

Arson Analysis Newsletter

CONTENTS

PAGE

"CAPILLARY GAS CHROMATO-
GRAPHY OF ISOPARAFFINIC
ACCELERANTS"65

By: Michael A. Garten
Arizona Department
Of Public Safety

"Relative Hydrocarbon
Detectability by Flame
Ionization Detection for
Various Isolation
Methods"73

By: Donald G. Kubler
Carlotta Stackhouse
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Chemistry
Furman University

AAN NOTES.....83

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The AAN solicits contributions from forensic scientists, arson investigators, and interested parties which have some unique or routine analysis which helps in the identification of flammable liquid or explosive residues. Articles herein express the views and opinions of the authors, which are not necessarily those of the AAN or Systems Engineering Associates (SEA).

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CAPILLARY GAS CHROMATOGRAPHY
OF ISOPARAFFINIC ACCELERANTS

by

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INTRODUCTION

This paper will describe a number of isoparaffinic products that have been encountered in arson casework. Isoparaffins are branch chained hydrocarbons rather than normal hydrocarbons (straight chain), naphthenes. (cycloparaffins), olefins (carbon double bond) or aromatic hydrocarbons. Common petroleum distillate products contain varying amounts of one or more of these five hydrocarbon groups. Exxon Company, U.S.A. produces a series of unusually pure isoparaffinic solvents that are marketed under the trade name "ISOPAR". There are seven grades of ISOPAR solvents; ISOPAR C, E, G, H, K, L, and M. The solvents are predominantly isoparaffinic with only trace levels of impurities and thus have unique solvent, evaporation and odor characteristics. ISOPAR solvents find use in a wide variety of applications including paint formulations, copier fluids, lighter fluids, lamp oil, and polymer manufacture.

EXPERIMENTAL

INSTRUMENT: A Hewlett-Packard Model 5880A gas chromatograph equipped with temperature programming, flame ionization detector, and a 50-M OV-101 fused silica (Hewlett-Packard) capillary column.

CHEMICALS: Carbon disulfide (Fisher Reagent ACS, C-184) was used to dilute all samples 10:1. ISOPAR solvents C, E, G, H, K, L, and M were obtained from Exxon Company, U.S.A.

G.C. CONDITIONS: The chromatographic conditions used in all separations were:

Initial temperature 35°C for minutes, to 180°C at 3.5°C/min. then 180°C to 210°C at 7°C/min., and held at final temperature for 20 minutes, injector temperature 220°C, detector temperature 300°C, flow rate of helium 1 ml/min.; injector split ratio 100:1, and sweep 1 ml/min.

The following table lists the boiling ranges of the ISOPAR solvent series:^{1/}

TABLE I

<u>ISOPAR</u>	<u>BOILING RANGE °C</u>
C	98-106 Flammable
E	116-134 Flammable
G	156-176 Combustible
H	176-188 Combustible
K	177-207 Combustible
L	180-202 Combustible
M	207-260 Combustible

Figures 1-2 have been arranged to illustrate the progressive increase of boiling ranges found in the ISOPAR solvent series. While isoparaffinic solvents are available from several sources, the wide boiling range of the ISOPAR solvent series lends itself to compilation of chromatograms that can be used to quickly distinguish isoparaffinic products from more common petroleum distillates in those cases where the examiner has recovered an accelerant that does not match chromatograms of known petroleum distillates. Such situations are likely to occur for two reasons:

the first is the widespread use of isoparaffinic solvents in products that arson examiners may encounter such as copier toners, lighter fluids, aerosol mixtures and insecticides and;

the second is the use of less expensive, more common petroleum distillates in the same types of products.

Due to the isoparaffinic composition of the ISOPAR solvent series, chromatograms of the various ISOPAR solvents differ significantly from more common petroleum distillates of similar boiling ranges.

These differences are readily discernable in the chromatograms of separations performed by use of capillary G.C. and are the basis used to distinguish isoparaffinic solvents from common petroleum distillates, Figure 3 illustrates such differences. Although the isoparaffinic charcoal lighter fluid "Gulf Lite" and the paint thinner have similar boiling ranges, examination of Figure 4 illustrates that Gulf Lite is an isoparaffinic product. This product has been encountered in several arson cases and is indeed an isoparaffinic product as reported by the manufacturer. Figure 5 shows ISOPAR G and a commercially available copier dispersant recovered in a recent arson case. The manufacturer indicated that an isoparaffinic solvent was used in the formulation of this product.

In conclusion, a series of isoparaffinic solvents have been described and chromatograms prepared for use as a quick reference that will enable isoparaffinic material to be distinguished from common petroleum distillates. The detection and reporting of isoparaffinic solvents in arson cases can add a greater degree of certainty to laboratory reports and provide invaluable investigative aid for use in the corroboration of stories, the matching of the M.O. or in the building of a case.

ACKNOWLEDGMENT

The author thanks Exxon Company for providing samples and technical information.

1/ Exxon Company, ISOPAR data sheets.

[FIGURE 1
ISOPARS C E G H]

