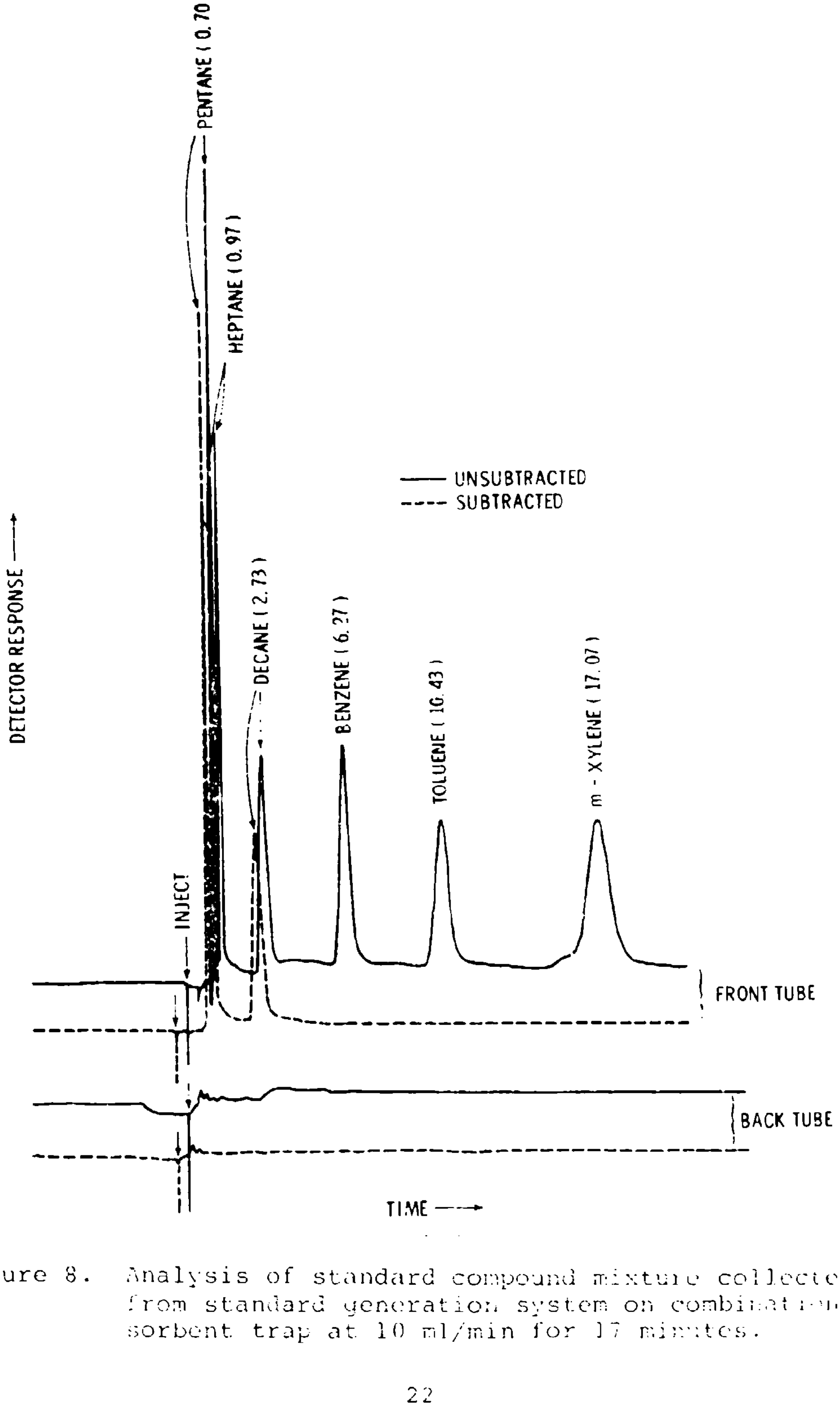


Figure 8. Analysis of standard compound mixture collected from standard generation system on combination sorbent trap at 10 ml/min for 17 minutes.

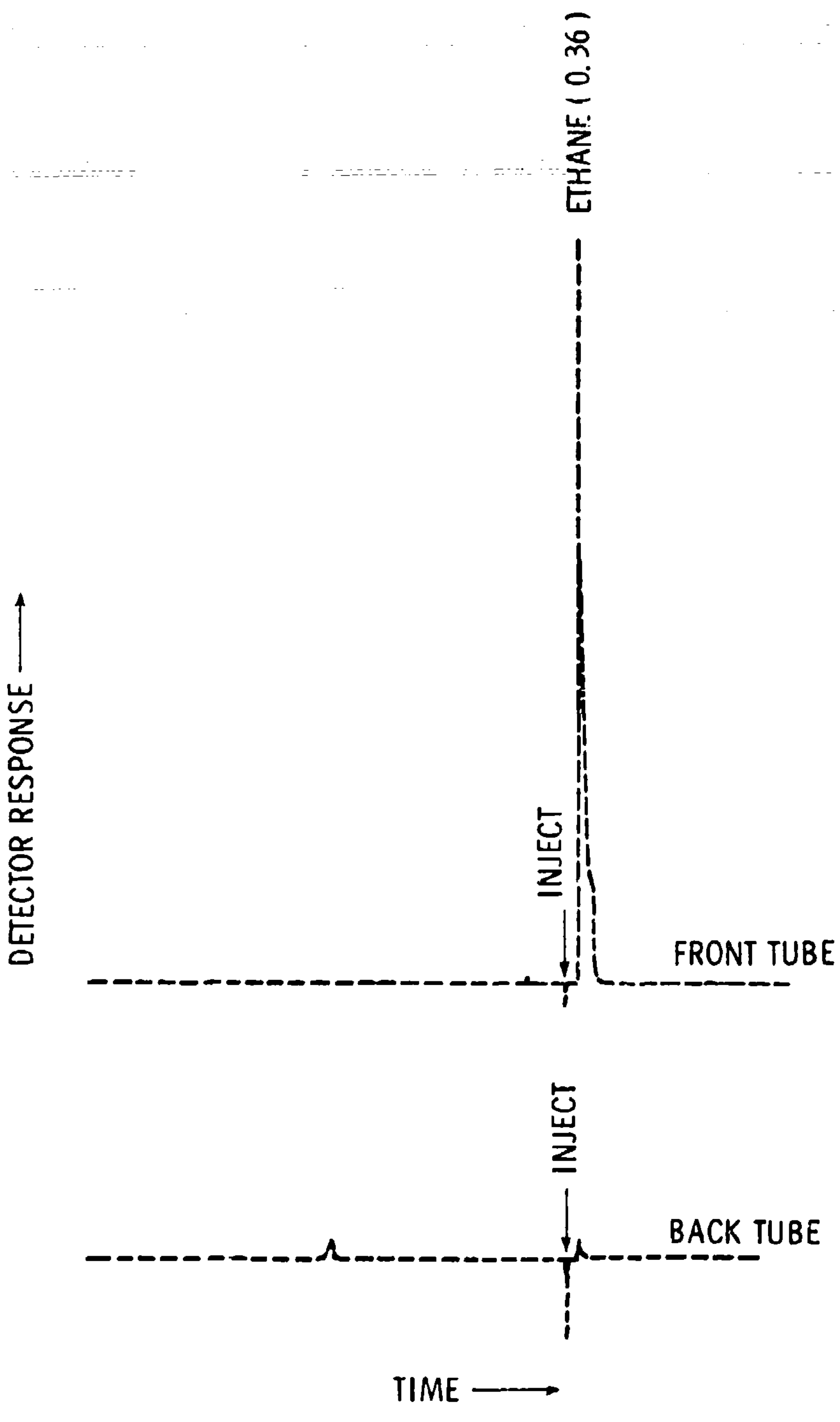


Figure 9. Analysis of ethane from sampling tube and backup tube collected at 1025 ppm at 10 ml/min for 10 minutes.

Material - The sampling tubes used in the 1975 studies were glass. As discussed earlier, the tubes used in this study were stainless steel for added strength.

Tube Capacity - In both cases the sample tubes were made of ¼ in. (0.6 cm) O.D. tubing and were 6 in. (15.2 cm) long. However, the tubes used in 1975 had a 2 mm I.D. while the current tubes have a 5 mm I.D. providing for ~6 times the volume of sorbent material.

Sorbent Material - In both studies, combination sorbent traps were used. In 1975 the sorbents were Tenax-GC and Carbosieve B. The current tubes contain Ambersorb XE-340 rather than Carbosieve B.

Sampling Mode - In 1975 the traps were cooled to dry ice temperature during sampling. The current studies were conducted at room temperature.

Sampling Rate - In 1975 the sampling rate was ~60-70 ml/min. The current studies used sampling rates of 10 ml/min.

Sampling Time - Typical sampling times during the 1975 studies were ~13 minutes. Ten-minute sampling times were normally used for these studies.

Flow Rate Control
and Measurement - In 1975 the flow through the sampling tube was controlled by a needle valve, and measurements of the flow rate were made continuously during the sampling period using a soap bubble meter. The flows charged appreciably during the sampling period. The current method used a mass flow sensor/controller to maintain the flow at a preset 10 ml/min during the sampling period.

In summary, all three of the areas (sorbent material, quantity of material, and sample volume) that most significantly affect sampling capacity were modified in the current sampling system to produce a more effective system for collecting organics in jet engine exhaust. The success of these modifications is illustrated by the THC recovery data compared with on-line data presented in the section on "Sampling and Analysis of Jet Engine Exhaust" (p. 35).

Development of the Analytical System

Evaluation of Aromatic/Oxygenate Differentiation Techniques

One of the major improvements of the analytical method that was sought during these studies was a technique for separately estimating the aromatic and oxygenate content of the exhaust samples. The previous analyses (March 1975) had lumped these into a single category (aromatics and oxygenates) of "reactive" hydrocarbons. Two approaches were evaluated as possible solutions to the aromatic/oxygenate differentiation.

The first approach was to use $PdSO_4/H_2SO_4$ on Chromosorb W as a subtractor column. This material had already been shown to be an effective oxygenate subtractor as demonstrated by the removal efficiencies in Table 7.

TABLE 7. EFFICIENCY OF $PdSO_4/H_2SO_4$ AS AN OXYGENATE SUBTRACTOR (80°C)

Compound	Conc., µg	Efficiency, % compound removed
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

It was hoped that aromatic compounds passing through this subtractor would not be retained and thus a basis for the differentiation of aromatic from oxygenated species would be realized.

The initial experiment to examine this possibility showed promise. An eight-port switching valve was configured in such a way as to allow a ∿25 cm section of Teflon tubing (∿2 mm I.D.) packed with $PdSO_4/H_2SO_4$ on Chromosorb W to be manually switched in or out of the chromatographic column flow system. The responses from the FID detection of samples of benzene with and without the subtractor at a temperature of 30°C are shown in Figure 10. The responses are essentially identical indicating that only an insignificant amount, if any, of the benzene was retained by the subtractor.

The case for toluene, Figure 11, was much different. A comparison of the FID responses for toluene with and without the subtractor at 30°C (Fig. 11) showed that a significant portion

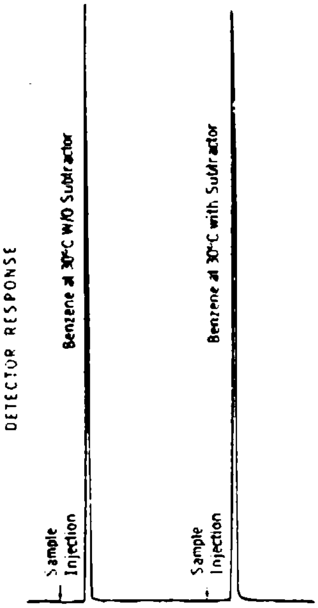


Figure 10. FID response for identical 0.2 μl (176 μg) injections of benzene without (w/o) and with a $PdSO_4/H_2SO_4$ subtractor in the chromatographic column flow system at a temperature of 30°C.

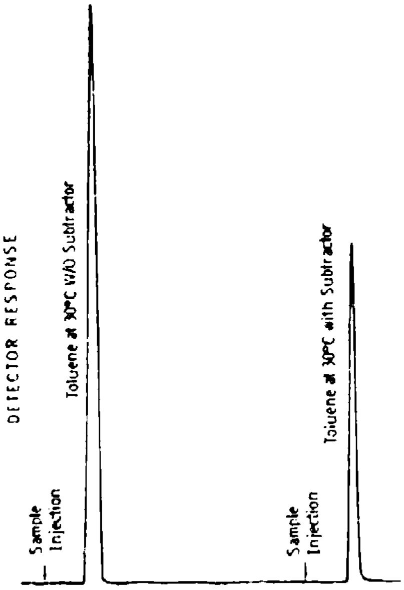


Figure 11. FID response for identical 0.2 μl (173 μg) injections of toluene without (w/o) and with a $PdSO_4/H_2SO_4$ subtractor in the chromatographic flow system at a temperature of 30°C.

of the toluene was removed by the subtractor. The effect was more dramatically illustrated with *m*-xylene in which case no FID response was obtained with the subtractor in the system indicating total removal of the *m*-xylene.

At elevated temperatures the subtraction efficiency of $PdSO_4/H_2SO_4$ for aromatics was increased. Figure 12 contains the FID responses for samples of benzene with and without the subtractor at 100°C. Only a very small portion of the benzene was unretained. Both toluene and *m*-xylene were completely removed at 100°C. It was hoped that perhaps at elevated temperatures the efficiency of $PdSO_4/H_2SO_4$ for oxygenate removal might be reduced. Methanol was selected as a representative oxygenate and evaluated with $PdSO_4/H_2SO_4$ at 100°C. The removal efficiency was still 100%. A summary of these data is contained in Table 8.

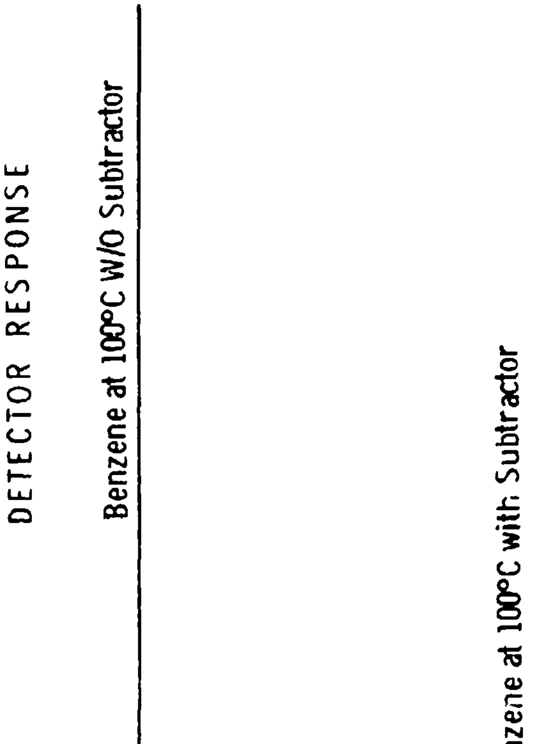


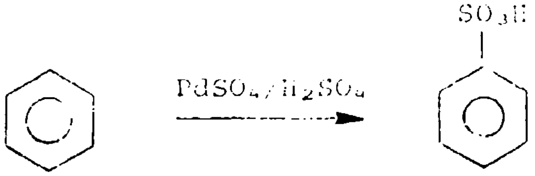
Figure 12. FID response for identical 0.2 μl (176 μg) injections of benzene without (w/o) and with a $PdSO_4/H_2SO_4$ subtractor in the chromatographic flow system at a temperature of 100°C.

TABLE 8. $PdSO_4/H_2SO_4$ SUBTRACTOR EFFICIENCY DATA

Compound	Mass (μg)	% Removed @30°C	% Removed @100°C
Benzene	176	0.74	89.8
Toluene	173	58.4	100
m-Xylene	173	100	100
Methanol	159	100	100

These data show that $PdSO_4/H_2SO_4$ is definitely not suitable for obtaining aromatic/oxygenate differentiation.

