

TECHNICAL NOTE

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Fractionation of Accelerants and Arson Residues by Solid Phase Extraction

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ABSTRACT: Adsorption elution extracts of fire debris are separated on solid phase extraction columns to divide the sample into aliphatic and aromatic hydrocarbon fractions. The fractions are analyzed by gas chromatography (GC) and compared with standard accelerants similarly treated.

KEYWORDS: criminalistics, arson, accelerants, chromatographic analysis, arson accelerant analysis, pyrolyzate contamination

As arson residue recovery techniques become more sensitive allowing the identification of minute quantities of accelerants (on the order of 1 μ L), the problem of equivalent amounts of interfering pyrolysis products grows correspondingly. It does little good to be capable of detecting 1 μ L of gasoline if it is obscured by 2 μ L of a pyrolysis product.

Currently, labs that have the capabilities of mass spectroscopy (MS) can utilize mass chromatography [1,2]. The MS has also been used to characterize the pyrolysis residues of debris thereby eliminating false positive responses [3]; however, not all laboratories are so well equipped. In an earlier paper [4], this analyst described a thin-layer chromatographic (TLC) method of cleaning arson residue samples. Further development of this technique and its modification to use solid phase extraction (SPE) concepts has provided a significant improvement in accelerant identification and pyrolyzate elimination.

With the use of solid phase extraction, the problem pyrolysis material can be successfully handled. In addition, the accelerant is manipulated in such a way that it produces more identifying data. Solid phase extraction permits significant manipulation of the stationary and mobile phases. This ability allows for fine-tuning the separations in a rapid, simple, and elegant manner. Many SPE products are available (Sep-Pak [Waters], Bond Elute [Analytichem], Baker-SPE), and all allow a type of simplified high pressure liquid chromatography (HPLC) approach to adsorption-elution arson residue samples.

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Technique and Equipment

Sep-Pak Silica Cartridges (51900) produced by Waters Associates, Inc. were used as the SPE product in this work. All solvents were omnisolve grade consisting of hexane, benzene, and carbon disulfide. Charcoal traps (MCB: 20 to 40 mesh) were produced in glass pipettes similar to the method suggested by the Bureau of Alcohol, Tobacco and Firearms (ATF).

All chromatography was performed on a PE Sigma 3B gas chromatograph with a Sigma 15 data station. Column parameters were as follows: 10M, OV-101 (Altech cat C-FSOT-25) 0.25-mm inside diameter (ID), 0.2- μ m film thickness; injector/detector at 275°C; program of 50°C for 1 min, rate 30°C/min to 250°C, hold for 2 min. The carrier gas was helium at 4.5-kg (10-lb) split ratio of approximately 40:1.

To prepare standards of the accelerants used in this paper (gasoline and diesel fuel, and so forth) the following procedure was used:

Of the accelerant 1 μ L was placed in approximately 0.2 mL of carbon disulfide (CS₂). This solution was pipetted onto a prewashed Sep-Pak cartridge and dried with a gentle stream of air.

A spiked pyrolysis adsorption-elution standard was prepared by burning nylon carpet and polyurethane and then placing them in a 3.8-L (1-gal) can. The can was heated to 70 to 90°C for 30 min while pulling air through the can and charcoal trap by means of lab vacuum. Extraction of the trap was accomplished with CS₂ yielding a finished volume of 1 mL. This solution was spiked with 1 μ L of 87% evaporated leaded regular gasoline. The test solution was placed on the prewashed cartridge by the above method after evaporating at room temperature with air to approximately 0.2 mL.

All elutions from the SPE cartridges were accomplished with approximately 4 mL of hexane:benzene (95:5) in a 5-mL glass syringe. (All cartridges were washed with 5 mL of hexane and dried before use.) The syringe was attached to the cartridge and the eluting solvent added along with the plunger. Gentle pressure on the plunger allowed delivery of the eluant dropwise. Multiple fractions were taken in tubes consisting of five drops each and each fraction was identified as a set. Individual fractions or combinations of fractions were injected into the GC in 3- μ L quantities.

Results and Discussion

In the prior work [4], petroleum accelerants were separated into two areas on the TLC plate: I: R_f 0.3 to R_f 0.7, II: the solvent front. Those compounds in Area I responded to Marquis reagent yielding colors consistent with aromatic compounds. The compounds in Area II failed to color with Marquis. When they were extracted and run on the GC (under conditions previously described), the chromatogram was rich in *n*-alkanes. Retrieval of the materials was difficult so a more effective procedure was sought. SPE appeared to offer an equivalent separating ability and easier recovery.