ISOPAR C

ISOPAR E

ISOPAR G

ISOPAR H

TIME MINUTES

5

10

15

20

25

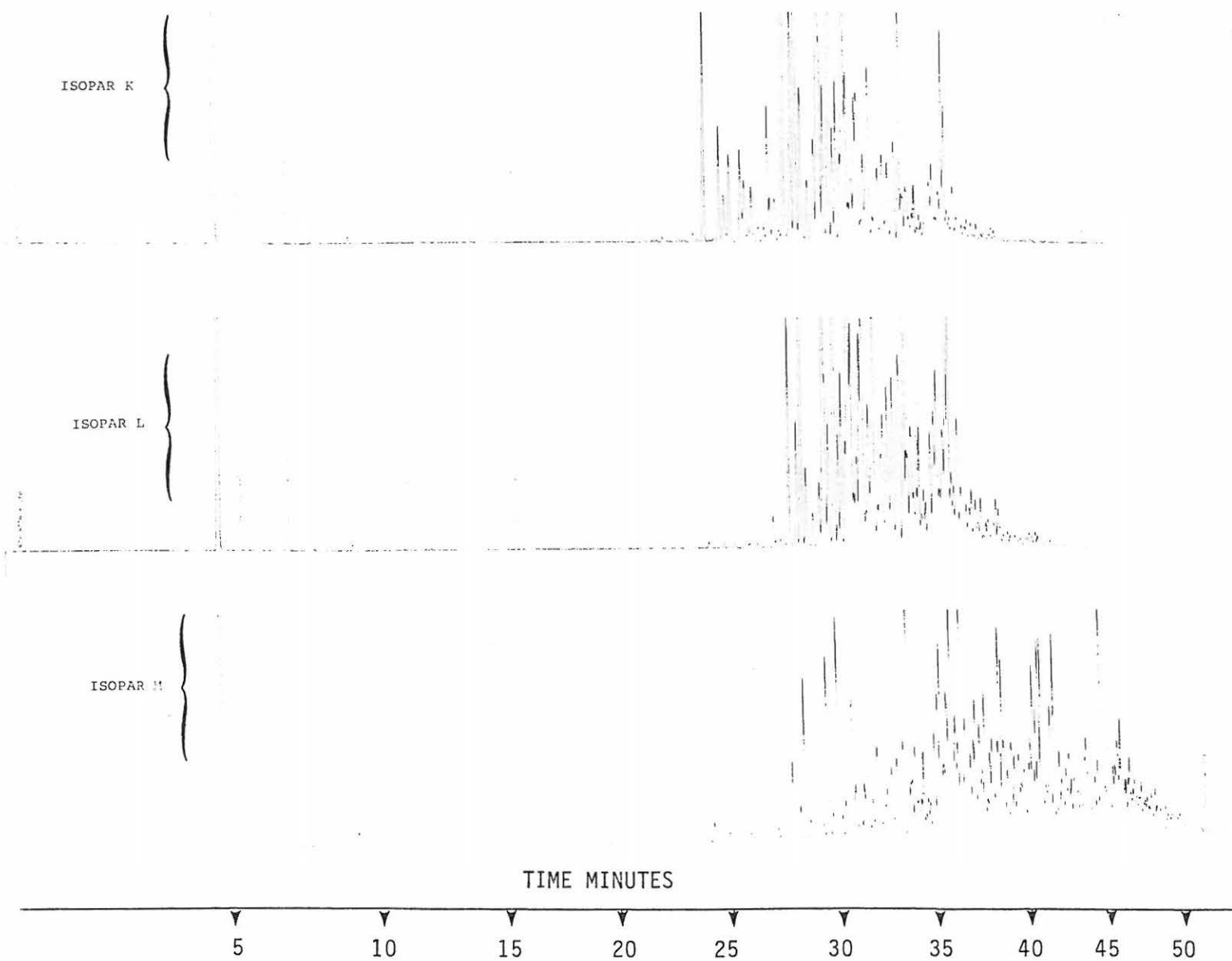
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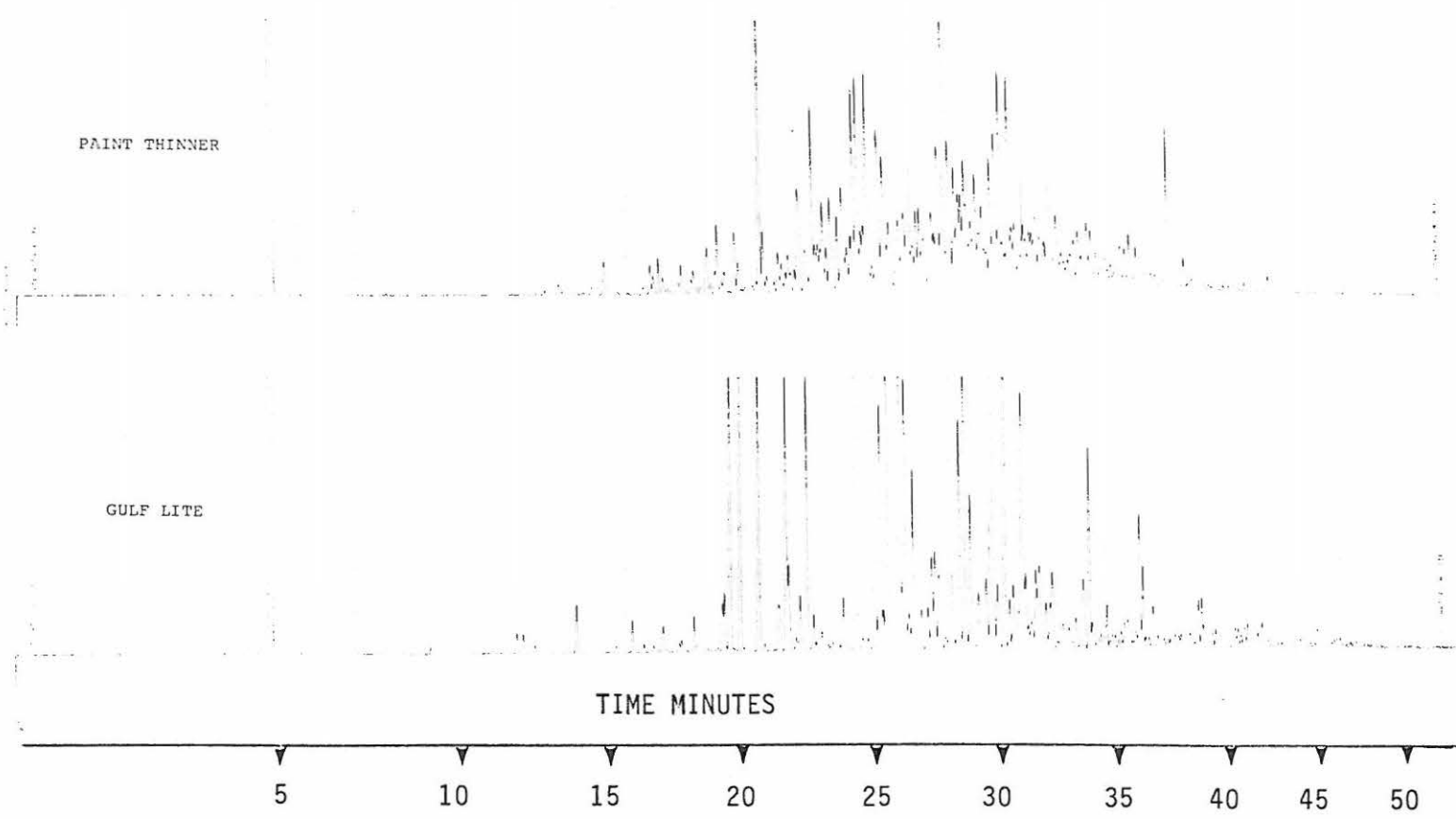
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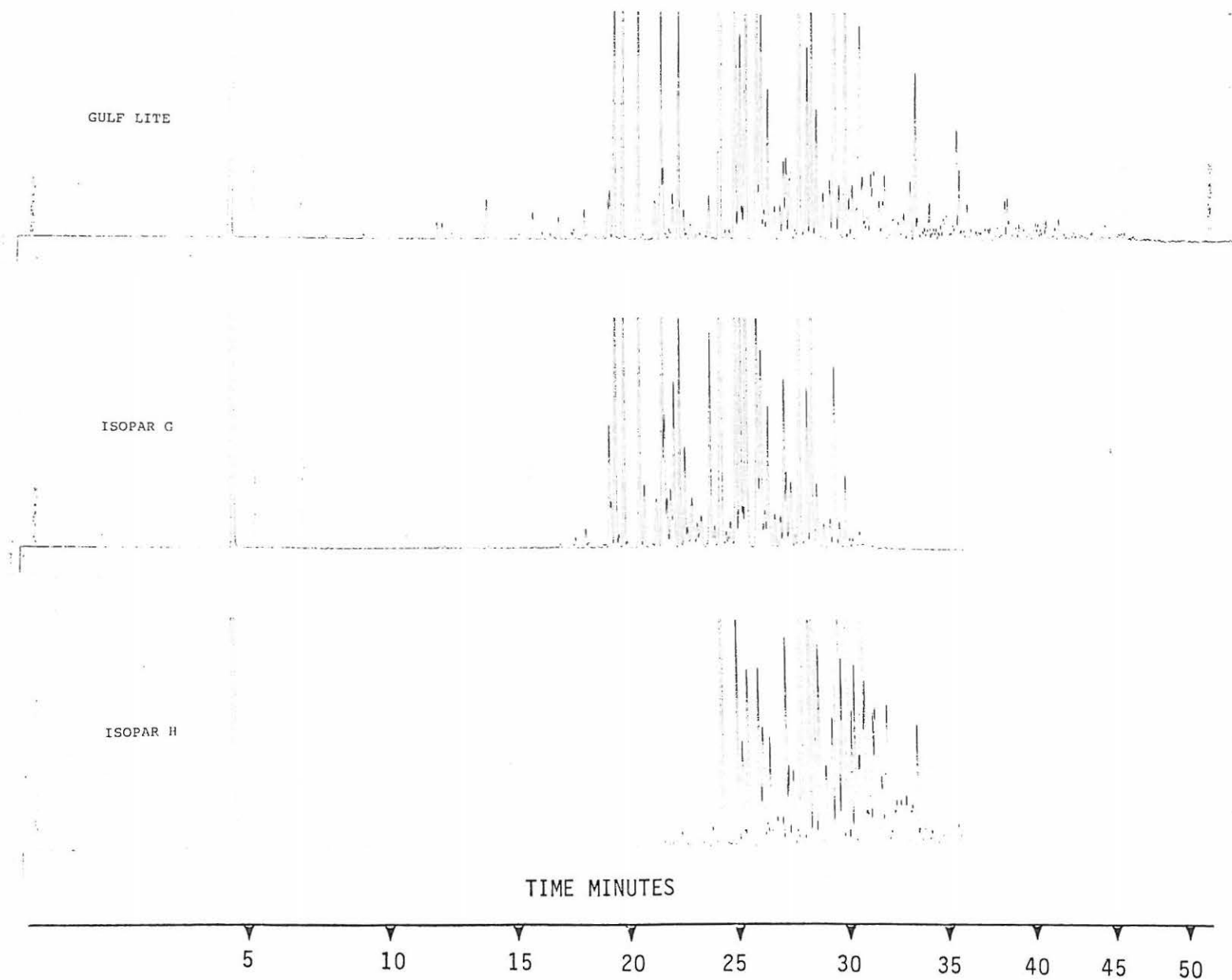
[FIGURE 2
ISOPARS K L M]