The explanation for the removal of aromatic compounds by $PdSO_4/H_2SO_4$ most likely involves the formation of the aromatic sulfonic acid according to the reaction



which is probably catalyzed by the palladium. The resulting sulfonic acid is then retained through specific interaction with the Pd in the liquid phase. Such an explanation is consistent with the more facile removal of toluene and xylene compared to benzene since the sulfonation of these compounds is more readily accomplished due to the activation effect of the methyl groups. A higher temperature would also be expected to promote this reaction as was observed.

Because the $PdSO_4/H_2SO_4$ subtractor also efficiently removed aromatic compounds, it was of no value in differentiating between oxygenates and aromatics. This subtraction ability was used, however, to achieve a more accurate interpretation of the data for the aromatics and oxygenate fraction than was obtained in the previous study (see section on "Output from Analysis," p. 33).

A second approach that was evaluated for the differentiation of aromatics/oxygenates involved the use of the lanthanide chelate, tris-(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato)europium (III), commonly called $Eu(fod)_3$. The rationale behind this approach is that $Eu(fod)_3$ interacts with oxygenated compounds due to its capacity for accommodating extra electron donors in its coordination sphere. This interaction forms the basis for the so-called "nmr shift reagent" phenomenon of which $Eu(fod)_3$ is one of the more widely used (8). $Eu(fod)_3$ has been incorporated into the stationary phase of a chromatographic column in order to study the interactions between oxygenate compounds and the europium chelate (2). It was hoped that a similar approach could be used to selectively retard oxygenated compounds while allowing the aromatics to pass through the column, thus achieving the aromatic/oxygenated differentiation.

To test this concept a column was prepared as follows. A 0.13 molar solution of Eu(fod)$_3$ was prepared by dissolving 0.2022 g Eu(fod)$_3$ in 1.5 g squalane. The solution was dissolved in 10 ml CH_2Cl_2 and added to a slurry of 8.5 g Chromosorb P (60/80 mesh) in 20 ml CH_2Cl_2. After mixing, the CH_2Cl_2 was removed using a rotary evaporator and a water aspirator at room temperature. This packing was placed in a 4 in. x ¼ in. O.D. (10 cm x 0.6 cm) x 2 mm I.D. glass column and conditioned overnight at 100°C.

Retention times obtained on this column for a selected group of compounds at 80°C and carrier flow (He) of 60 ml/min are given in Table 9.

TABLE 9. RETENTION TIMES FOR SELECTED COMPOUNDS ON Eu(fod)$_3$ COLUMN

Compound	Minutes
n-Hexane	0.55
n-Decane	14.78
Methanol	0.29
Acetone	0.32
Benzene	0.82

From these retention times it is obvious that such a column is unsatisfactory for achieving the oxygenate/aromatic differentiation. The problem lies in the fact that it is necessary to incorporate the Eu(fod)$_3$ in some solution as the stationary phase in order to achieve the best contact for the oxygenate interaction (i.e., in solution). Unfortunately this "solvent" (in this case squalane) functions as a normal chromatographic stationary phase and retains the compounds that do not interact with Eu(fod)$_3$ (e.g., aromatics) according to normal chromatographic principles (i.e., vapor pressure, solubility, polarity). The interactions between the oxygenates and the Eu(fod)$_3$ are too weak to offset the gross effect of the squalane solvent, and the column functions very similarly to a column which has squalane as its liquid phase.

Subsequent to these studies we have learned of the successful use of Eu(fod)$_3$ coated on controlled porosity glass beads without a solvent as an oxygenate subtractor (9). The details of this work were unavailable at the time that the sampling was conducted so that this technology could not be used in the current studies. It does, however, offer a possible solution to the problem for future applications.

The lack of success in these attempts to further extend the compound class characterization technique by developing a method for differentiating between aromatics and oxygenates led to the decision to deemphasize this effort. This decision was based on limitations of funding and time and the belief that more beneficial information could be obtained by applying the remaining resources to the area of sampling technology.

Improved Speed and Ease of Operation

The analytical system that was used in the March 1975 studies had some features that made the analysis slow and relatively cumbersome. For example, the use of a two-column system (Fig. 2) with a manual valve switch during the analytical run and the requirement for two identically collected samples to obtain a single analysis greatly encumbered the analytical method. A major emphasis in this program was directed toward improving the analytical method in terms of speed and ease of operation.

The purpose of the Chromosorb 105 column in the previous system (Fig. 2) was to allow the water to pass through rapidly while retaining the oxygenated and aromatic compounds. However, the relatively high concentrations of water in the actual samples never proved to be a problem in the analyses since the FID response associated with the presence of water was insignificantly small compared to the hydrocarbon response. This lead to the conclusion that the Chromosorb 105 column performed an unnecessary function and could be eliminated. By eliminating this column it was no longer necessary to modify the gas chromatograph so that a column with separate heating capabilities could be located external to the oven. This also eliminated the requirement for switching the carrier flow during the analysis.

A second modification that was made in the analytical system was to split the column effluent such that half of the flow passed directly into a flame ionization detector while the other half was directed through the olefin and oxygenate subtractor column (Ag_2SO_4/H_2SO_4 and $PdSO_4/H_2SO_4$) and subsequently into a second flame ionization detector. This provided for both "subtracted" and "unsubtracted" analyses on a single sample eliminating the need for duplicate samples. The basic flow schematic for the analytical system used in these studies is shown in Figure 13.

The implementation of these modifications cut the analysis time by more than 50% and eliminated several manual operations (e.g., valve switching and insertion of subtractors) from the analytical process.

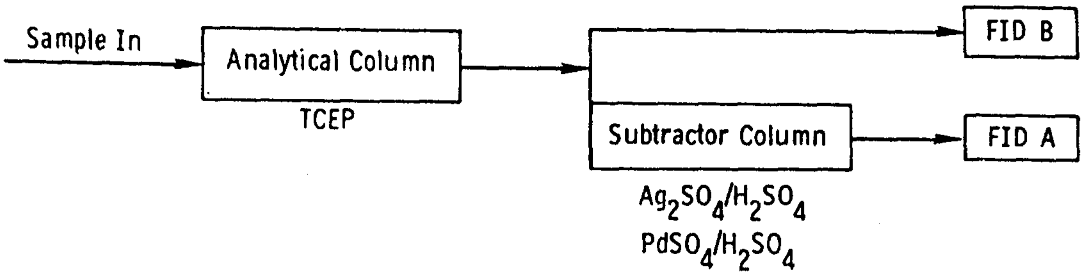


Figure 13. Flow diagram for analytical system.

Instrumentation

The analytical system used for the jet engine exhaust samples centered around a conventional gas chromatograph (GC) equipped with dual flame ionization detectors (FID). The unique features of this system were the method of sample introduction and the data processing capabilities.

The chromatograph used in these analyses was a Hewlett-Packard Model 5710 GC. The samples were introduced by means of a modified Chromalytics Concentrator (Model 1047). This unit normally functions to thermally desorb samples from sorbent sampling tubes and reconcentrate or "focus" the sample on a second sorbent trap. This second trap is then switched into the normal carrier system and heated to desorb the sample in a backflush mode onto the analytical column. The necessity to "focus" samples and introduce them onto the analytical column in a single "slug" is most acute when sampling has been done over an extended period (e.g., hours) and the sample has become significantly dispersed throughout the sampling tube.

For the jet engine exhaust sampling the time necessary to desorb and reconcentrate the sample on the second trap was comparable to the total sampling time so that no advantage would be realized in this reconcentration step. Consequently, the Chromalytics unit was modified so that the sampling tube itself could be switched into the normal carrier flow path and thermally desorbed in a backflush mode onto the analytical column (see section on "Chromatographic Analysis," p. 40).

Through various tests and evaluations it was determined that the optimum thermal desorption procedure was a 30-second preheat period at 300°C under no-flow conditions before switching the sorbent trap into the carrier flow path. The temperature was maintained at 300°C and the tube remained in the carrier flow path throughout the entire analysis. The switching valve was maintained at 250°C continuously. The Chromalytics Concentrator has very good thermal desorption characteristics because of its rapid temperature rise capabilities (e.g., room temperature to

300°C in <15 seconds). The sorbent materials (Tenax-GC and Ambersorb XE-340) are quite compatible with thermal desorption techniques since they both have high thermal stability (>350°C). Figure 14 is a typical chromatogram from a "blank" combination Tenax/Ambersorb sorbent sampling tube showing the residual background under these desorption conditions. This is small compared with the actual exhaust concentrations.

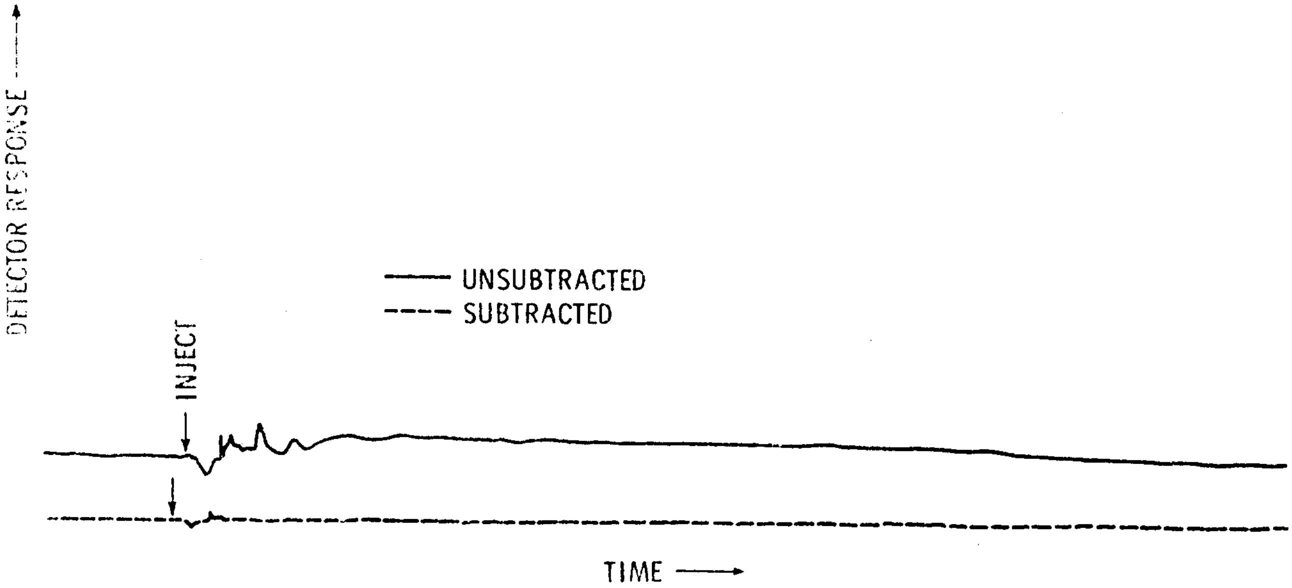


Figure 14. Background from thermal desorption of combination Tenax-GC/Ambersorb XE-340 sampling tube.

The other unique feature of the analytical system was the data interface with a Hewlett-Packard Model 3354 laboratory data system equipped with a 32K computer and dual disc data storage capability. This meant that the data collected during the analyses could be stored for subsequent computer reduction. This capability greatly expedited the processing of the data from the exhaust sampling studies.

Analytical Column

The analytical column to be used for the jet engine exhaust studies is a 12 ft. x 1/8 in. (366 cm x 0.3 cm) O.D. nickel column packed with 10% 1,2,3 tris-(2-cyanoethoxy)propane (TCEP) on 100/120 mesh Chromosorb G (acid washed) (Supelco, Inc.). The choice of this column is based on previous experience (4, 8) that demonstrated the ability of TCEP for retaining oxygenated and aromatic compounds. The performance characteristics are such that essentially all oxygenated compounds (except acetaldehyde) and all aromatics have longer retention times than saturated and olefinic hydrocarbons of carbon numbers 10 or less. The separation characteristics of this column are demonstrated with the test mixture in Figure 8. Note that benzene elutes after decane. Actually, undecane was also found to elute before methanol, acetone, and benzene. A mixture of compounds including heptane, decane, benzene, toluene, and xylene was used to calibrate the detector response over the range of compounds collected in the jet exhaust samples. Each of these compounds was used as a standard for a particular area of the chromatogram. This made it possible to compare the areas under the chromatograms from the exhaust samples with compounds having similar characteristics and retention times. It was believed that this would be a more accurate way of assessing the hydrocarbon content rather than calibrating with a single standard. The analytical column was operated at an isothermal temperature of 80°C and flow rate of 50-60 ml/min for the jet exhaust samples.

Subtractor Column

A subtractor column was used to remove olefinic, oxygenate, and aromatic compounds. The subtractor column consisted of a 6 in. x ¼ in. (15.2 cm x 0.6 cm) O.D. x 4 mm I.D. glass tube containing two sections: Ag_2SO_4/H_2SO_4 on Chromosorb W (0.5 g) and $PdSO_4/H_2SO_4$ on Chromosorb W (0.5 g). The Ag_2SO_4/H_2SO_4 served as an efficient olefin and aromatic subtractor, while the $PdSO_4/H_2SO_4$ served as an oxygenate subtractor. The effectiveness of this trap for olefin subtraction was tested using 1-butene. The total removal is demonstrated in Figure 15. The effectiveness of aromatic subtraction is demonstrated in Figure 8. The subtractor was also tested with representative oxygenates, and 100% removal was obtained for acetone, methanol, ethanol, propanol, and butanol. These test compounds were run to verify the activity of the current preparations of the subtractor materials. Their efficiency for accomplishing these class subtractions is well documented (1).

The effluent from the analytical column was split so that one half passed directly into a FID while the other half passed through the subtractor column and then into a second FID. By simultaneously monitoring the signals from both FID's a comparison was made between the chromatograms of subtracted and unsubtracted sample.

Output From Analysis

The analysis accomplished by the subtractive chromatographic technique described above provides the following data:

FID A = Subtracted Sample

FID B = Unsubtracted Sample

Paraffinic ($\leq C_{10}$) = FID A (Heptane and Decane)

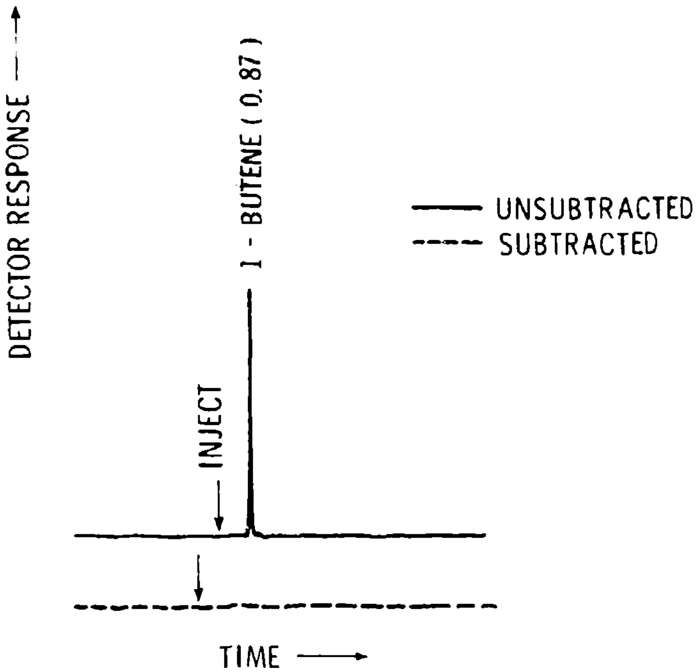


Figure 15. Demonstration of subtraction efficiency for olefins of combination Ag_2SO_4/H_2SO_4 and $PdSO_4/H_2SO_4$ subtractor.

Olefinic ($\leq C_{10}$) = FID B - FID A (Heptane and Decane)

Paraffinic ($>C_{10}$) = FID A (Benzene, Toluene, and Xylene)

Aromatic + Oxygenated + Olefinic ($>C_{10}$) = FID B - FID A (Benzene, Toluene, and Xylene)

The compounds in parentheses are the standards by which the various classes were calibrated. The above relationships demonstrate how the data were processed to assess the contributions from the various classifications of compounds. The paraffinic compounds were indicated by the subtracted sample response (FID A). Those of C_{10} or less were obtained by summing the contributions from the areas of the chromatogram calibrated against heptane and decane. Those $>C_{10}$ were obtained by summing the areas calibrated against benzene, toluene, and xylene. The olefinic contribution ($\leq C_{10}$) was obtained by subtracting the subtracted sample response (FID A) from the unsubtracted response (FID B) during that portion of the chromatogram calibrated against heptane and decane. That area of the chromatogram that was calibrated against benzene, toluene, and xylene produced the contribution due to oxygenates, aromatics, and olefins $>C_{10}$ by subtracting the subtracted sample response (FID A) from the unsubtracted response (FID B) during this time period.