The usual accelerants involved in arson cases are petroleum distillants. As such, they are made up of families of compounds which can be loosely classified as aliphatic hydrocarbons, single ring substituted aromatics, and fused ring aromatics. Pyrolyzate materials are more difficult to characterize but possibly possess compounds in each of these classes along with additional polar components (that is, oxygenated and nitrogenous compounds). With the judicious use of eluant strength it is possible to separate the different hydrocarbon families in a pyrolyzate sample or an accelerant sample. The polar compounds pose little problem because it is easy to retain polar materials in a sample on silica gel by using nonpolar eluting solvents [5].

To demonstrate the separation of these families, a test solution consisting of equal amounts of the *n*-alkanes (C12, C14, C16, C18), Tenneco Oil Co. solvent T-500-100, and naphthalene was prepared for testing (Solvent T-500-100 contains the compounds listed in Table 1 repre-

TABLE 1—Gas chromatographic analysis, Tenneco Oil Company, T-500-100 TK 220 ID T-83-72.

	% by Weight
Toluene	0.15
Ethylbenzene	2.65
<i>p</i> -xylene	1.91
<i>m</i> -xylene	9.20
<i>o</i> -xylene	6.91
<i>iso</i> -propylbenzene	0.82
<i>n</i> -propylbenzene	4.01
1-methyl-3-ethylbenzene	15.35
1-methyl-4-ethylbenzene	6.10
1-methyl-2-ethylbenzene	5.70
1,3,5-trimethylbenzene	8.20
1,2,4-trimethylbenzene	26.25
1-methyl-3-isopropylbenzene	0.44
1,2,3-trimethylbenzene or 1-methyl-4-isopropylbenzene or both	4.66
1-methyl-2-isopropylbenzene or indane or both	1.25
1,3-diethylbenzene	1.06
1-methyl-3- <i>n</i> -propylbenzene	0.99
<i>n</i> -butylbenzene	0.16
1,2-diethylbenzene or 1,4-diethylbenzene or 1-methyl-4- <i>n</i> -propylbenzene or all	0.82
1-methyl-2- <i>n</i> -propylbenzene	0.22
1,3-dimethyl-5-ethylbenzene	1.10
1,4-dimethyl-2-ethylbenzene	0.47
1,3-dimethyl-4-ethylbenzene	0.35
1,3-dimethyl-2-ethylbenzene or 1,2-dimethyl-4-ethylbenzene or both	0.80
1,2-dimethyl-3-ethylbenzene	0.25
1,2,4,5-tetramethylbenzene	0.08
1,2,3,5-tetramethylbenzene	0.10
Total	100.00

senting the C-8 through C-10 aromatic compounds in gasoline). This solution was fractioned (or separated) by Sep-Pak cartridge as previously described and the fractions (sets) run on GC. In Fig. 1 the chromatogram of the original test solution is displayed. Figures 2 and 3 show, respectively, Fractions $\frac{3}{4}$ and Fractions $\frac{1}{12}$. Although the separation of aliphatics from aromatics is not complete, it is certainly quite distinct. This agrees with the TLC responses seen in the earlier method [4].

It is known that gasoline has significant quantities of aliphatic hydrocarbons and aromatic hydrocarbons [6]. A fractioning procedure was performed on this fuel to generate a standard chromatogram of the aliphatic and aromatic fractions of gasoline. A fractioning process was also applied to a diesel fuel solution. The results for gasoline are seen in Figs. 4 (Fraction 5) and 5 (Fraction 9). The results for diesel fuel are seen in Figs. 6 (Fraction 8) and 7 (Fraction 12). Figures 4 and 6 represent compounds in the aliphatic region (found in Fractions 3 to 8 from the Sep-Pac cartridge). Figures 5 and 7 represent compounds in the aromatic region (found in Fractions 9 to 13 with this SPE product).