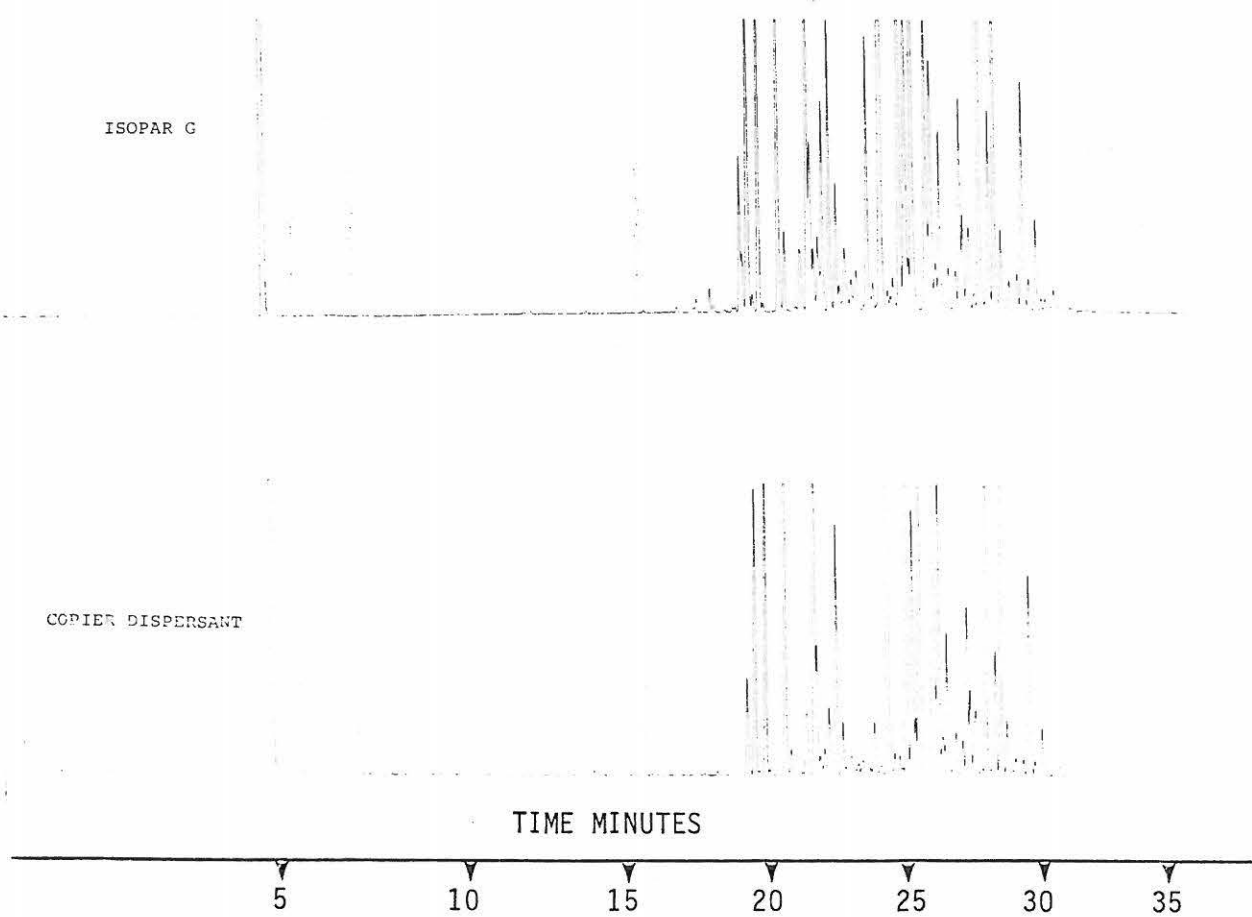
[FIGURE 3]