Differences From Previously Used Analytical System

The system used for the analysis of the jet exhaust samples collected in March 1975 differs significantly from that used in the current studies. The following is a summary of the most notable differences:

Deletion of the Chromosorb 105 Column - In the 1975 studies a Chromosorb 105 column was used in series with the TCEP to separate water from the oxygenate + aromatic fraction. Since water was found not to present a problem, this column was eliminated in the current analytical scheme.

Sample Splitting - In the 1975 studies two identically collected samples were required for a single analysis. One was analyzed with the subtractor in the system and the other without the subtractor. Because of the changes in the analytical system, the current studies required only a single sample which was split to obtain subtracted and unsubtracted results.

Data Obtained - The use of the subtractor has been extended in the current system to oxygenates and aromatics. Previously it was assumed that all compounds eluting after a certain time were either oxygenates or aromatics. The new technique accounts for higher paraffins ($>C_{10}$) that may be present.

Data Reduction - The current analytical system is interfaced with a laboratory data system that was used to accomplish the total data reduction for the jet exhaust studies. In 1975 the data were reduced using an integrator and manual manipulation (planimetry). The speed and ease of data reduction were significantly increased.

The changes that were made in the analytical system not only improved the quality of the data but also greatly facilitated the analysis of the jet engine exhaust samples.

Sampling and Analysis of Jet Engine Exhaust

Exhaust Sample Collection

On 18-20 January 1978 exhaust samples were collected from a J85-5 jet engine at the Aero-Propulsion Laboratory, Wright-Patterson Air Force Base, Ohio. This sampling and analysis program involved three organizations:

1. Aero-Propulsion Laboratory (APL) - operation of jet engine and on-line total hydrocarbon analyses.

2. Monsanto Research Corporation (MRC) - solid sorbent sampling and subtractive chromatographic analysis.

3. USAF School of Aerospace Medicine (SAM) - cryogenic and solid sorbent sampling and GC/MS analysis.

MRC collected a total of 15 samples during this series of tests. The test matrix indicating the conditions and numbers of samples is given in Table 10. Additional samples (numbers in parentheses, Table 10) were collected on 9 February 1978 when it appeared that a computer malfunction at MRC had resulted in the loss of a substantial portion of the 18-20 January data. Fortunately, these data were later recovered.

TABLE 10. TEST MATRIX FOR MRC SAMPLES

J85-5 Conditions			No. of samples at stated conditions		
Power	Fuel	Approx. APL THC	10 min @ 10 ml/min	20 min @ 10 ml/min	Other
IDLE 46% rpm	JP-4	~600	5(2)[a]	-	-
IDLE 46% rpm	Alt. fuel[b]	~200	5(3)	-	2(2)
CRUISE 75% rpm	JP-4	~500	(3)	3	-

---

[a] Numbers in parentheses indicate samples collected on 9 February 1978.

[b] Alternate fuel is a blend of JP-4 with xylene added to bring the total aromatic content to 25.1%.

The system depicted in Figure 16 was used to transport the exhaust samples to the on-line THC analyzer (Beckman Model 402) and the collection system. All sample transfer lines were heated to ~110°C. A schematic of the sample collection system is shown in Figure 17. Only the MRC trap was used to collect samples during the 9 February tests.

The MRC collection system (Fig. 18) consisted of a ¼ in. (0.6 cm) stainless steel toggle valve (Whitey Valve Company), a combination Ambersorb XE-340/Tenax-GC sorbent trap, and a Brooks Model 5841 thermal mass flow sensor/controller to maintain a precise flow rate during the sampling period.

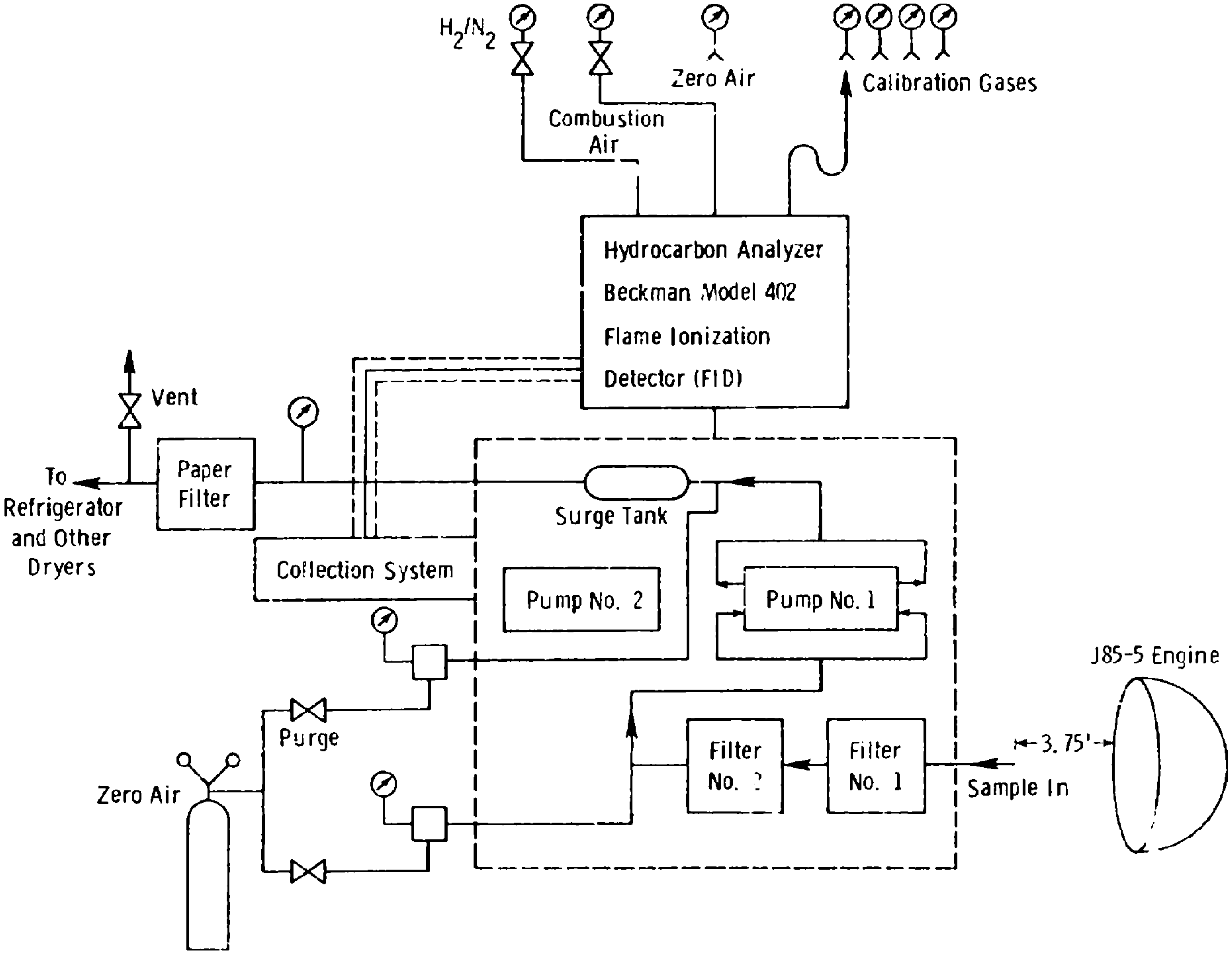
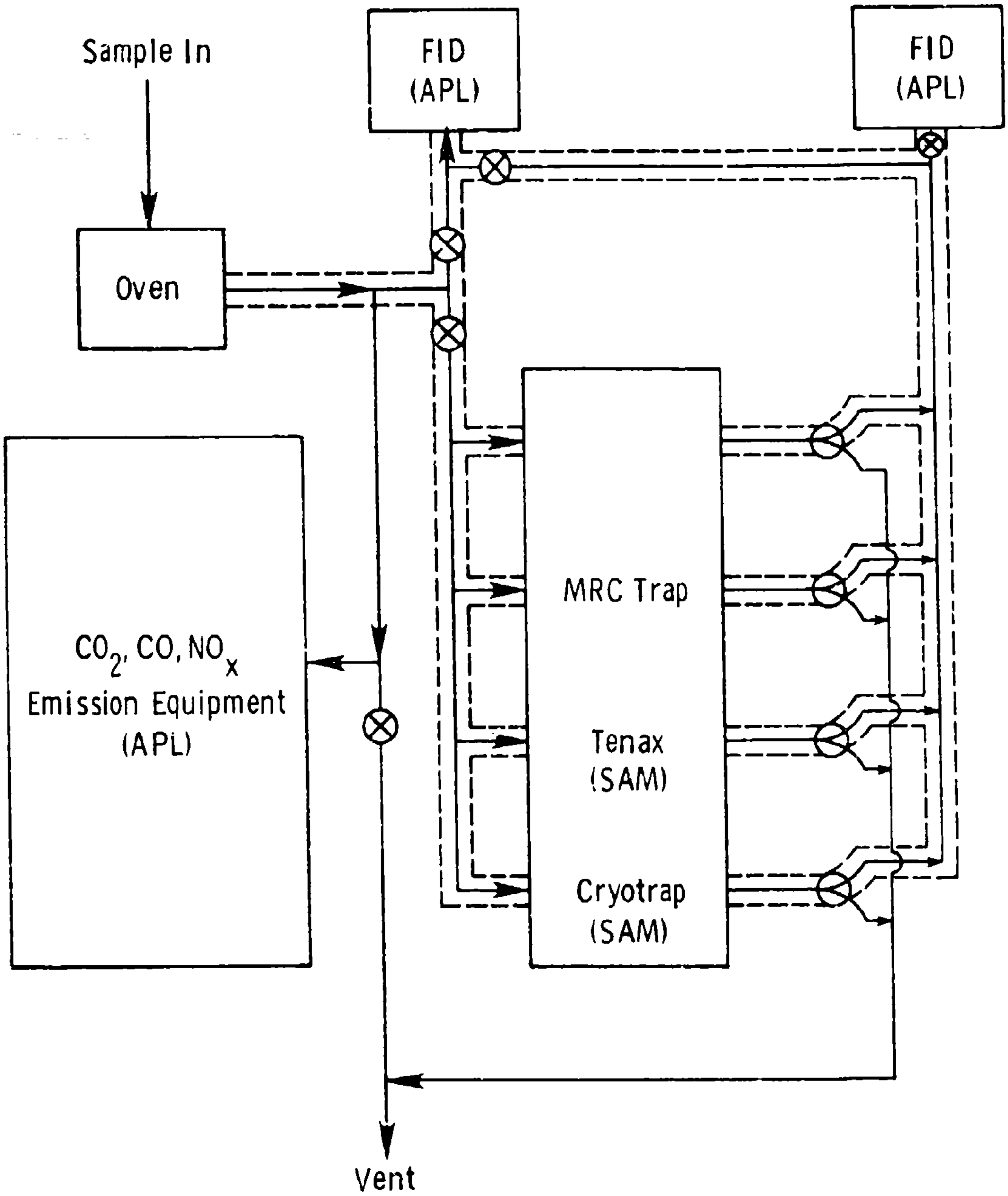


Figure 16. Exhaust sample transport system.



MRC - Monsanto Research Corporation
SAM - School of Aerospace Medicine
APL - Aero-Propulsion Laboratories

Figure 17. Exhaust sample collection system.

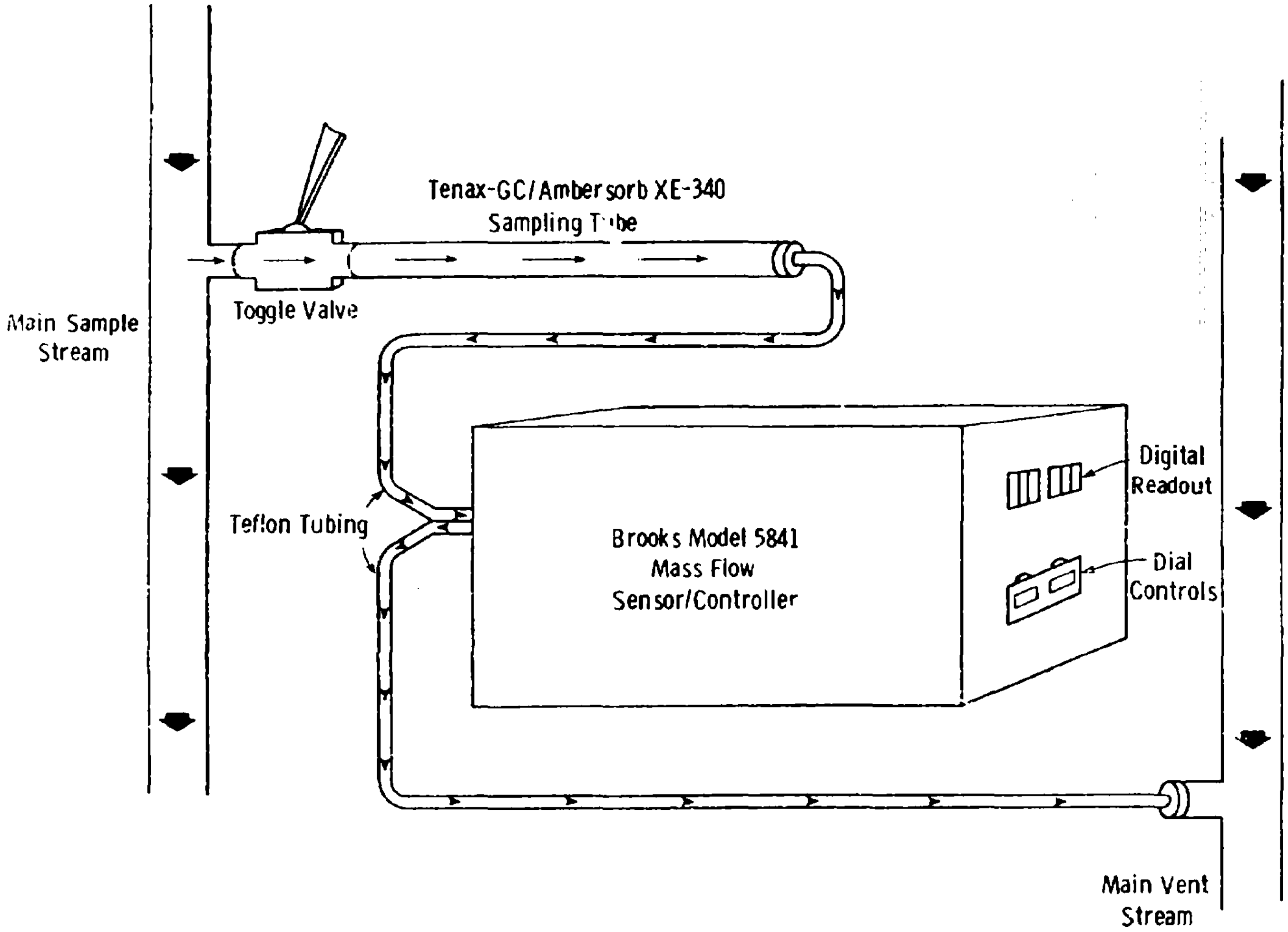


Figure 18. MRC sample collection system.

In several instances a second sorbent tube was placed in series with the first to evaluate the possibility of sample breakthrough. In addition, the on-line THC analyzer could be configured by appropriate valving to monitor the effluent from the sampling devices. The sampling time was defined by timing the period between opening and closing of the toggle valve.