The resulting chromatograms are reproducible from one fractioning procedure to the next. This separation of aliphatic hydrocarbons from aromatic hydrocarbons yields two sets of analytical data on which to base an identification of these accelerants (the aliphatic hydrocarbon content [AHC] and the aromatic hydrocarbon content [ARHC]). If the problem pyrolyzate material in a case sample is primarily aliphatic, the ARHC of an accelerant would be relatively

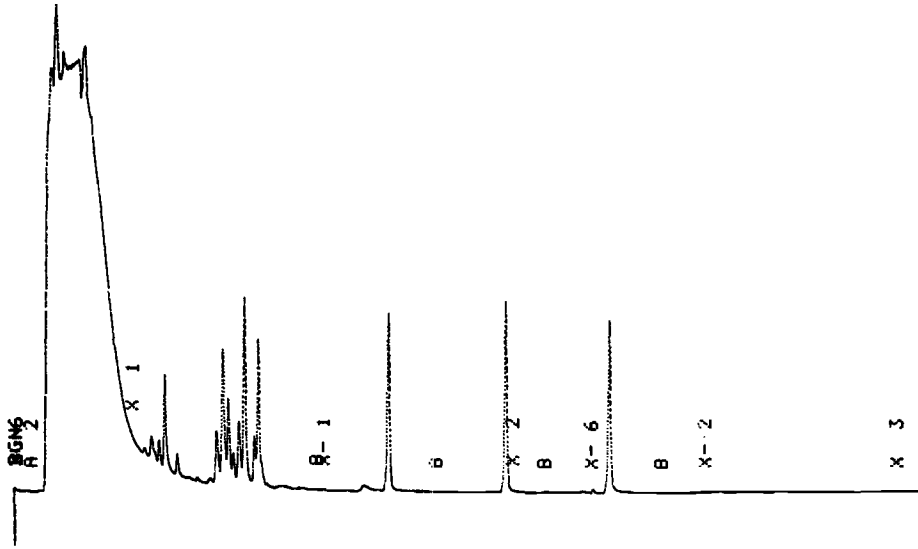


FIG. 1—Test solution.

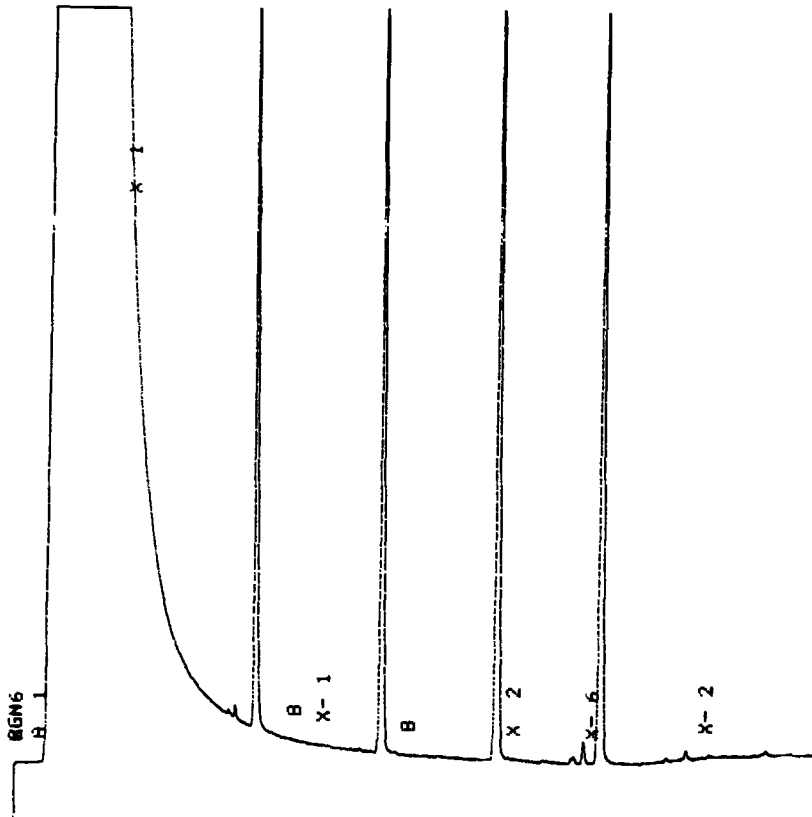


FIG. 2—Fraction $\frac{3}{4}$.