[FIGURE 4]



[FIGURE 5]



Relative Hydrocarbon Detectability by Flame Ionization
Detection for Various Isolation Methods

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We have recently contrasted basic aspects of the isolation of accelerants from fire debris by head space sampling and by steam distillation.¹ The successful use of the gas purge and trap method (GPT) for this purpose demonstrated many advantages over either head space sampling or steam distillation.^{2,3} However, we lacked quantitative information about our ability to "see" accelerants by the various methods. To provide such information we have run detectability tests with a flame ionization detector with selected hydrocarbons isolated by head space sampling, by steam distillation, and by GPT.

Experimental

Instrument. The gas chromatograph was a Varian-3700 with dual columns and dual flame ionization detectors. The columns were 1/8" x 6' stainless steel packed with 3% OV-101 on 60/80 Chromsorb GCRA. Samples were run isothermally at 140°C with an injection temperature of 200°C, a detector temperature of 290°C

and a helium flow rate of 30 ml. per minute. The recorder was a Sargent MR series (1 mv) with a chart speed of 1" per minute.

Standard Hydrocarbon Mixture. A mixture of 12.84 mg each of C-13, C-15 and C-16 normal hydrocarbons (Aldrich) was prepared in 100 ml (volumetric flask) of carbon disulfide solution and stored in a septum sealed bottle. Various aliquots of this mixture were used for the isolation and detection tests. The Varian 3700 instrument is capable of detecting 3×10^{-12} g at maximum sensitivity and the company provides a detectability test and a test solution of C-14, C-15 and C-16 in isooctane for this purpose.⁴ Because we had problems with impurities in our sources of isooctane, we switched to carbon disulfide as the solvent and we switched to C-13 from C-14 because of availability. We used the C-13 and C-15 peaks as indicator peaks and measured detectability for the C-16 peak. By detectability is meant the mass of a component required to give a 1% deflection of a peak over the baseline at maximum sensitivity.

Head Space Sampling. For this test, 0.50 ml (syringe) of the standard hydrocarbon solution was dispersed on a Kimwipe in a clean one gallon paint can. The carbon disulfide was allowed to evaporate for a few minutes and then the can was sealed. The can was placed in a Blue M oven at 100° for 30 minutes and a 5.0 ml vapor sample was removed by means of a Precision Sampling gas syringe. The sample was directly injected into the gas chromatograph.

Steam Distillation. Water (100 ml) and 10.0 ml (pipet) of the standard hydrocarbon mixture were placed in a 2 liter resin flask set up for steam distillation (see ref. 1 for a description of this apparatus). The mixture was steam distilled until a total of 200 ml of distillate collected. The head, the condenser and receiver were rinsed with two 25 ml portions of carbon disulfide and added to the distillate. The layers were shaken vigorously and the separated carbon disulfide layer was evaporated (rotary evaporator) to 3 ml and stored in a septum sealed vial until chromatographed. One μ l of the solution was chromatographed. The procedure was run in triplicate with the gas chromatograph at three different attenuations. The procedure was then triplicated for 1.4 ml of hydrocarbon solution steam distilled with the gas chromatograph run at three different attenuations.