The rationale for the selection of Ambersorb XE-340 (Rohm and Haas) and Tenax-GC (Applied Science Laboratories, Inc.) as the sorbent materials is presented in the section on "Choice of Sorbent Materials," p. 12. A schematic of the sampling tubes is presented in Figure 4. The tubes were constructed of ¼ in. O.D. x 3/16 in. I.D. x 6 in. long (0.6 cm O.D. x 0.5 cm I.D x 15.2 cm) stainless steel tubing and contained ~0.2 g Tenax-GC (60/80 mesh) and ~0.4 g Ambersorb XE-340 (unsieved) with silanized glass wool plugs at both ends and separating the sorbent materials. The sorbent materials were preconditioned as described in the section on "Conditioning of Sorbent Materials," p. 16. The traps were thermally desorbed at 300°C under N_2 flow for 16 hours prior to sampling. The tubes were capped with plastic tubing caps during transfer and storage to prevent contamination.

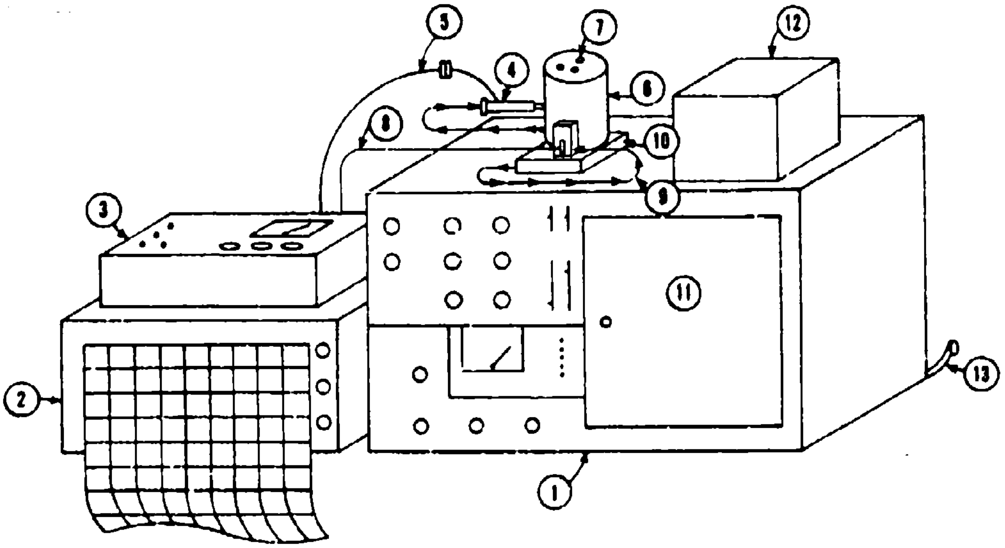
The sampling tubes were positioned such that the flow was directed through the Tenax-GC first and then through the Ambersorb XE-340. Our previous evaluations (see section on "Choice of Sorbent Materials," p. 12) led to the use of the following sampling parameters:

Flow Rate = 10 ml/min
Sampling Time = 10 min
Sampling Temp. = Ambient

A few samples were collected under other conditions. These can be identified in Table 10. A more complete description of the samples is contained in Appendix B.

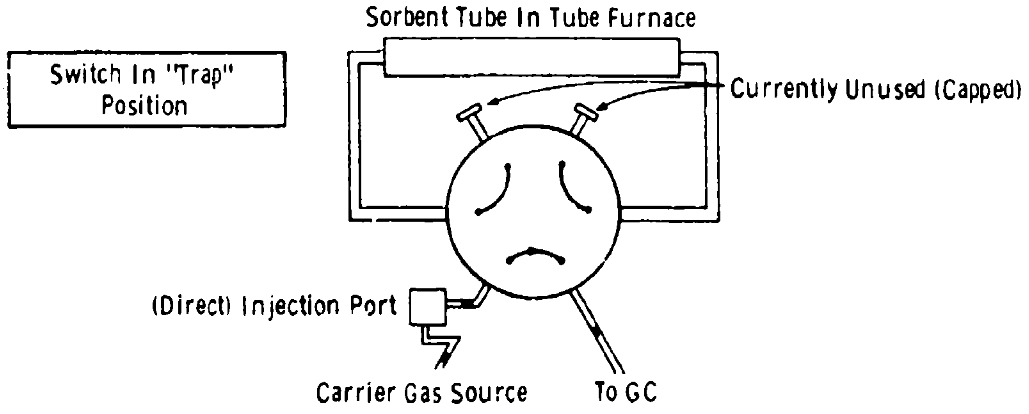
Chromatographic Analysis

The samples collected at APL were analyzed at MRC using thermal desorption and subtractive chromatography techniques. The analytical instrumentation consisted of a Chromalytics Model 1047 Concentrator for thermal desorption and introduction into a Hewlett-Packard Model 5710 gas chromatograph equipped with a dual flame ionization detector (FID). This desorption/analytical system is depicted in Figure 19. Note that the Chromalytics Concentrator oven contains a six-port, two-position valve which is sketched in Figure 20. This valve offers the alternative of direct syringe injection of a standard or thermal desorption of a sampling tube. The analytical column was a 12 ft. x 1/8 in. O.D. (366 cm x 0.3 cm O.D.) nickel column packed with 10% 1,2,3-tris(2-cyanoethoxy)propane (TCEP) on 100/120 mesh Chromosorb G (Supelco). The effluent from the analytical column

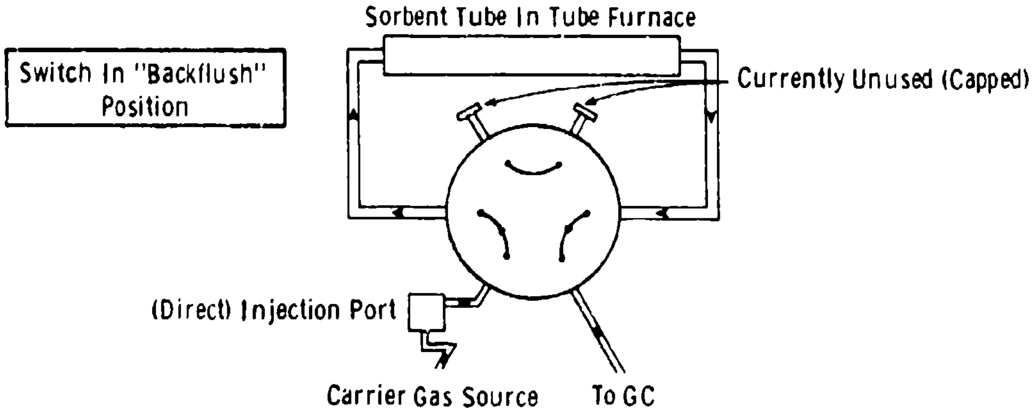


① 5710A Hewlett Packard Gas Chromatograph
② 7132A Hewlett Packard Chart Recorder
③ Chromalytics® Thermal Controller to 1047 Concentrator System
④ Chromalytics® Tube Desorption Chamber to 1047 Concentrator System (300 °C)
⑤ Thermocouple Connection from Desorption Chamber to Thermal Controller
⑥ Chromalytics® Oven with Valve to 1047 Concentrator System (240 °C)
⑦ Injection Port for Direct Injections
⑧ Thermocouple Connection from Oven to Thermal Controller
⑨ Nitrogen Carrier Gas (30 ml/min) into Chromalytics Valve
⑩ Chromalytics® Oven/GC Injection Port Connection
⑪ GC Oven Containing Analytical and Subtractor Columns (Described in Text)
⑫ Dual FID's
⑬ GC Cable to Central 3350 Hewlett Packard Computer System

Figure 19. Desorption/analytical system used in jet engine exhaust evaluations.



DIRECT INJECTION OF STANDARDS INTO GC



THERMAL DESORPTION OF TUBES INTO GC

Figure 20. Diagram of six-port, two-position valve within Chromalytics oven.

was split with one half passing directly into one of the FID's while the other half passed through a 6 in. (15.2 cm) column containing 0.5 g Chromosorb W coated with Ag_2SO_4/H_2SO_4 and 0.5 g of Chromosorb W coated with $PdSO_4/H_2SO_4$ before passing into the second FID. This column served as an efficient olefin, oxygenate, and aromatic subtractor. The details of this analytical system are discussed previously in this report (see section on "Development of The Analytical System," p. 25).

Typical chromatograms for the three engine/fuel settings are shown in Figures 21, 22, and 23. Figure 21 is the chromatogram from the analysis of a sample collected at the IDLE (46% rpm) engine setting using JP-4 fuel. The solid line represents the detector response for the unsubtracted sample (i.e., that portion passing directly from the column into an FID), while the dashed line represents the detector response for the subtracted sample (i.e., that portion passing through the Ag_2SO_4/H_2SO_4 and $PdSO_4/H_2SO_4$ subtractors before passing into the FID). A backup tube was also used on this sample to check for any sample breakthrough. The bottom two traces of Figure 21 represent the unsubtracted and subtracted analyses of the backup tube. This shows that there was no significant breakthrough of sample during the collection period, since the backup tube chromatogram compares very similarly with the typical trap blank (background) shown in Figure 14 (see section on "Instrumentation," p. 31). Figure 22 contains a typical chromatogram (subtracted and unsubtracted) for the CRUISE (75% rpm) setting using JP-4, while Figure 23 contains the similar representation for the IDLE (46% rpm) setting using the alternate (JP-4 + xylene) fuel. In every case where backup tubes were used, no significant breakthrough was detected. The raw data from all of the analyses were stored on a disc in the MRC Hewlett-Packard Model 3354 laboratory data system for later reduction.

A calibration standard consisting of heptane, decane, benzene, toluene, and m-xylene in carbon disulfide was run daily during the analysis period. The raw data from these calibration runs were also stored on the computer disc.

This calibration standard used a mixture of compounds rather than a single one to provide a more accurate comparison of detector response to sample size over several regions of the sample chromatogram. Furthermore, the concentrations of the calibration compounds were determined by comparing their peak heights to the peak heights of a preliminary sample (MRC-O, the first sample collected), thereby ensuring a proper order of magnitude for sample quantitation. The composition of the calibration standard is given in Table 11.

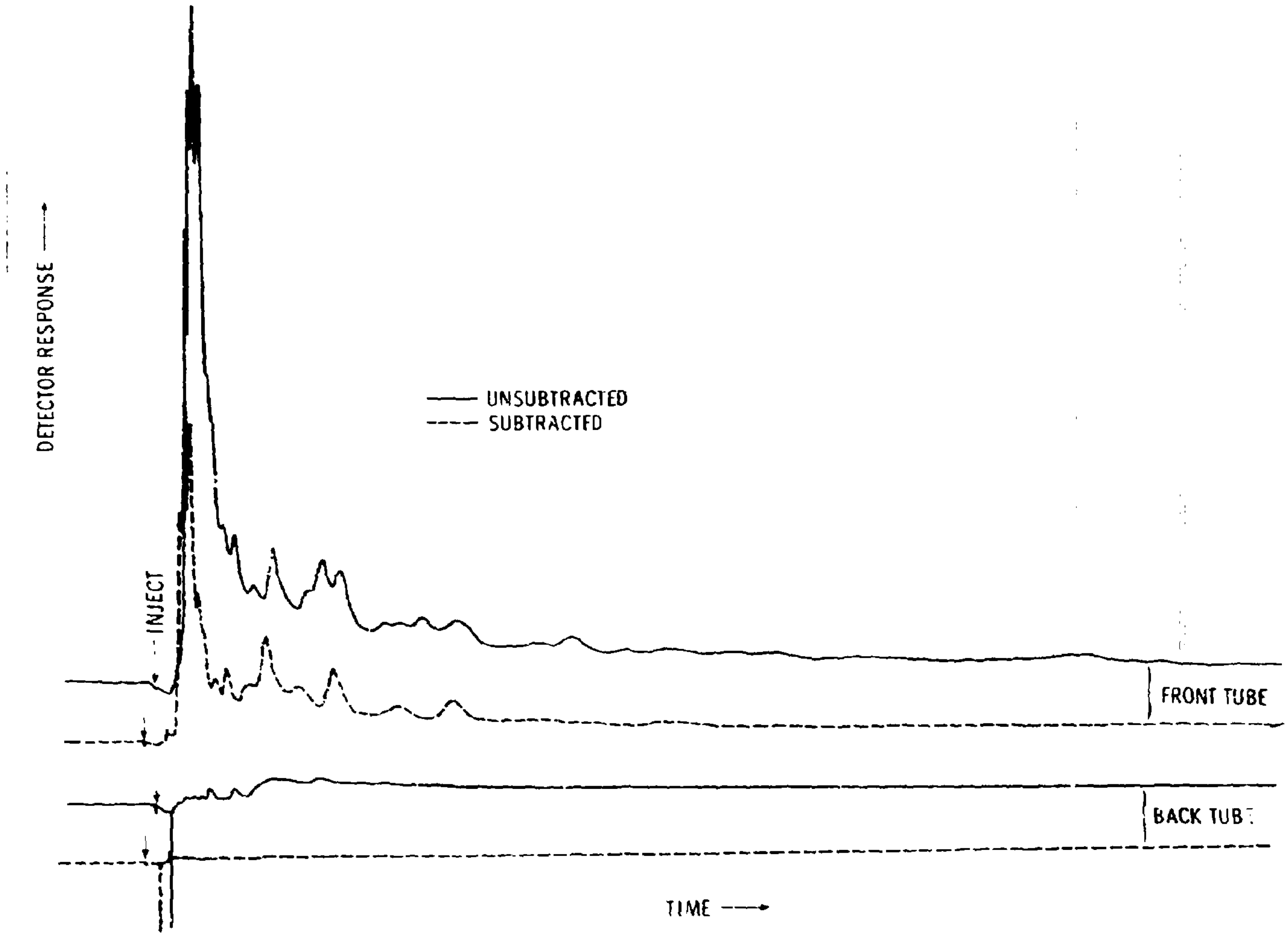


Figure 21. Typical chromatogram for sample collected at *IDLE* (463 rpm) using JP-4 fuel.

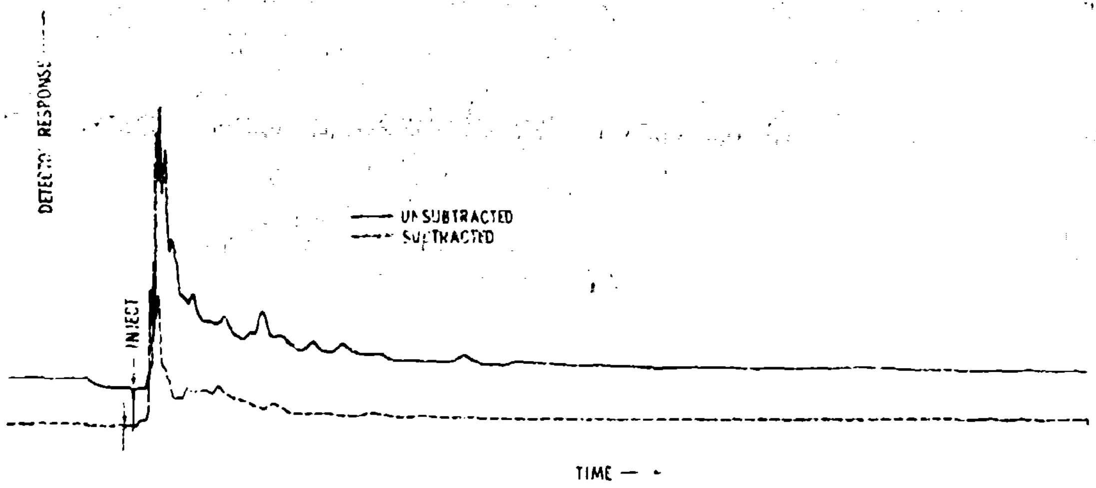


Figure 22. Typical chromatogram for sample collected at CRUISE (75% rpm) using JP-4 fuel.