Gas Purge and Trap Isolation. A 2.0 ml (pipet) sample of the hydrocarbon mixture was placed in a clean quart jar of the GPT assembly (see reference 2 for a description of this assembly). The nitrogen flow was adjusted to about 2-3 liters per minute for 15 minutes at an oven temperature of 80°C. The charcoal trap was removed and eluted with carbon disulfide to give 2.0 ml of eluate in a septum sealed vial. One μ l samples of the solution were chromatographed. The procedure was repeated with 0.5 ml, 0.1 ml, 10.0 μ l and 1.0 μ l samples of the standard hydrocarbon solution.

Results. The C-13 and C-15 hydrocarbons were used as indicator peaks and the detectability (D) was measured for the C-16 peak. The results for the three isolation methods are summarized in Table I. Typical gas chromatograms are shown as Figures 1, 2, 3, and 4.

Table 1
Detectability of Hexadecane^a

A. By Gas Purge and Trap^b

<u>Sample Size</u>	<u>%Deflection</u> ^c	<u>Attenuation</u>	<u>D, g</u> ^d
2.0 ml	79.5	80	2.6×10^{-11}
0.5 ml	37.7	80	2.9×10^{-11}
0.1 ml	15.5	80	1.7×10^{-11} (5.0×10^{-11} gm) ^f
10 μ l	4.7	80	1.1×10^{-11}
1 μ l	0.5	80	1.0×10^{-11}

B. By Steam Distillation^e

10.0 ml	19.5	800	4.1×10^{-11}
10.0 ml	15.0	2000	3.7×10^{-11}
10.0 ml	2.0	8000	4.0×10^{-11}
1.4 ml	35.0	80	3.3×10^{-11} (2.5×10^{-11} gm) ^f
1.4 ml	2.5	800	4.5×10^{-11}
1.4 ml	0.3	8000	3.7×10^{-11}

C. By Headspace^g

0.5 ml	0.5	80	2.1×10^{-9} (6.0×10^{-9} gm) ^f
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^aThe solution of standard hydrocarbon contained 12.84 mg. each of C-13, C-15, and C-16 in 100 ml of carbon disulfide. The specified sample size was added to the particular separation system. The isolated hydrocarbons were chromatographed isothermally at 140°C.

^bThe sample size refers to the sample subjected to the particular isolation method. For the GPT method, a 1.0 μ l sample of the trapped sample was injected into the GC.

^cThe percent deflection was measured from peak base to maximum peak height.

$$^d D = \text{detectability} = \text{sample weight} \times \frac{\mu\text{l injected}}{\mu\text{l of elute}} \times \frac{1}{\text{attn}} \times \frac{1}{\% \text{ deflection}}$$

^eFor the steam distillations, the final volume of carbon disulfide solution was 3.0 milliliters; a 1.0 μ l sample of this solution was injected into the GC.

^fNumbers in parentheses are reported by Roberta Given in her senior thesis.⁵ Her results were obtained at a later time (5 months) by a replication of the procedure reported here. Her values agree sensibly with the cited values.

^gThe head space sample was 5.0 ml of vapor. The results cited are the average of three runs.

It is evident from the results shown in the last column of Table 1 that both the GPT method and the steam distillation method allow one to isolate hydrocarbons from samples at a level near the limit of detectability of the instrument. However, the head space isolation method is less sensitive by a factor of about 100. The use of charcoal to simulate charred fire samples to retain accelerants was briefly evaluated for the recovery of hydrocarbons. By all three recovery methods considerably lower hydrocarbon detectability (by a factor of about 10 to 30) was observed. The important conclusions we would emphasize are the following (1) both GPT and steam distillation are considerably more efficient than head space isolation for the recovery of hydrocarbons. (2) the GPT method is preferred over the steam distillation primarily because of the time requirement and the simplicity of operation, (3) a hydrocarbon mixture of the type we have used is of value to compare resolution and detectability of gas chromatographs over periods of time at any given laboratory and between different laboratories. We strongly urge the adoption of such a calibration mixture, which could be readily furnished by various chromatographic supplier such as Applied Science Laboratories.⁶ We would be happy to cooperate with any interested groups in establishing such a calibration mixture and the necessary calibration procedure.

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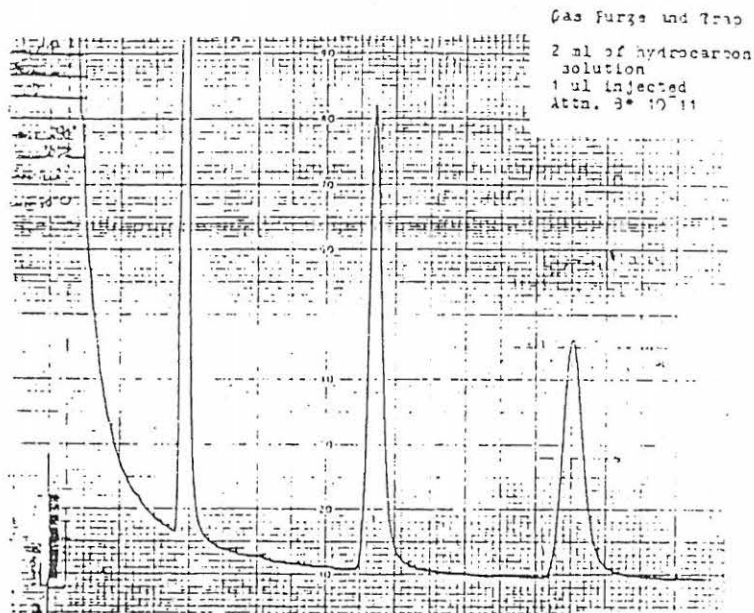
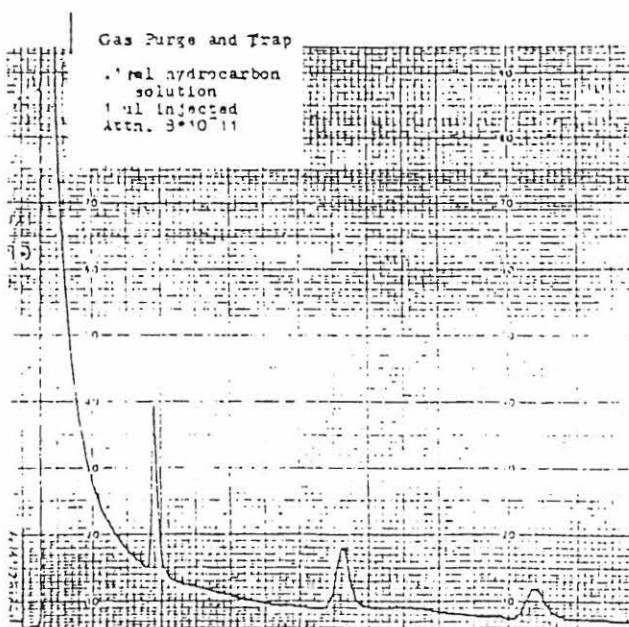
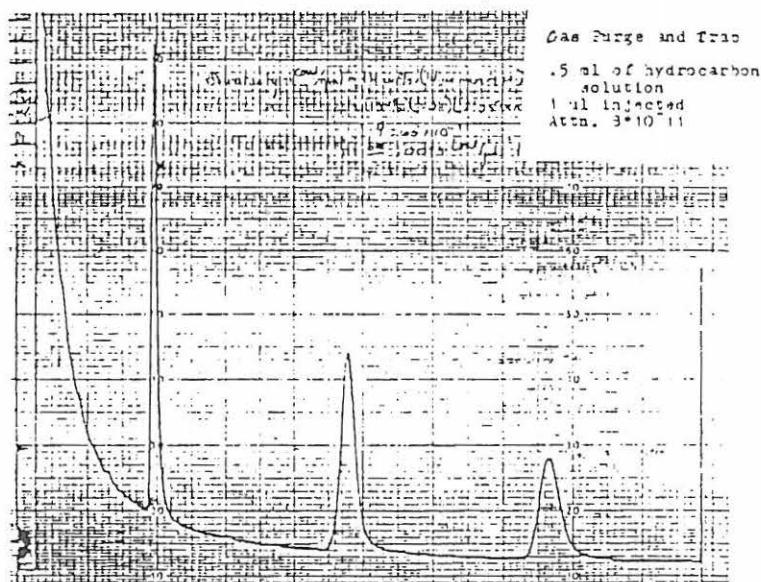


FIGURE 1:

Gas Purge and
Trap Studies



Steam Distillation
 10 ml hydrocarbon solution
 1 ul injected
 Attn. 8×10^{-11}

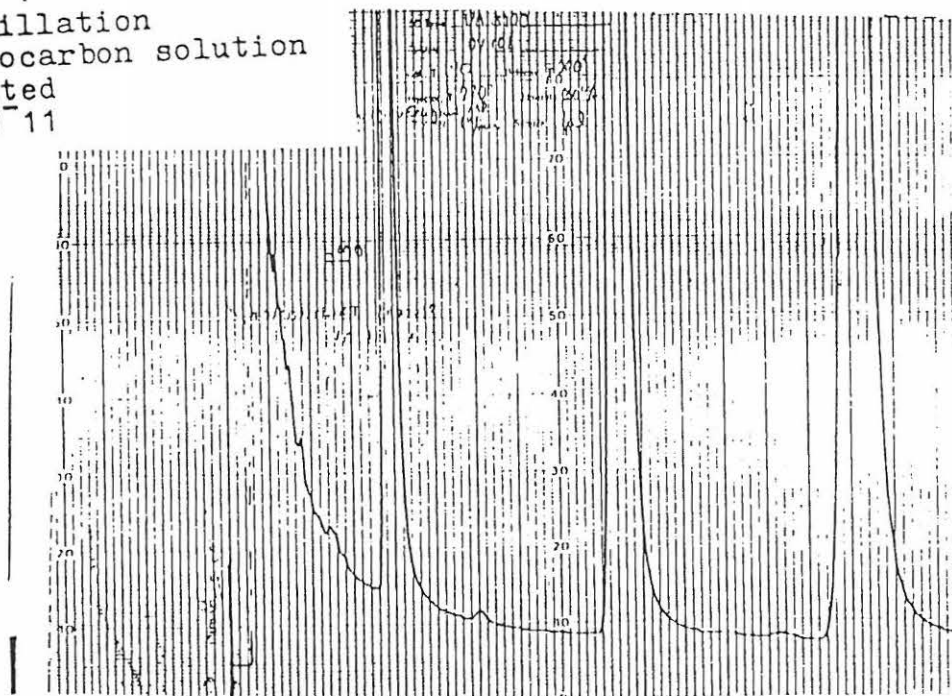
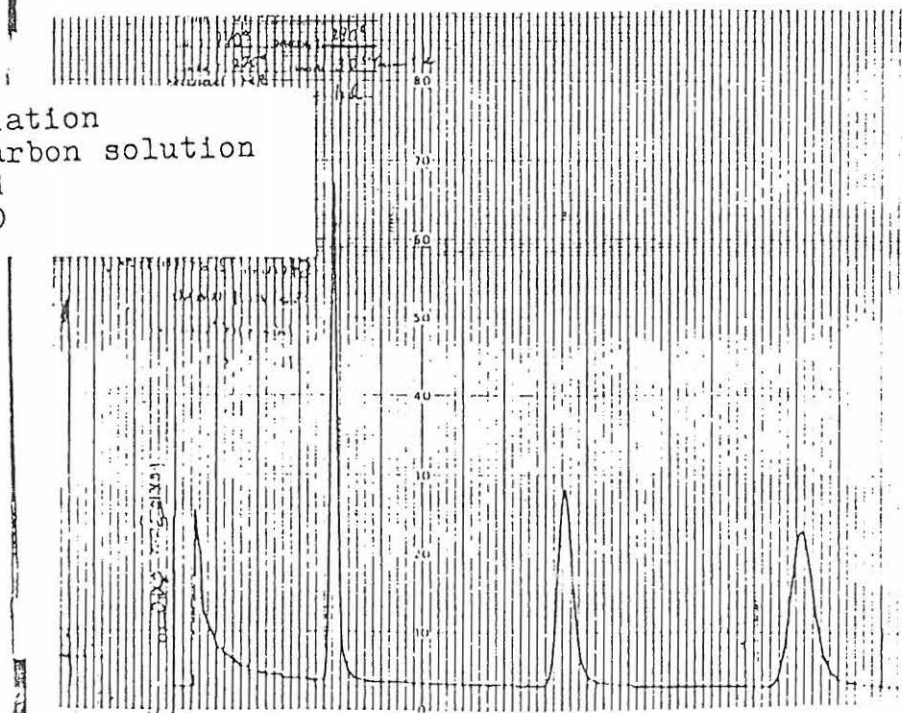