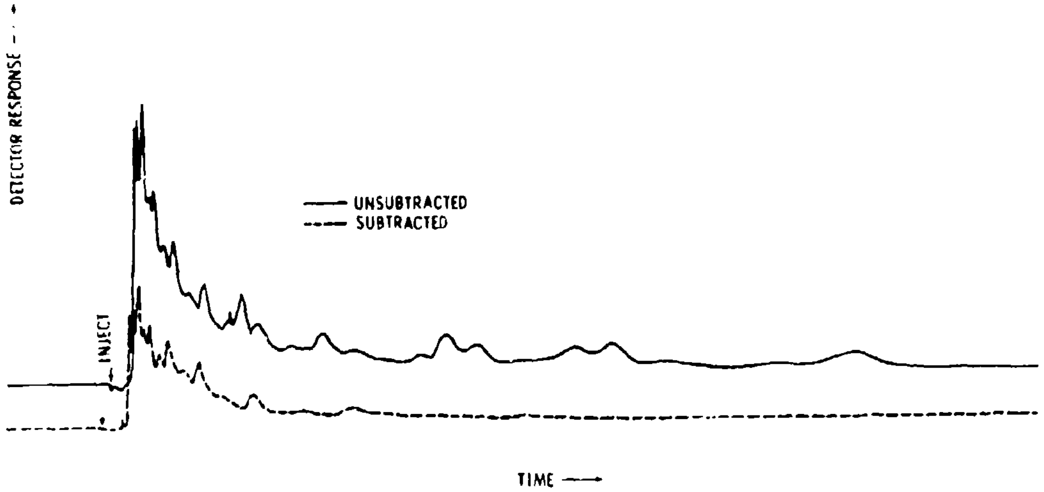


Figure 23. Typical chromatogram for sample collected at IDLE (46% rpm) using alternate fuel (JP-4 + xylene).

TABLE 11. CALIBRATION STANDARD FOR JET ENGINE EXHAUST SAMPLES

Compound	Volume (μl) of pure compound diluted to 50 ml with CS_2	Amount (μg) of compound in a 1 μl injection of standard	Equivalent ppmC in a 1 μl injection of standard
Heptane	75	0.99	19.6
Decane	60	0.87	15.0
Benzene	54	0.95	17.7
Toluene	43	0.85	13.8
Xylene	51	0.88	16.3
		Total:	82.4

An example of the chromatogram from a typical calibration standard is given in Figure 24.

Data Interpretation

As stated previously, the raw data from the jet engine exhaust samples and calibration standards were stored on the data disc of a Hewlett-Packard Model 3354A laboratory data system. These data are collected by the system in the form of "area slices" during the course of the chromatographic analysis. Each area slice contains the area under the chromatographic trace during a set time interval (e.g., normally 0.5 seconds). The areas are accumulated and transmitted to the computer by an analog-to-digital (A/D) converter at the chromatograph.

This method of collecting and storing data is illustrated in Figure 25. Note that the computer has an established baseline of -10 mV, and the amplitude of the signal is measured in terms of voltage (microvolts) relative to this baseline. The area is obtained by forming the product of the area slice width (time interval) and the amplitude during that interval. The chromatographic baseline is generally near 0 mV so that the area between the chromatographic baseline and the computer baseline is included in each of the area slices. Once the raw data have been accumulated the system software processes these data, determines the existence of peaks based on certain integration criteria, and corrects for the area between the chromatographic and system baselines to obtain the area under each peak. This process is illustrated in Figure 26.

The calibration standard analyses consisted of chromatographically distinct peaks so that the standard method of collecting (0.5 sec intervals) and analyzing the raw data was used. The areas of peaks integrated by this method are given in the units of counts (1 count = 0.5 microvolt-second). Dividing the calibration standard peak areas by the number of micrograms

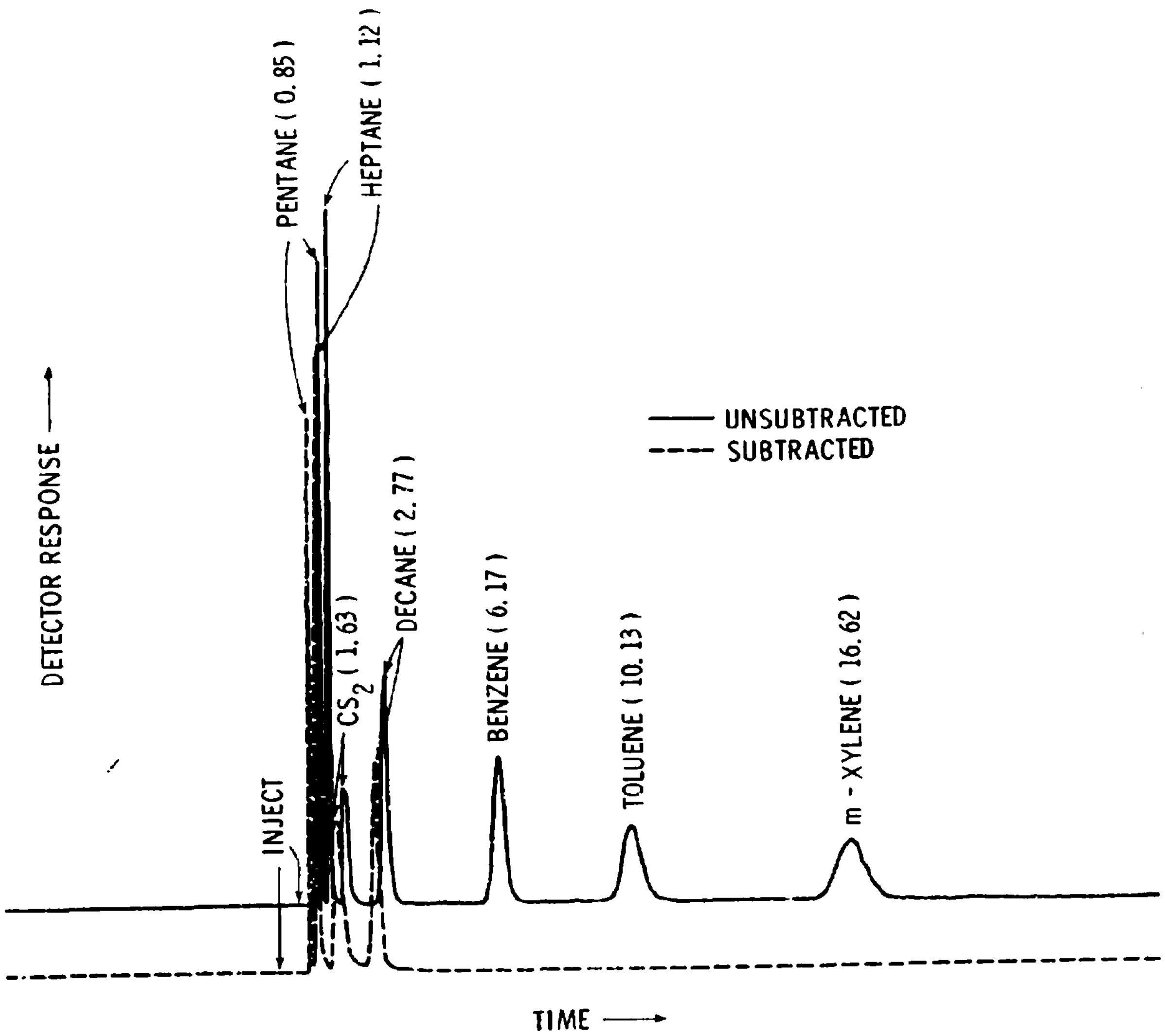


Figure 24. Chromatogram of calibration standard.

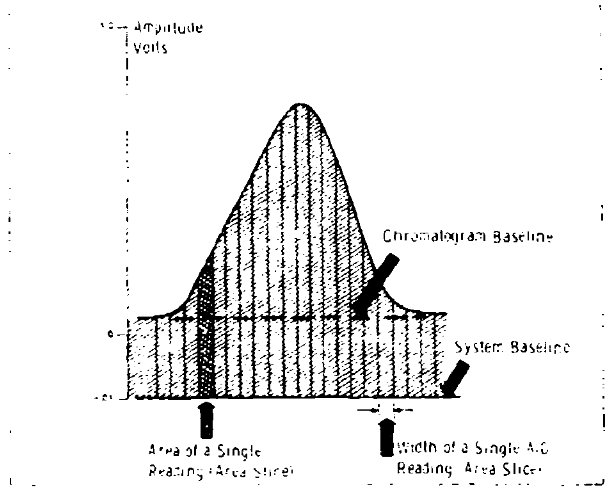


Figure 25. Method of raw data collection used by computer system.

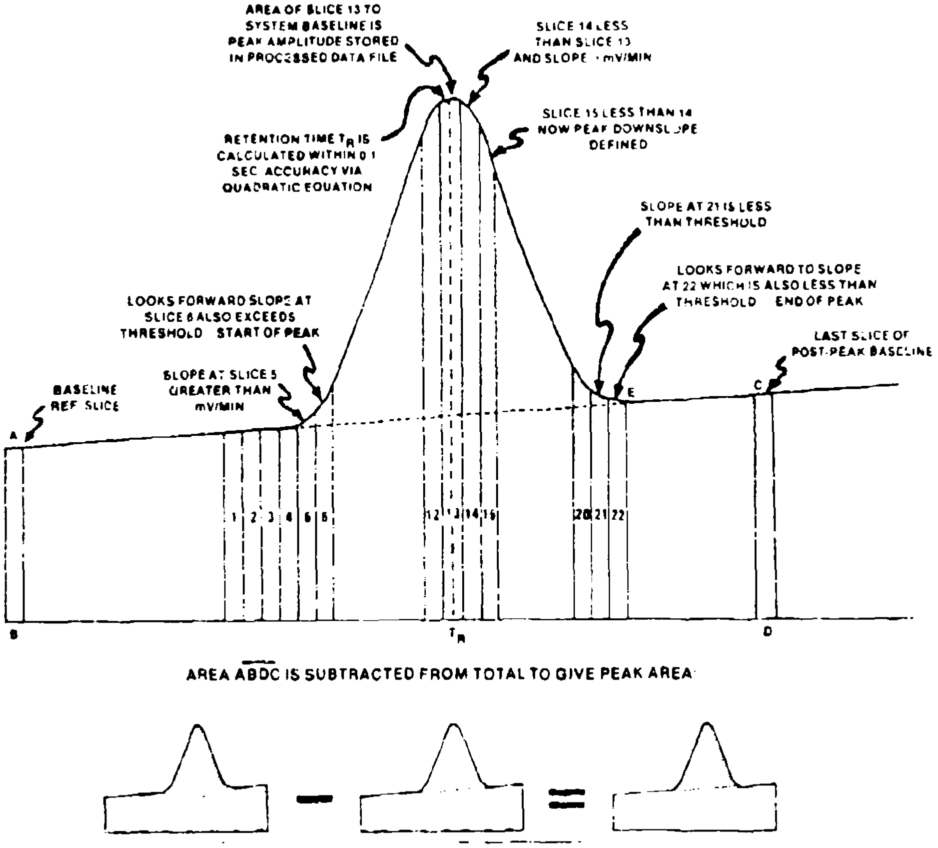


Figure 26. Standard integration of peak areas (ref. 7).

of each calibration compound in a standard injection produced the calibration factors (counts/μg) used to quantify the jet engine exhaust samples. Therefore, for the calibration runs, the calibration factors were determined for each of the five standard compounds from the unsubtracted (straight to FID) portion of the sample split. However, due to the presence of the subtractor columns the split ratio was not exactly 1:1, although it was consistent. Therefore, the subtracted portion of the sample was analyzed also and the calibration factors determined for heptane and decane since these compounds were not removed by the subtractor. Calibration factors for three subtracted compounds (benzene, toluene, and m-xylene) were then determined on the basis of the split ratio by taking the average of the subtracted/unsubtracted values for heptane and decane and multiplying by the unsubtracted calibration factors for benzene, toluene, and m-xylene. These calibration factors are tabulated in Appendix B, Table B-2.

The actual jet exhaust data were not processed by the normal peak integration technique since the chromatograms consisted of envelopes of response rather than distinct peaks. The important data for this method of analysis are the accumulative area over a particular span of the chromatogram. Therefore, larger area slices (10 sec) were collected and stored for processing by a special computer program that related the areas to the appropriate calibration standards. The basic program (called "JET") used to process these data is listed in Appendix C. The areas of the samples were determined by subtracting a baseline value from the entire chromatographic run, similar to the standard method. The baseline value for each analysis was selected at the minimum of the sample chromatogram at or near the end of the run. This was found to eliminate most of the sample tube background contribution to area along with the baseline subtraction. The analysis of each sample was optimized by individually selecting the baseline values.

The total areas of the samples were then divided into five regions for quantitation with the five calibration standards. These regions were defined at points selected from the calibration runs in chromatographic valleys, halfway between two calibration compound peaks. This is illustrated by Figure 27.

Three parts in this program were varied according to the sample being analyzed: (1) the point at which the baseline value was obtained, (2) the point at which sample integration was stopped, and (3) a value which was altered according to the sample size. These variables are discussed in Appendix C with the listing of the program, and the values used for each analysis are included in Table B-1 of Appendix B along with the sampling information. The appropriate calibration factors (counts/μg), the sample raw file name, the report title, and the average APL on-line THC values were the required inputs for the program.

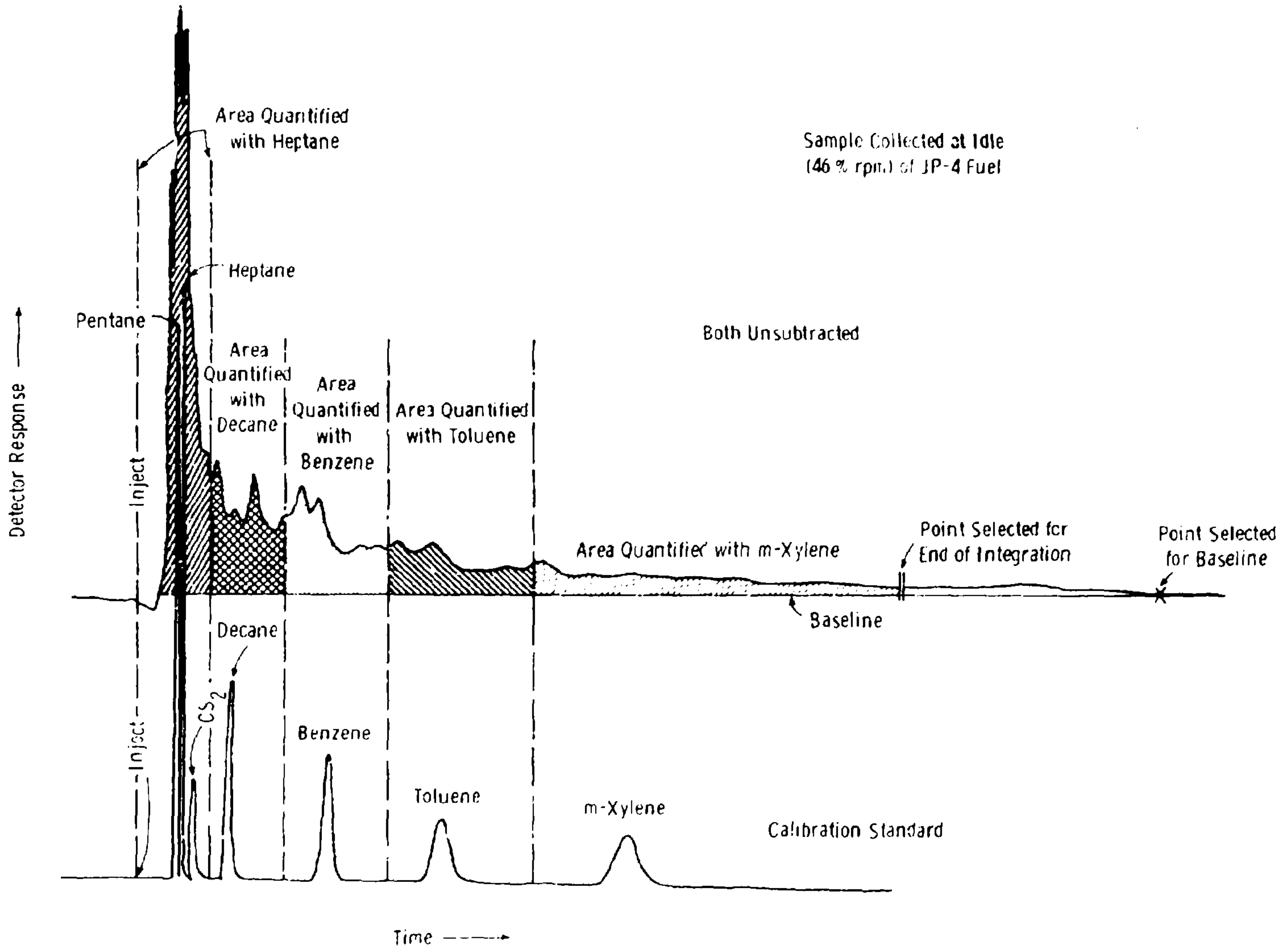


Figure 27. Definition of regions quantified by each of the five calibration standards.