FIGURE 2:

Steam Distillation
 Studies

Steam Distillation
 10 ml hydrocarbon solution
 1 ul injected
 Attn. 8×10^{-10}



Steam Distillation
1.4 ml hydrocarbon solution
1 ul injected
Attn. 8×10^{-11}

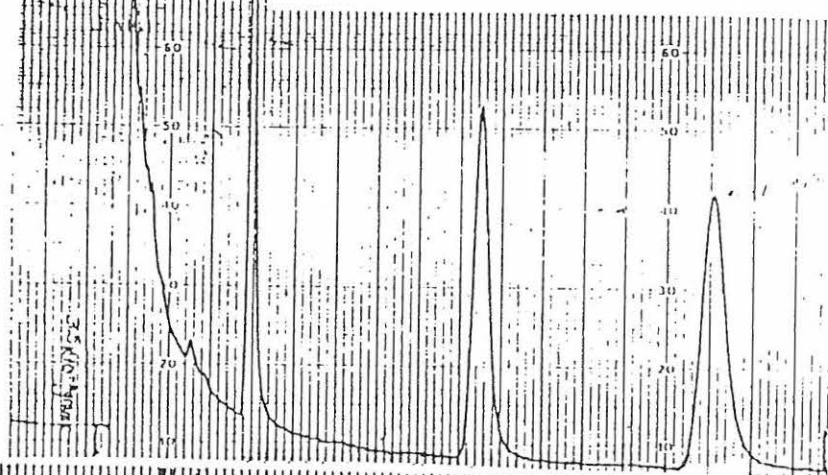
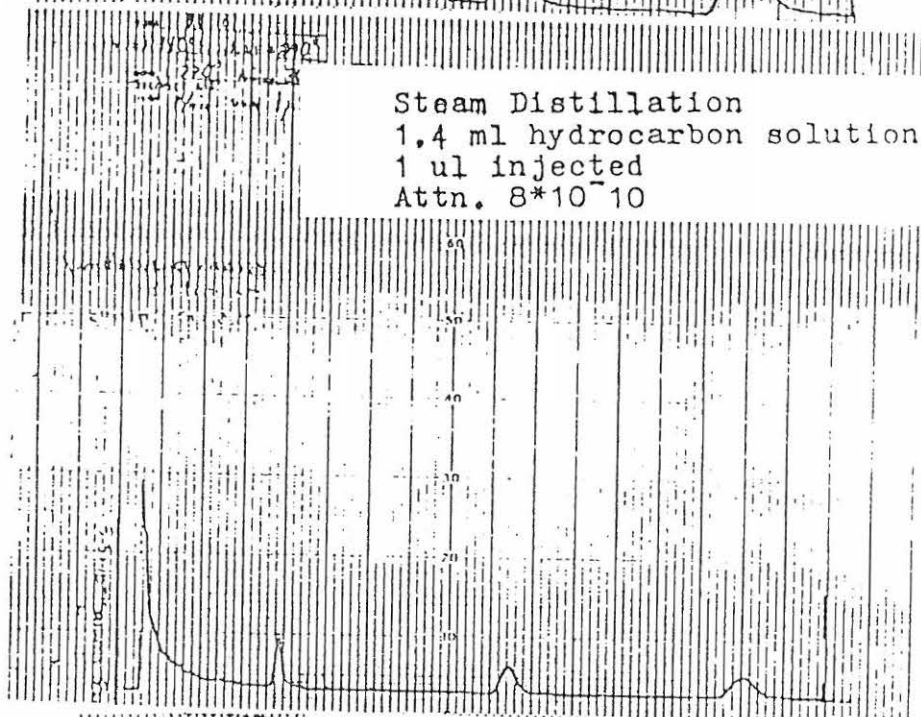


FIGURE 3:

Steam Distillation
Studies

Steam Distillation
1.4 ml hydrocarbon solution
1 ul injected
Attn. 8×10^{-10}



Steam Distillation
1.4 ml hydrocarbon solution
1 ul injected
Attn. 8×10^{-9}

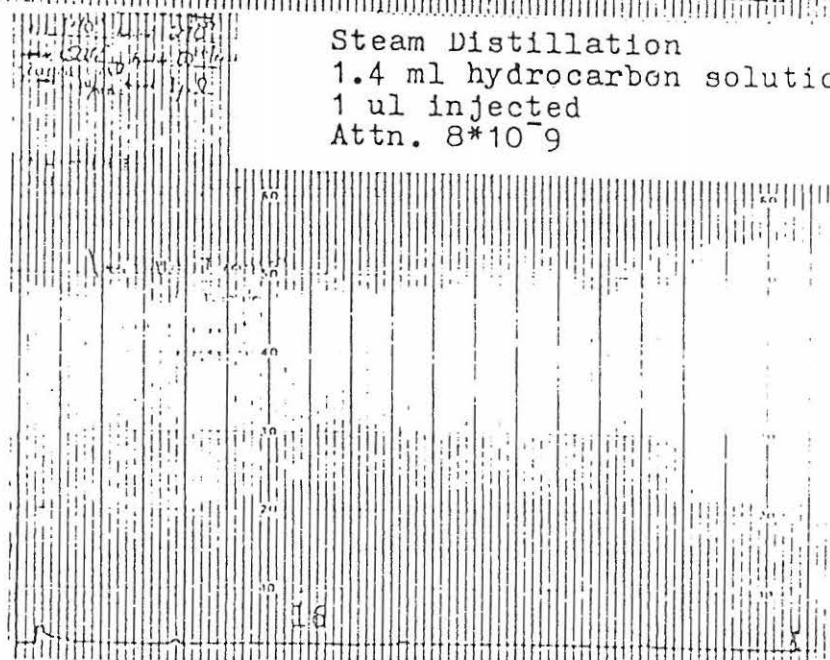
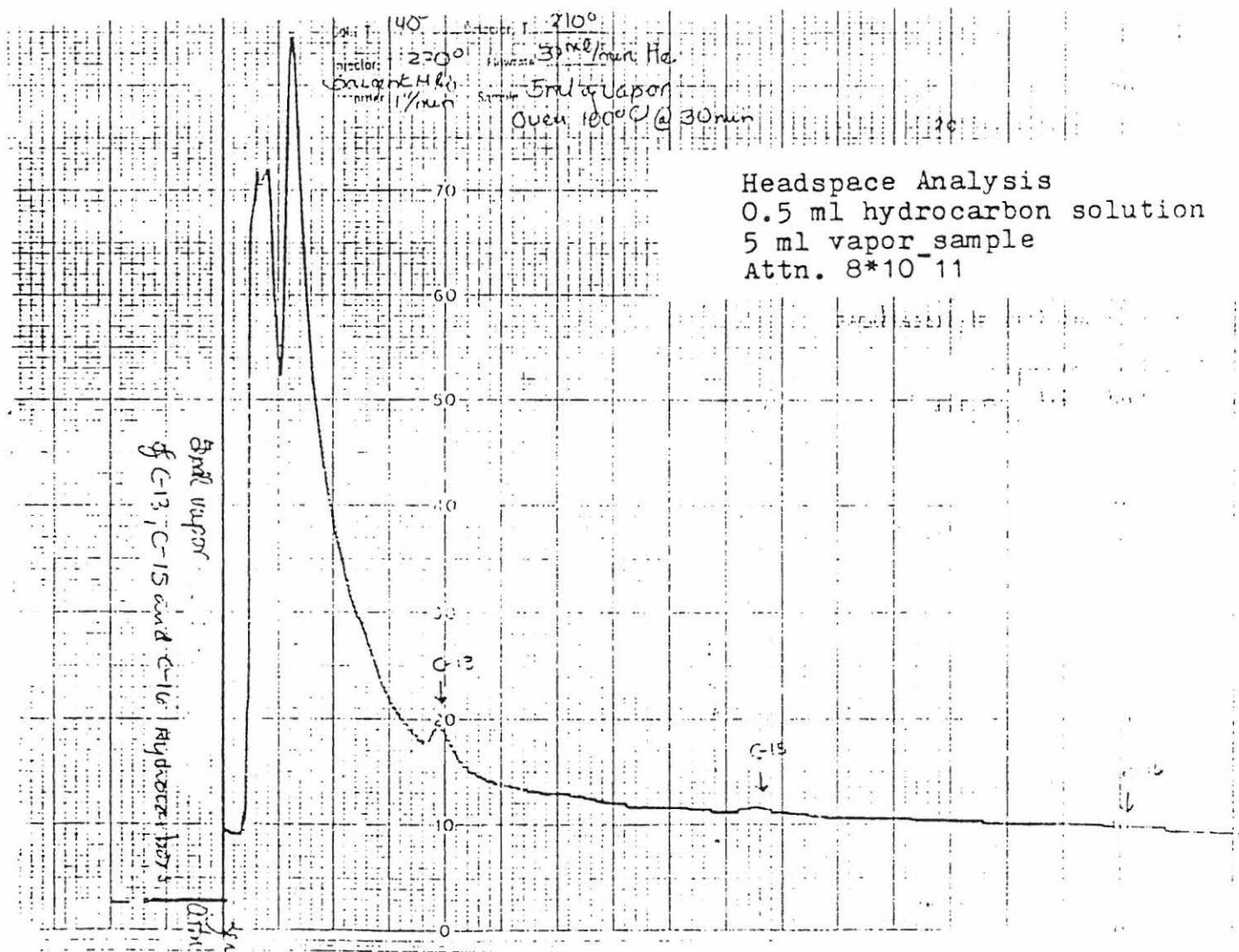


FIGURE 4:

Headspace Sampling Studies



AANotes

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Secondly, the rate of re-newal is behind last years rate. Tell your associates in other facilities to renew the publication.

- * From the Journals:
 - ** An article titled "Automated Sampling and Computer-Assisted Identification of Hydrocarbon Accelerants" appeared in the Journal of Forensic Science this year, p., 710-714, by, R. E. Tontarshi and R. A. Strobel.