Results

An example of a typical report resulting from the reduction of exhaust sample data with the BASIC program, "JET", is given in Figure 28 for both the unsubtracted and subtracted analyses. The total amount of hydrocarbons (ppmC) analyzed is obtained directly from the total ppmC in the "UNSUBTRACTED" report. The quantities of the different classes of chemicals are obtained as follows:

Paraffins ($\leq C_{10}$)	[Eq. ppmC of Heptane + Decane, Subtracted]
Olefins ($\leq C_{10}$) & light Oxygenates	[Eq. ppmC of Heptane + Decane, Unsubtracted] -[Paraffins ($\leq C_{10}$)]
Paraffins ($>C_{10}$)	[Eq. ppmC of Benzene, Toluene and m-Xylene, Subtracted]
Olefins ($>C_{10}$), Oxygenates & Aromatics	[Eq. ppmC of Benzene, Toluene and m-Xylene, Unsubtracted] -[Paraffins ($\geq C_{10}$)]

The total hydrocarbon data and chemical class data are compiled in Tables 12 and 13, respectively.

These data are further reduced to show the average values for a particular sampling condition in Tables 14 and 15 for the total hydrocarbon and chemical class information, respectively.

Three of the samples (MRC-10, 11, and 12) were collected on tubes that had been inadvertently packed such that the sample passed through the Ambersorb first rather than the Tenax. Therefore, no results were obtained for these samples. Two other samples collected on the same day (20 January) at the same conditions [Alt. Fuel, Idle (46% rpm)] gave results that were abnormally low for these engine conditions because of a leak in the exhaust sample transfer line. These results were reflected in both the on-line and the MRC THC values. More typical values were obtained for this condition from the 9 February samples.

Discussion of Results

It is informative to consider the results of these analyses both on an individual basis and in comparison with similar fuel or power settings. The results are tabulated in Table 15 for the three fuel and power settings sampled.

The average THC values show that the more efficient cruise setting produces a lower level of organic emissions by a factor of 2.5-3 compared with an idle setting. There appears to be no significant difference in the total organic emissions from the JP-4 and the alternate fuel (JP-4 + xylene to give 25.1% aromatics) under identical power settings (Idle, 46% rpm).

```
MRC-9,IDLE (46% rpm) ALT FUEL,SUBTRACTED,100 ml
THE ON-LINE THC VALUE WAS 475     PPMC


CALIBRATION          EQUIVALENT          EQUIVALENT          EQUIVALENT
 COMPOUND                UG                  PPM                 PPMC
-----------          ----------          ----------          ----------

HEPTANE              2.47068             7.01033             49.0723

DECANE               2.86126             4.91691             49.1691

BENZENE              2.61758             8.19356             49.1613

TOLUENE              1.27477             3.38306             23.6814

M-XYLENE             2.7441              6.32002             50.5602
                                                             ----------
                                                TOTAL PPMC = 221.644

THE PERCENT OF ON-LINE THC VALUE RECOVERED IS 46.662        %

MRC-9,IDLE (46% rpm) ALT FUEL,UNSUBTRACTED,100 ml
THE ON-LINE THC VALUE WAS 475     PPMC


CALIBRATION          EQUIVALENT          EQUIVALENT          EQUIVALENT
 COMPOUND                UG                  PPM                 PPMC
-----------          ----------          ----------          ----------

HEPTANE              5.42024             15.3795             107.656

DECANE               4.51325             7.75575             77.5575

BENZENE              4.67541             14.635              87.8099

TOLUENE              2.86367             7.59977             53.1984

M-XYLENE             8.88641             20.4665             163.732
                                                             ----------
                                                TOTAL PPMC = 489.954

THE PERCENT OF ON-LINE THC VALUE RECOVERED IS 103.148       %
```

Figure 28. Typical exhaust sample analysis report.

TABLE 12. TOTAL HYDROCARBON (THC) DATA FOR INDIVIDUAL JET ENGINE EXHAUST SAMPLES

Run	Sample size	Power setting	Fuel	On-line THC ppmC	MRC THC ppmC	% On-line THC
MRC-1	100 ml	Idle (46% rpm)	JP-4	632 ± 22	525	83
MRC-2	100 ml	Idle (46% rpm)	JP-4	630 ± 28	567	90
MRC-3	100 ml	Idle (46% rpm)	JP-4	620 ± 18	577	93
MRC-4	100 ml	Idle (46% rpm)	JP-4	610 ± 18	619	102
MRC-5	100 ml	Idle (46% rpm)	JP-4	632 ± 28	551	87
MRC-R1	100 ml	Idle (46% rpm)	JP-4	605 ± 25	505	83
MRC-R2	100 ml	Idle (46% rpm)	JP-4	570 ± 30	548	96
MRC-3 (backup)	100 ml	Idle (46% rpm)	JP-4	620 ± 18	127	21
MRC-R3	100 ml	Cruise (75% rpm)	JP-4	230 ± 15	222	96
MRC-R4	100 ml	Cruise (75% rpm)	JP-4	225 ± 10	237	105
MRC-R5	100 ml	Cruise (75% rpm)	JP-4	222 ± 13	251	113
MRC-6	200 ml	Cruise (75% rpm)	JP-4	205 ± 10	200	98
MRC-7	200 ml	Cruise (75% rpm)	JP-4	200 ± 10	165	82
MRC-8	200 ml	Cruise (75% rpm)	JP-4	197 ± 12	177	90
MRC-9	100 ml	Idle (46% rpm)	Alt. fuel	475 ± 85	490	103
MRC-13	100 ml	Idle (46% rpm)	Alt. fuel	407 ± 23	380	93
MRC-R6	100 ml	Idle (46% rpm)	Alt. fuel	583 ± 13	600	103
MRC-R7	100 ml	Idle (46% rpm)	Alt. fuel	564 ± 16	614	109
MRC-R8	100 ml	Idle (46% rpm)	Alt. fuel	555 ± 15	565	102
MRC-9 (backup)	100 ml	Idle (46% rpm)	Alt. fuel	475 ± 85	54	11
MRC-10, 11, & 12	100 ml	Idle (46% rpm)	Alt. fuel	-[a]	-[a]	-[a]
MRC-14	500 ml	Idle (46% rpm)	Alt. fuel	405 ± 15	302	74
MRC-14 (backup)	500 ml	Idle (46% rpm)	Alt. fuel	405 ± 15	23	6
MRC-R9	1000 ml	Idle (46% rpm)	Alt. fuel	552 ± 16	370	67
MRC-R10	1000 ml	Idle (46% rpm)	Alt. fuel	552 ± 16	379	69
MRC-15 (Tenax only)	100 ml	Idle (46% rpm)	Alt. fuel	405 ± 15	294	73
MRC-15 (backup)	100 ml	Idle (46% rpm)	Alt. fuel	405 ± 15	110	27

[a] Sampling tubes packed improperly.

TABLE 13. CHEMICAL CLASS DATA FOR INDIVIDUAL JET ENGINE EXHAUST SAMPLES

			Paraffins ($\leq C_{10}$)			($\leq C_{10}$) Olefins and light oxygenates			Paraffins ($\geq C_{10}$)			Olefins ($\geq C_{10}$), oxygenates and aromatics		
Run	Sample	Fuel	ppmC	% MRC THC	% APL[a] THC	ppmC	% MRC THC	% APL THC	ppmC	% MRC THC	% APL THC	ppmC	% MRC THC	% APL THC
MRC-1	Idle (46% rpm)	JP-4	101	19	16	136	26	22	127	24	20	161	31	25
MRC-2	Idle (46% rpm)	JP-4	110	19	17	117	21	19	176	31	28	164	29	26
MRC-3	Idle (46% rpm)	JP-4	114	20	18	134	23	22	179	31	29	150	26	24
MRC-4	Idle (46% rpm)	JP-4	118	19	19	149	24	24	176	28	29	175	28	29
MRC-5	Idle (46% rpm)	JP-4	121	22	19	142	26	22	159	29	25	129	23	20
MRC-R1	Idle (46% rpm)	JP-4	95	19	16	135	27	22	104	21	17	170	34	28
MRC-R2	Idle (46% rpm)	JP-4	94	17	16	134	25	24	135	25	24	186	34	33
MRC-3 (backup)	Idle (46% rpm)	JP-4	2	2	0.3	4	3	0.6	26	20	4.2	95	75	15.3
MRC-R3	Cruise (75% rpm)	JP-4	36	16	16	56	25	24	52	23	23	79	36	34
MRC-R4	Cruise (75% rpm)	JP-4	35	15	16	59	25	26	43	18	19	100	42	44
MRC-R5	Cruise (75% rpm)	JP-4	46	18	21	50	20	23	65	26	29	90	36	41
MRC-6	Cruise (75% rpm)	JP-4	40	20	20	44	22	21	45	23	22	72	36	35
MRC-7	Cruise (75% rpm)	JP-4	33	20	17	38	23	19	40	24	20	54	33	27
MRC-8	Cruise (75% rpm)	JP-4	34	19	17	38	22	19	41	23	21	64	36	32
MRC-9	Idle (46% rpm)	Alt. fuel	98	20	21	87	18	18	122	25	26	181	37	38
MRC-13	Idle (46% rpm)	Alt. fuel	76	20	19	51	13	13	93	25	23	159	42	39
MRC-R6	Idle (46% rpm)	Alt. fuel	127	21	22	137	23	23	105	18	18	232	39	40
MRC-R7	Idle (46% rpm)	Alt. fuel	131	21	23	118	19	21	113	18	20	252	41	45
MRC-R8	Idle (46% rpm)	Alt. fuel	126	22	23	121	21	22	98	17	18	220	39	40
MRC-9 (backup)	Idle (46% rpm)	Alt. fuel	3	5.6	0.6	1	1.9	0.2	15	28	3.2	50	93	10.5
MRC-14	Idle (46% rpm)	Alt. fuel	73	24	18	50	17	12	61	20	15	118	39	29
MRC-14 (backup)	Idle (46% rpm)	Alt. fuel	1	4.3	0.2	4	17	1.0	4	17	1.0	14	61	3.5
MRC-R9	Idle (46% rpm)	Alt. fuel	89	24	16	47	13	8.5	79	21	14	155	41	28
MRC-R10	Idle (46% rpm)	Alt. fuel	95	25	17	65	17	12	76	20	14	143	38	26
MRC-15 (Tenax only)	Idle (46% rpm)	Alt. fuel	69	24	17	39	13	10	74	25	16	112	38	28
MRC-15 (backup)	Idle (46% rpm)	Alt. fuel	4	3.6	1.0	24	22	5.9	20	18	4.9	62	56	15

---

[a] The APL THC values were obtained by an on-line THC analyzer.

TABLE 14. AVERAGE PERCENT OF ON-LINE THC VALUES FOR EACH POWER SETTING

Run	Power setting	Fuel	Sample size	Average % of the on-line (APL) THC value
MRC-1	Idle (46% rpm)	JP-4	100 ml	91%
MRC-2				
MRC-3				
MRC-4				
MRC-5				
MRC-R1				
MRC-R2				
MRC-R3	Cruise (75% rpm)	JP-4	100 ml	105%
MRC-R4				
MRC-R5				
MRC-6	Cruise (75% rpm)	JP-4	200 ml	90%
MRC-7				
MRC-8				
MRC-9	Idle (46% rpm)	Alt. fuel	100 ml	102%
MRC-13				
MRC-R6				
MRC-R7				
MRC-R8				
All 100 ml & 200 ml runs (i.e., all above runs)	(<u>Overall</u>)		100 ml & 200 ml	96% (range: 82% to 113%) std. dev.: 9%
MRC-3 (backup)	Idle (46% rpm)	JP-4	100 ml	21%
MRC-9 (backup)	Idle (46% rpm)	Alt. fuel	100 ml	11%
MRC-R9	Idle (46% rpm)	Alt. fuel	1000 ml	68%
MRC-R10				
MRC-14	Idle (46% rpm)	Alt. fuel	500 ml	74%
MRC-14 (backup)	Idle (46% rpm)	Alt. fuel	500 ml	6%
MRC-15 (Tenax only)	Idle (46% rpm)	Alt. fuel	100 ml	73%
MRC-15 (backup)	Idle (46% rpm)	Alt. fuel	100 ml	27%

TABLE 15. AVERAGE PERCENT COMPOSITION OF JET ENGINE EXHAUST SAMPLES

Fuel and power setting	Avg. THC (ppmC)	No. of replicates	% Paraffins ($\leq C_{10}$)	% Olefins ($\leq C_{10}$) + light oxygenates	% Paraffins ($>C_{10}$)	% Oxygenates + aromatics + olefins ($>C_{10}$)
JP-4 Idle (46% rpm)	556	7	19 (17-22)[a]	25 (21-27)	27 (21-31)	29 (23-34)
JP-4 Cruise (75% rpm)	209	6	18 (15-20)	23 (20-25)	23 (18-26)	37 (33-42)
Alt. fuel Idle (46% rpm)	435[b] 593	2 3	21 (20-22)	19 (13-21)	21 (17-25)	40 (37-42)

---

[a] Numbers in parentheses indicate range of values obtained from replicate samples.

[b] This value is abnormally low due to a leak in the exhaust sample delivery system that resulted in dilution of samples collected on this day (20 January).

The data can further be reduced by combining the less reactive paraffins into a single category and the more reactive olefins, oxygenates, and aromatics into another category. These data are presented in Table 16.

TABLE 16. JET EXHAUST EMISSION DATA SUMMARIZED AS TOTAL PARAFFINS AND TOTAL OLEFINS + OXYGENATES + AROMATICS

Fuel and power setting	% Paraffins	% Olefins, oxygenates, aromatics
JP-4 Idle (46% rpm)	46	54
JP-4 Cruise (75% rpm)	41	59
Alt. fuel Idle (46% rpm)	42	58

It can be seen that in every case the majority of the organic emissions can be characterized as belonging to the more reactive categories (olefins, oxygenates, and aromatics). Presented in this manner, the % compositions for the JP-4 at Cruise (75% rpm) and the Alternate Fuel at Idle (46% rpm) emissions are very similar although the total organic emissions are much lower for the cruise condition.

There appears to be a significantly higher percentage of the sample attributable to oxygenates, aromatics, and olefins ($>C_{10}$) in the emissions from JP-4 at cruise condition compared to idle (Table 15). This would be expected since the cruise power setting results in more efficient combustion which should increase the degree of partial oxidation in the emitted hydrocarbons.

Another significant comparison can be made by considering the effect of different fuels at the same power setting. Both JP-4 and the alternate fuel were run in the engine at an idle (46% rpm) power setting. The alternate fuel is JP-4 with xylene added to bring the total aromatics up to 25.1%. This special blend was created to simulate expected higher aromatic concentrations in shale and coal-derived fuels. The added aromatic concentration was reflected in a higher percentage contribution from the oxygenates + aromatics + olefins ($>C_{10}$) category in the emissions data for the alternate fuel. Therefore, an increased aromatic content does significantly increase the content of the more reactive species in the exhaust.

A significant difference between the results obtained in these studies and those obtained in March 1975 is that the data from the earlier studies probably contained erroneously high values for the aromatic + oxygenate category because of the assumption that all of the emissions falling in the area of the chromatogram at retention times greater than decane were due to aromatics and oxygenates. Figure 29 is a chromatogram of a typical JP-4 fuel (5). From this chromatogram it is obvious that a significant portion of the paraffin content of this fuel is $>C_{10}$. In fact, the average paraffin carbon number is 8.7. Since these larger paraffin molecules would be more difficult to burn, it is reasonable to expect $>C_{10}$ paraffins in the exhaust.

The changes made in the analytical system that resulted in the subtractor column being used throughout the chromatographic analysis (see section on "Development of the Analytical System," p. 25) resulted in the ability to assess the $>C_{10}$ paraffin content in these studies.

CONCLUSIONS

It is appropriate to consider the conclusions reached during the course of this study in two separate areas: (1) sampling and analysis methodology, and (2) jet engine exhaust results.

The conclusions that can be made concerning the sampling and analysis methodology are summarized in the following statements:

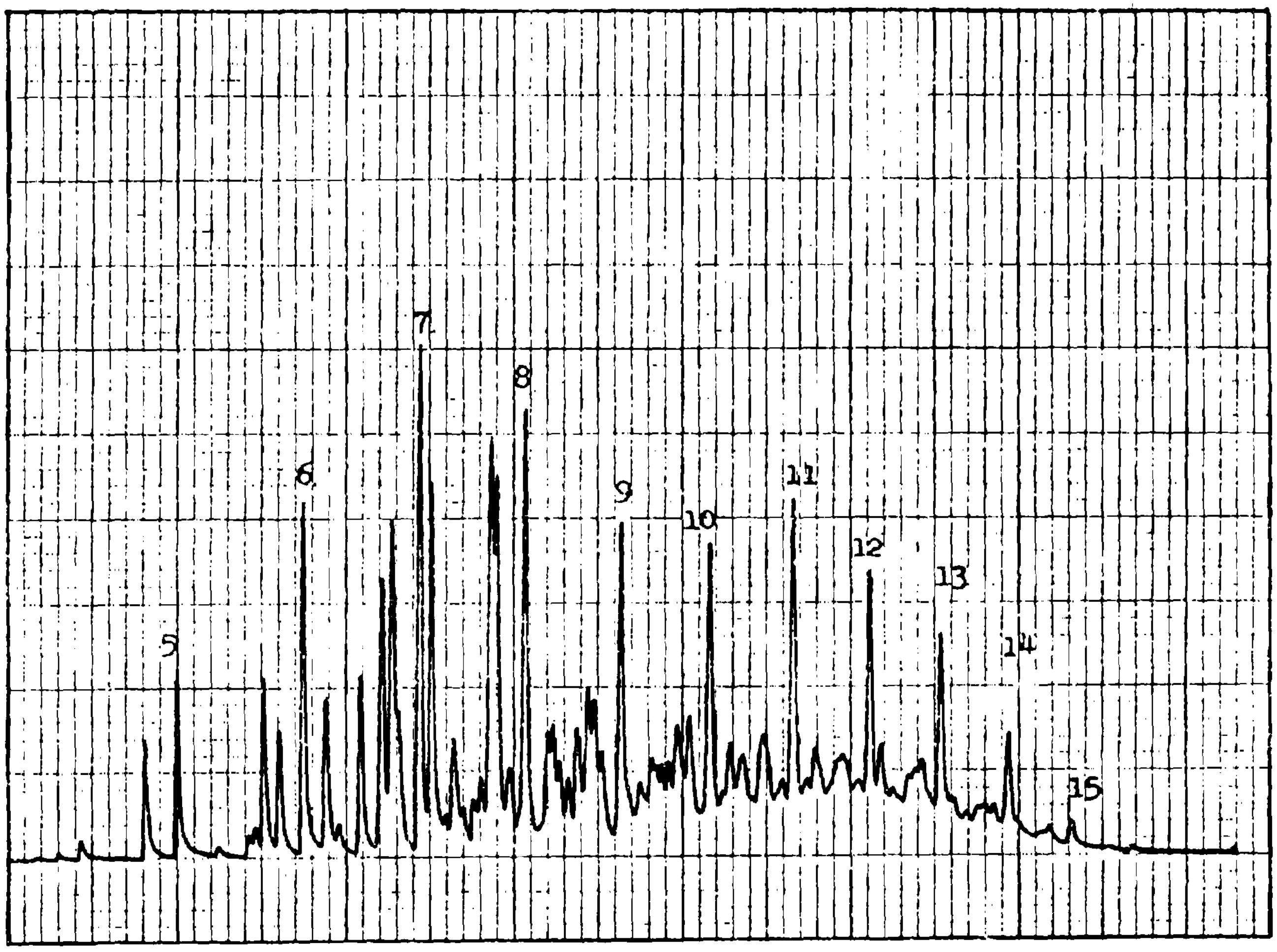


Figure 29. Chromatogram of JP-4. Numbers indicate carbon numbers of n-paraffins.

1. The combination Tenax/Ambersorb XE-340 trap proved to be a highly efficient (96% average recovery) method of recovering the organic emissions from jet engine exhaust using the prescribed sampling parameters.

2. A sampling rate of 10 ml/min for 10 minutes (100 ml total sample volume) proved to be a good value (for the amount of sorbents used) in terms of providing adequate sample for the analysis and avoiding major breakthrough of sample.

3. The organic class analyses gave a reasonable profile of the composition of the exhaust such that the total contribution from the more environmentally significant classes (oxygenates + aromatics + olefins) could be assessed.

4. The modifications to the analytical system represent a major advancement over the system used in previous studies (March 1975) because of the ability to measure the $>C_{10}$ paraffin contribution.

5. The ease and speed of analysis have been greatly enhanced due to modifications that eliminate the requirement for two samples to obtain a single analysis.

The conclusions that can be drawn from the results of the jet exhaust analyses are:

1. A power setting corresponding to a cruise condition (75% rpm) produces lower total organic emissions than a power setting corresponding to idle (46% rpm).

2. For all power settings and fuels examined the major contributions to the organic emissions were in the more reactive category corresponding to olefins, aromatics, and oxygenates.

3. The percent contribution corresponding to oxygenates + aromatics + olefins ($>C_{10}$) was significantly greater for JP-4 at cruise than at idle, probably reflecting a greater degree of partial oxidation of the emitted organics for the more efficient combustion at cruise conditions.

4. There was a significant increase in the percent contribution corresponding to oxygenates + aromatics + olefins ($>C_{10}$) when an alternate fuel blend containing an increased aromatic concentration was used, probably reflecting a corresponding increase in the aromatic composition of the exhaust.

RECOMMENDATIONS

The results from the jet exhaust analyses indicate a major advance in both the sampling and analytical systems compared with those used in the March 1975 studies. Some additional improvements, however, can be made to further increase the value of this type of analysis. The following are areas of research and suggested improvements that should be explored:

1. Although the recovery of organic emissions using the combination Tenax/Ambersorb XE-340 trap was very impressive compared with on-line THC values, additional evaluation of this system should be made to establish that sample integrity is maintained (i.e., what goes onto the tube is also what comes off the tube and is analyzed).

2. Further optimization as to quantity of sorbent material should be made.

3. The use of glass or glass-lined stainless steel should be considered for trap tube construction to further reduce background levels.

4. Although the efforts to accomplish aromatic/oxygenate differentiation in this program were unsuccessful, it now appears that the technology may be available to accomplish this task (9). This should be pursued as a very desirable additional class separation that can be incorporated into the system.

REFERENCES

1. Black, M. S., et al. Gas chromatographic technique for compound class analysis of jet engine exhaust. J Chromatogr 142:809 (1977).

2. Brooks, J. J., and R. E. Sievers. Gas chromatographic studies of interactions between selected organic nucleophiles and the NMR shift reagent, tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato) europium (III). J Chromatogr Sci 11:303 (1973).

3. David, D. J., D. S. West, and J. J. Brooks. Development of a portable miniature collection system for the exposure assessment within the microenvironment for carcinogens, precarcinogens, and cofactors. EPA Contract No. 68-02-2774, Progress Report No. 5, Mar 1978.

4. David, D. J., D. S. West, and J. J. Brooks. Development of a portable miniature collection system for the exposure assessment within the microenvironment for carcinogens, precarcinogens, and cofactors. EPA Contract No. 68-02-2774, Progress Report No. 6, Apr 1978.

5. Hodgson, F. N. Report No. 77-35, USAF Contract No. F33615-76-C-2014, 10 Nov 1977.

6. Holzer, G., et al. Collection and analysis of trace organic emissions from natural sources. J Chromatogr 142:755 (1977).

7. Laboratory Automation Products 3354-Operator's Reference, Hewlett-Packard, Feb 1977.

8. Rondeau, R. E., and R. E. Sievers. New superior paramagnetic shift reagents for nuclear magnetic resonance spectral clarification. J Am Chem Soc 93:1522 (1971).

9. Sievers, R. E. Dept. of Chemistry, University of Colorado, Boulder, Colorado. Personal communication (1978).

APPENDIX A

STANDARD SAMPLE GENERATION SYSTEM

To evaluate the sorbent sampling systems used in this project it was necessary to have a method for generating known concentrations of organic compounds in dynamic gas streams. MRC has developed a dynamic standard sample generation system based on the controlled syringe injection of organic liquids into a flowing stream of gas (N_2), vaporization, and subsequent dilution. This system was used to evaluate the sorbent tubes for the jet engine exhaust studies.

Figure A-1 is a schematic diagram of the sample generation system. The main frame of the system is a modified F&M Model 700 gas chromatograph. The chromatograph has been stripped of the protective metal covering and the detector removed. The oven (12 in. x 12 in. (30.5 cm x 30.5 cm) was relocated from the right to the left side of the main frame. Four heated zones were available on the original GC. One of these zones controls the oven temperature while the other three are available for heating various components of the sample generation system. Two of these are used to separately control the temperature of the two 3-port injection blocks (see Figure A-1). The final one is available for heating transfer lines for direct interfacing with a detector for frontal analysis capacity studies. A Simpson pyrometer (0-500°C) has been added along with a selection switch and necessary circuit modifications to allow the monitoring of temperatures in the four zones.

Additional modifications included an 18 in. x 18 in. x ¼ in. (45.7 cm x 45.7 cm x 0.6 cm)) aluminum plate attached to the main frame to the right of the oven to accommodate the syringe drives and a 13 in. x 12 in. x ¼ in. (33 cm x 30.5 cm x 0.6 cm) aluminum plate attached to the main frame in front of the oven to accommodate the flow controller instrumentation. The necessary bulkhead fittings, toggle valves, needle valves, tubing and pressure gages were also added to accomplish the configuration indicated in Figure A-1.

The generation system functions in the following manner. A source of carrier gas (N_2) is introduced and split into a primary and secondary flow. The primary flow passes through a Brooks Model 5841 mass flow sensor/controller which maintains the flow at a preset value (0-1000 ml/min). This flow passes through individually heated and controlled injection blocks which are designed to each accept three syringes mounted on Sage Model 355 variable control syringe drives. This allows for the simultaneous introduction of six pure liquid components or potentially many more if mixtures of compounds are used in

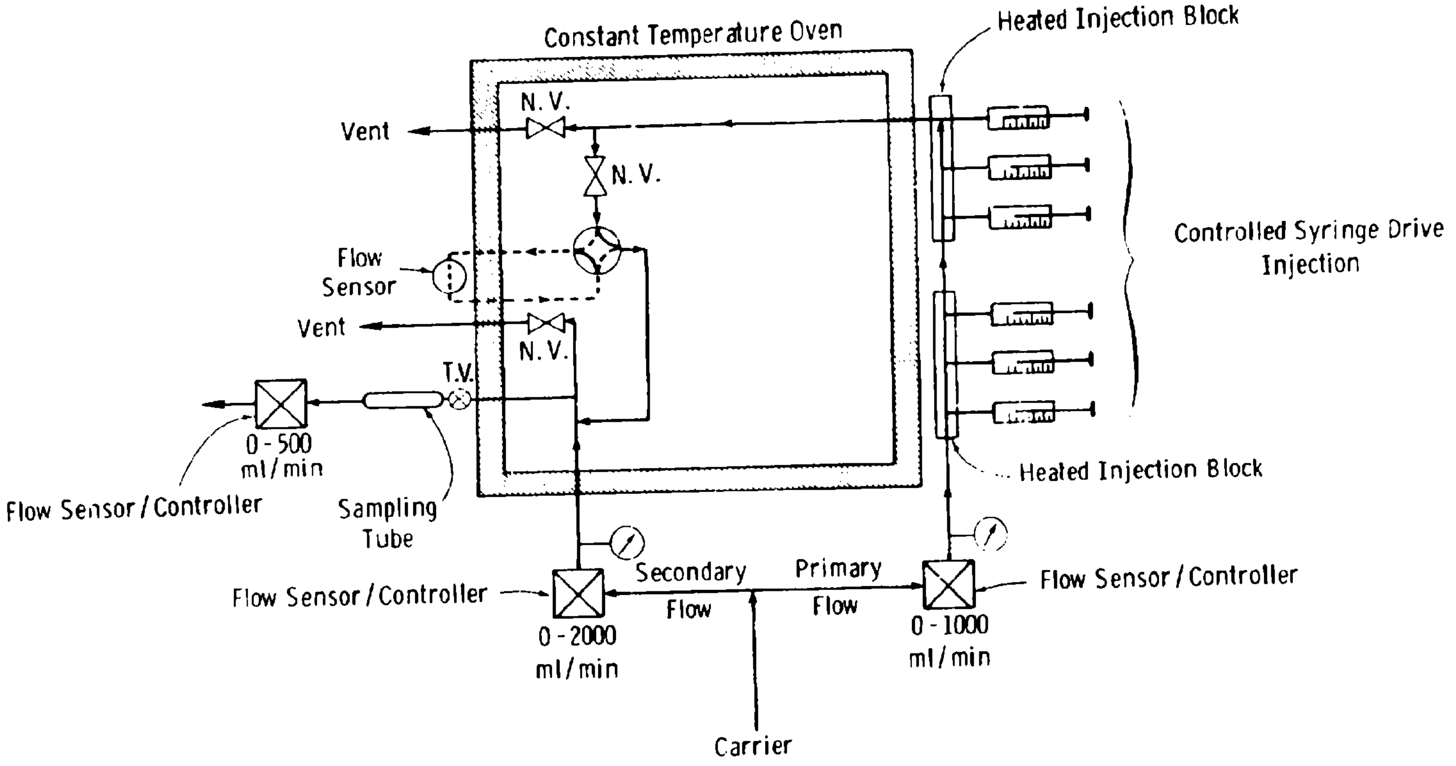


Figure A-1. Schematic of MRC dynamic gaseous sample generation system.

the syringes. The rate of injection can be varied from sub microliter/hour to milliliter/minute rates by choice of syringe size and drive rate. The liquid samples are vaporized in the injection block and swept with the carrier gas into a constant temperature oven.

The major portion of the primary flow passes through the oven, passes through a needle valve used to regulate the pressure in the primary flow path, and is expelled to vent. A small portion (usually ~10 ml/min) of the primary flow is split off through a second needle valve and passes into a switching valve. The switching valve makes it possible to switch a Hastings Model LF-100 (0-100 ml/min) mass flow sensor into the flow path (dashed line in Figure A-1) to measure the exact split on the primary flow. The portion of the primary flow that is split out passes from the switching valve and is combined with the secondary carrier flow which enters the constant temperature oven through a Brooks Model 5841 mass flow sensor/controller 0-2000 ml/min). As in the case of the primary flow, the major portion of the secondary flow passes through the oven and is expelled to vent through a needle valve. A small portion of the secondary flow is split off through a toggle valve to a solid sorbent sampling tube. The rate of sampling (0-500 ml/min) is controlled by a Brooks Model 5841 mass flow sensor/controller at the tube exit.

With the sample generation system in this configuration it is possible to achieve dynamic sample generation of pure compounds down to low ppb concentrations. For example, a concentration of ~20 ppb can be achieved using pure benzene in a 25 µl syringe at a syringe drive rate of 25% of the 1/1000 of full range setting and primary and secondary flows of 1000 ml/min and 2000 ml/min, respectively, using a 10 ml/min split from the primary flow. Under these conditions, the syringe drive mechanism delivers 0.0143 µl/min.

The data in Table A-1 show the results of numerous syringe delivery rate determinations for the sample generation system.

The final column entitled "Equivalence" has been added to provide a common basis for comparison of the various settings by converting to the equivalent delivery rate assuming a 25 µl syringe at a setting of 100% of the 1/100 range. These data show good agreement in general and excellent agreement for repeat measurements of the same setting (e.g., 25 µl syringe at 25% of 1/100 range). Some problems of nonlinearity are encountered at lower percent of range settings, and these are reflected in the data obtained for the delivery at 5% of 1/1000 range. Generally settings below 25% of any range will not be used. The value obtained for the 100 µl syringe agreed surprisingly well with those obtained with the 25 µl syringe. This will not necessarily be the case from syringe to syringe

TABLE A-1. SYRINGE DELIVERY RATE DATA

Syringe size (µl)	Amount delivered (µl)	(min)	Rate (µl/min)	Range	Equivalence[a] (µl/min)
25	4	27.67	0.145	1/100 @ 25%	0.580
25	1	70.00	0.0143	1/1000 @ 25%	0.572
25	1	52.50	0.0190	1/1000 @ 31.9%	0.596
25	5	34.23	0.146	1/100 @ 25%	0.584
25	5	34.37	0.145	1/100 @ 25%	0.580
25	5	34.18	0.146	1/100 @ 25%	0 584
25	2.5	978.0	0.0026	1/1000 @ 5%	0.512
100	18	7.37	2.44	1/100 @ 100%	0.610

---

[a] Assuming 25 µl syringe at 100% of 1/100 range.

since the graduations along the syringe barrels will not necessarily be the same. Although the linearity of delivery is in most cases good, this is used only to obtain a rough approximation of the delivery rate at a particular setting. An accurate measurement is made with each experiment to determine the precise delivery rate.

To give some indication of the accuracy the system for generating standard vapor concentrations, the following data were obtained using acrylonitrile as the test compound. The conditions were as follows:

Primary flow: 1000 ml/min
Split flow: 10 ml/min
Secondary flow: 2000 ml/min
Sample flow: 10 ml/min
Dilution factor: $(10/1000)\ (10/2010) = 4.975 \times 10^{-5}$
Syringe size: 25 µl
Syringe drive settings: 1/100 @ 25%
Delivery rate: 0.146 µl/min

Table A-2 contains the results of two sampling experiments using Porapak N sampling tubes and sampling times of 30 and 60 minutes.

TABLE A-2. RECOVERY OF ACRYLONITRILE FROM STANDARD SAMPLE GENERATION SYSTEM

Sampling time (min)	Theoretical amount (μg)	Actual amount (μg)	% Recovery
60	0.35	0.36	103
30	0.17	0.18	106

The acrylonitrile was analyzed by thermally desorbing the Porapak N tubes at 150°C onto a Porapak Q analytical column (at 150°C) and subsequent detection by a nitrogen specific FID. Agreement to within 10% of theoretical values has consistently been obtained from samples generated on the system.

APPENDIX B

COMPILATION OF SAMPLING AND ANALYSIS PARAMETERS

Table B-1 describes each sample that was taken, the date sampled, the sampling parameters, the date analyzed, and various analysis parameters. The analysis parameters include the separation of the subtracted and unsubtracted information into different files, a coded reference of calibration factors, and the program variables (which are discussed in Appendix C). Table B-2 is a listing of the calibration factors by the coded reference used in Table B-1.

TABLE B-1. JET ENGINE EXHAUST SAMPLING AND ANALYSIS INFORMATION

Run	Sample	Date sampled	Sampling time (min)	Flow rate (ml/min)	Sample size (ml)	Date analyzed	Raw files	Sub-tracted	Calib. factors	Program variables		
										Base-line	Run time	Sample size
MRC-1	Idle (46% rpm) JP-4	1/18/78	10	10	100	1/21/78	R11:JP S11:JP	No Yes	1a 1b	240 220	166 166	244.5 244.5
MRC-2	Idle (46% rpm) JP-4	1/18/78	10	10	100	1/23/78	R21:JB S21:JB	No Yes	2a 2b	290 300	201 201	244.5 244.5
MRC-3	Idle (46% rpm) JP-4	1/18/78	10	10	100	1/23/78	R31:JB S31:JB	No Yes	2a 2b	290 300	201 201	244.5 244.5
MRC-3	<u>Backup</u>	1/18/78	10	10	100	1/23/78	R32:JB S32:JB	No Yes	2a 2b	285 260	201 201	244.5 244.5
MRC-4	Idle (46% rpm) JP-4	1/18/78	10	10	100	1/23/78	R41:JB S41:JB	No Yes	2a 2b	295 305	201 201	244.5 244.5
MRC-5	Idle (46% rpm) JP-4	1/19/78	10	10	100	1/23/78	R51:JB S51:JB	No Yes	2a 2b	255 340	201 201	244.5 244.5
MRC-6	Cruise (75% rpm) JP-4	1/19/78	20	10	200	1/23/78	R61:JB S61:JB	No Yes	3a 3b	350 350	201 201	122.25 122.25
MRC-7	Cruise (75% rpm) JP-4	1/19/78	20	10	200	1/23/78	R71:JB S71:JB	No Yes	3a 3b	350 350	201 201	122.25 122.25
MRC-8	Cruise (75% rpm) JP-4	1/19/78	20	10	200	1/23/78	R81:JB S81:JB	No Yes	3a 3b	350 340	201 201	122.25 122.25
MRC-9	Idle (46% rpm) Alt. fuel	1/20/78	10	10	100	1/23/78	R91:JB S91:JB	No Yes	3a 3b	350 340	201 201	244.5 244.5
MRC-9	<u>Backup</u>	1/20/78	10	10	100	1/30/78	R92:JB S92:JB	No Yes	4a 4b	170 150	101 101	244.5 244.5
MRC-10	Idle (46% rpm) Alt. fuel	1/20/78	10	10	100	-[a]						
MRC-11	Idle (46% rpm) Alt. fuel	1/20/78	10	10	100	-[a]						
MRC-12	Idle (46% rpm) Alt. fuel	1/20/78	10	10	100	-[a]						
MRC-13	Idle (46% rpm) Alt. fuel	1/20/78	10	10	100	1/30/78	R131:JB S131:JB	No Yes	4a 4b	350 350	201 201	244.5 244.5
MRC-14	Idle (46% rpm) Alt. fuel	1/20/78	5	100	500	1/30/78	R141:JB S141:JB	No Yes	4a 4b	330 350	201 201	48.9 48.9

TABLE B-1 (continued)

Run	Sample	Date sampled	Sampling time (min)	Flow rate (ml/min)	Sample size (ml)	Date analyzed	Raw files	Sub-tracted	Calib. factors	Program variables		
										Base-line	Run time	Sample size
MRC-14	Backup	1/20/78	5	100	500	1/30/78	R142:JB S142:JB	No Yes	4a 4b	190 190	101 101	48.9 48.9
MRC-15	Idle (46% rpm) Alt. fuel	1/20/78	10	10	100	1/31/78	R151:JB S151:JB	No Yes	5a 5b	330 330	201 201	244.5 244.5
Tenax only												
MRC-15	Backup	1/20/78	10	10	100	1/31/78	R152:JB S152:JB	No Yes	5a 5b	200 200	101 101	244.5 244.5
MRC-R1	Idle (46% rpm) JP-4	2/9/78	10	10	100	2/10/78	RR11:DW SR11:DW	No Yes	6a 6b	250 270	201 201	244.5 244.5
MRC-R2	Idle (46% rpm) JP-4	2/9/78	10	10	100	2/10/78	RR21:DW SR21:DW	No Yes	6a 6b	350 330	201 201	244.5 244.5
MRC-R3	Cruise (75% rpm) JP-4	2/9/78	10	10	100	2/10/78	RR31:DW SR31:DW	No Yes	6a 6b	180 350	201 201	244.5 244.5
MRC-R4	Cruise (75% rpm) JP-4	2/9/78	10	10	100	2/10/78	RR41:DW SR41:DW	No Yes	6a 6b	340 270	201 201	244.5 244.5
MRC-R5	Cruise (75% rpm) JP-4	2/9/78	10	10	100	2/13/78	RR51:DW SR51:DW	No Yes	7a 7b	350 350	201 201	244.5 244.5
MRC-R6	Idle (46% rpm) Alt. fuel	2/9/78	10	10	100	2/13/78	RR61:DW SR61:DW	No Yes	7a 7b	330 330	201 201	244.5 244.5
MRC-R7	Idle (46% rpm) Alt. fuel	2/9/78	10	10	100	2/13/78	RR71:DW SR71:DW	No Yes	7a 7b	340 340	201 201	244.5 244.5
MRC-R8	Idle (46% rpm) Alt. fuel	2/9/78	10	10	100	2/13/78	RR81:DW SR81:DW	No Yes	7a 7b	280 270	201 201	244.5 244.5
MRC-R9	Idle (46% rpm) Alt. fuel	2/9/78	10	100	1000	2/13/78	RR91:DW SR91:DW	No Yes	7a 7b	330 350	201 201	24.45 24.45
MRC-R10	Idle (46% rpm) Alt. fuel	2/9/78	10	100	1000	2/13/78	RR101:DW SR101:DW	No Yes	7a 7b	350 350	201 201	24.45 24.45

---

[a] Sampling tubes packed improperly.

TABLE B-2. JET ENGINE EXHAUST SAMPLE CALIBRATION FACTORS

Run	Analysis date	Calib. factor #	Calibration factors (counts/μg)				
			Heptane	Decane	Benzene	Toluene	Xylene
MRC-1	1/21/78	1a	10416	10937	11223[a]	11285[a]	12082[a]
		1b	9878	10324	10623[a]	10677[a]	11431[a]
MRC-2 to MRC-5	1/23/78	2a	11715	11793	12727[a]	12592[a]	12950[a]
		2b	11285	11374	12267[a]	12137[a]	12482[a]
MRC-6 to MRC-9	1/23/78	3a	12136	12325	12995[a]	13060[a]	13619[a]
		3b	11646	11889	12502[a]	12565[a]	13103[a]
MRC-9 (backup) to MRC-14	1/30/78	4a	12032	12382	13057[a]	13080[a]	13619[a]
		4b	11709	12215	12793[a]	12816[a]	13344[a]
MRC-15	1/31/78	5a	11892	11970	12828[a]	12842[a]	13147[a]
		5b	11469	11722	12466[a]	12480[a]	12776[a]
MRC-R1 to MRC-R4	2/10/78	6a	9515	9409	10307[a]	10093[a]	10965[a]
		6b	8196	7922	8777[a]	8595[a]	9337[a]
MRC-R5 to MRC-R10	2/13/78	7a	12229	12330	13066[a]	13033[a]	14334[a]
		7b	10593	10295	11110[a]	11082[a]	12188[a]

---

[a] Determined by ratio.

APPENDIX C

LISTING AND EXPLANATION OF BASIC PROGRAM "JET"

Table C-1 is a listing of the Basic program "JET" that was used to reduce the data from the jet engine exhaust analyses. Three lines were modified depending upon the particular sampling and analysis parameters for each run:

```
130 FOR N =  1 TO 340                     (Baseline)
370 LET L = 201                           (Run Time)
500 LET P[M] = S[M]* 244.5 /Q             (Sample Size)
```

Line 130 is used to set the baseline value to a level that was appropriate for each particular chromatographic run. The example given (value of 340) is a typical value used and corresponds to the 10-second area slice at 3400 seconds into the run. Values were always chosen on the back side of the chromatogram (i.e., after the analytical peaks) when the trace had reached a stable baseline condition.

Line 370 is used to set the length for the final area of integration (calibrated with m-xylene). The analytical technique used multiple standards (heptane, decane, benzene, toluene, and m-xylene) to calibrate appropriate portions of the chromatogram. Lines 210 (heptane), 250 (decane), 290 (benzene), and 330 (toluene) determine the areas of the chromatogram to be calibrated against each of the other standards. The sum of the L values from these steps determines the total length of the chromatogram that was integrated (i.e., the effective run time). Line 370 being the final of these steps was adjusted to an appropriate value (normally 201) to include all of the remaining chromatogram that contained analytical information.

Line 500 is modified to correct the conversion factor for variations in sample size (usually 100 ml or a factor of 244.5). The actual values used in each of these steps for each of the individual analyses are included in Table B-1 of Appendix B.

TABLE C-1. LISTING OF BASIC PROGRAM "JET"

```
10  DIM A$[80]
20  FILES *
30  REM:  INPUT PARAMETERS
40  PRINT 'WHAT ARE THE CALIBRATION FACTORS';
50  INPUT C[1],C[2],C[3],C[4],C[5]
60  PRINT 'WHAT RAW FILE';
70  INPUT C$
80  PRINT 'REPORT TITLE';
90  INPUT A$
100  PRINT 'APL THC VALUE'
110  INPUT Z
120  ASSIGN C$,1,E
130  READ #1,2
140  REM:  THIS LOOP SETS BASELINE VALUE
150    FOR N=1 TO 340
160    IF  END #1 THEN 190
170    READ #1;B
180    NEXT N
190  LET S[1]=S[2]=S[3]=S[4]=S[5]=0
200  READ #1,2
210  REM:  SET PARAMETERS FOR DATA CALIBRATED WITH HEPTANE
220    FOR M=1 TO 5
230    IF M#1 THEN 280
240    LET L=11
250    LET Q=86.17
260    LET R=7
270    REM:  SET PARAMETERS FOR DATA CALIBRATED WITH DECANE
280    IF M#2 THEN 330
290    LET L=11
300    LET Q=142.28
310    LET R=10
320    REM:  SET PARAMETERS FOR DATA CALIBRATED WITH BENZENE
330    IF M#3 THEN 380
340    LET L=21
350    LET Q=78.11
360    LET R=6
370    REM:  SET PARAMETERS FOR DATA CALIBRATED WITH TOLUENE
380    IF M#4 THEN 430
390    LET L=26
400    LET Q=92.13
410    LET R=7
420    REM:  SET PARAMETERS FOR DATA CALIBRATED WITH XYLENE
430    IF M#5 THEN 480
440    LET L=201
450    LET Q=106.16
460    LET R=8
470    REM:  THIS LOOP SUMS AREAS
480      FOR N=1 TO L
490      READ #1;I
500      IF  END #1 THEN 530
```

TABLE C-1 (continued)

```
510       LET S[M]=S[M]+I
520       GOTO 550
530       LET L=N-1
540       GOTO 570
550       NEXT N
560     REM:  REDUCE AREAS TO uG AND ppmC EQUIVALENTS
570     LET S[M]=S[M]-(L*B)
580     LET S[M]=S[M]/(C[M]*4)
590     LET P[M]=S[M]*244.5/Q
600     LET A[M]=R*P[M]
610     NEXT M
620   REM:  SUM TOTAL ppmC
630   LET T[1]=A[1]+A[2]+A[3]+A[4]+A[5]
640   PRINT "POSITION PAPER AT BOTTOM OF PAGE, HIT SPACE, RETURN.";
650   REM:  OUTPUT DATA
660   INPUT D$
670     FOR N=1 TO 10
680     PRINT
690     NEXT N
700   PRINT A$
710   PRINT "THE ON-LINE THC VALUE WAS ";Z;" PPMC"
720     FOR N=1 TO 5
730     PRINT
740     NEXT N
750   PRINT "CALIBRATION";TAB(24);"EQUIVALENT";TAB(47);"EQUIVALENT";
760   PRINT TAB(70);"EQUIVALENT"
770   PRINT " COMPOUND";TAB(28);"UG";TAB(51);"PPM";TAB(73);"PPMC"
780   PRINT "-----------";TAB(24);"-----------";TAB(47);"-----------";
790   PRINT TAB(70);"----------"
800   PRINT
810   PRINT "HEPTANE";TAB(24);S[1];TAB(47);P[1];TAB(70);A[1]
820   PRINT
830   PRINT "DECANE";TAB(24);S[2];TAB(47);P[2];TAB(70);A[2]
840   PRINT
850   PRINT "BENZENE";TAB(24);S[3];TAB(47);P[3];TAB(70);A[3]
860   PRINT
870   PRINT "TOLUENE";TAB(24);S[4];TAB(47);P[4];TAB(70);A[4]
880   PRINT
890   PRINT "M-XYLENE";TAB(24);S[5];TAB(47);P[5];TAB(70);A[5]
900   PRINT TAB(70);"----------"
910   PRINT TAB(56);"TOTAL PPMC = ";T[1]
920   PRINT
930   REM:  CALCULATES % OF ON-LINE THC VALUE RECOVERED
940   LET Q=T[1]/Z*100
950   PRINT "THE PERCENT OF ON-LINE THC VALUE RECOVERED IS ";Q;" %"
960     FOR N=1 TO 15
970     PRINT
980     NEXT N
990   END
```