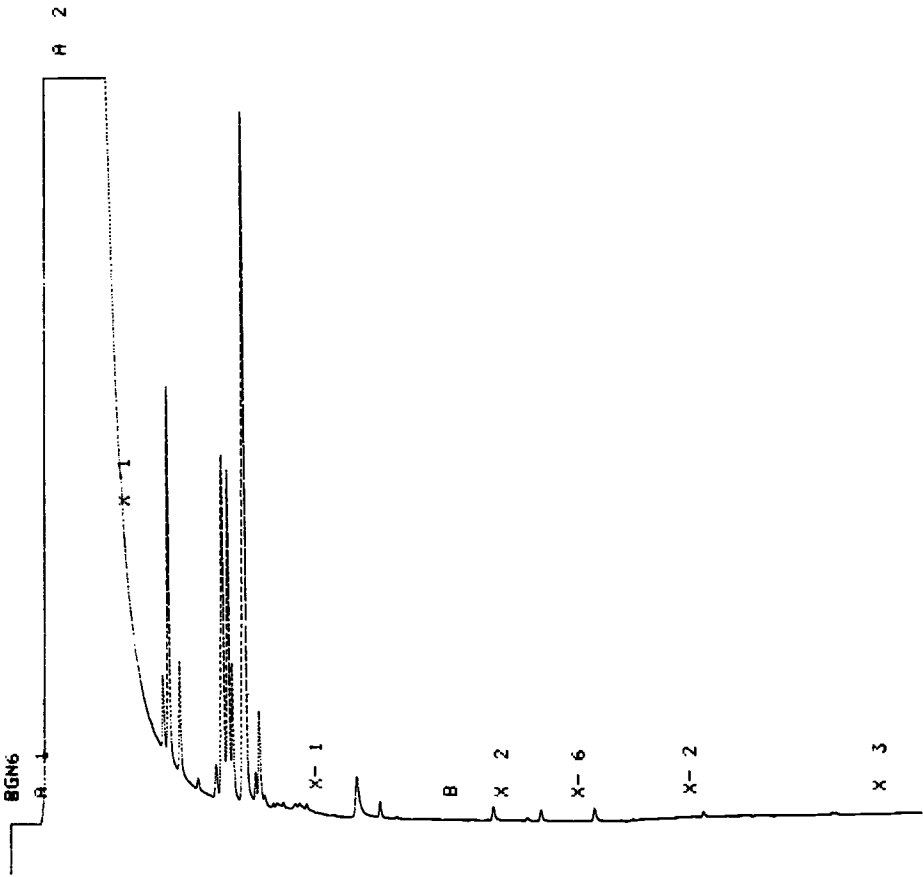


FIG. 3—Fraction 11/12.

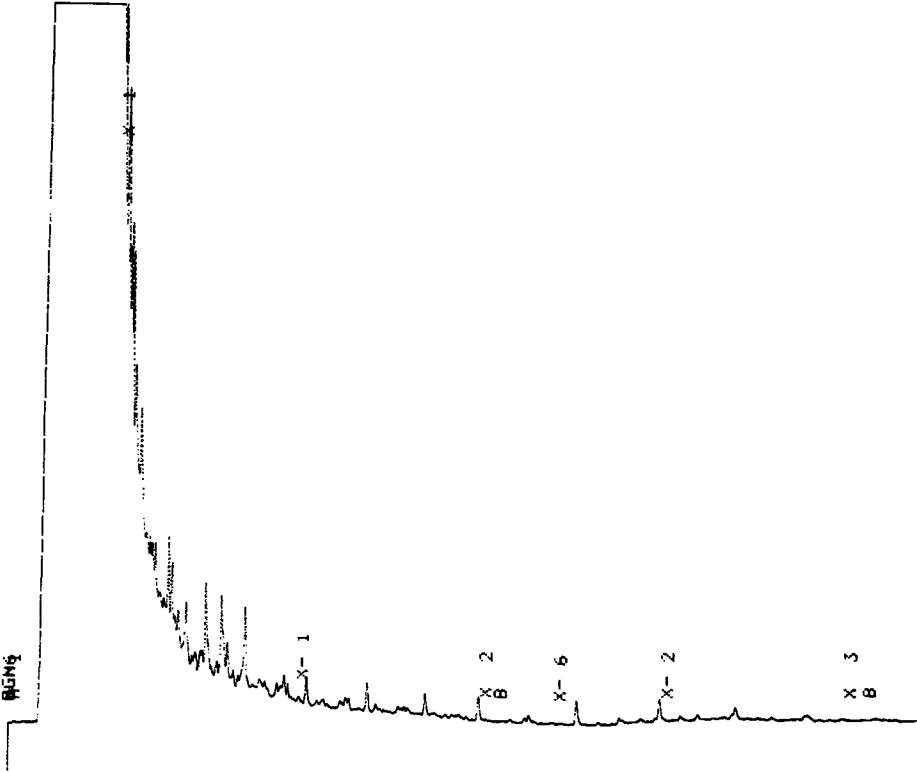


FIG. 4—Gasoline, Fraction 5.

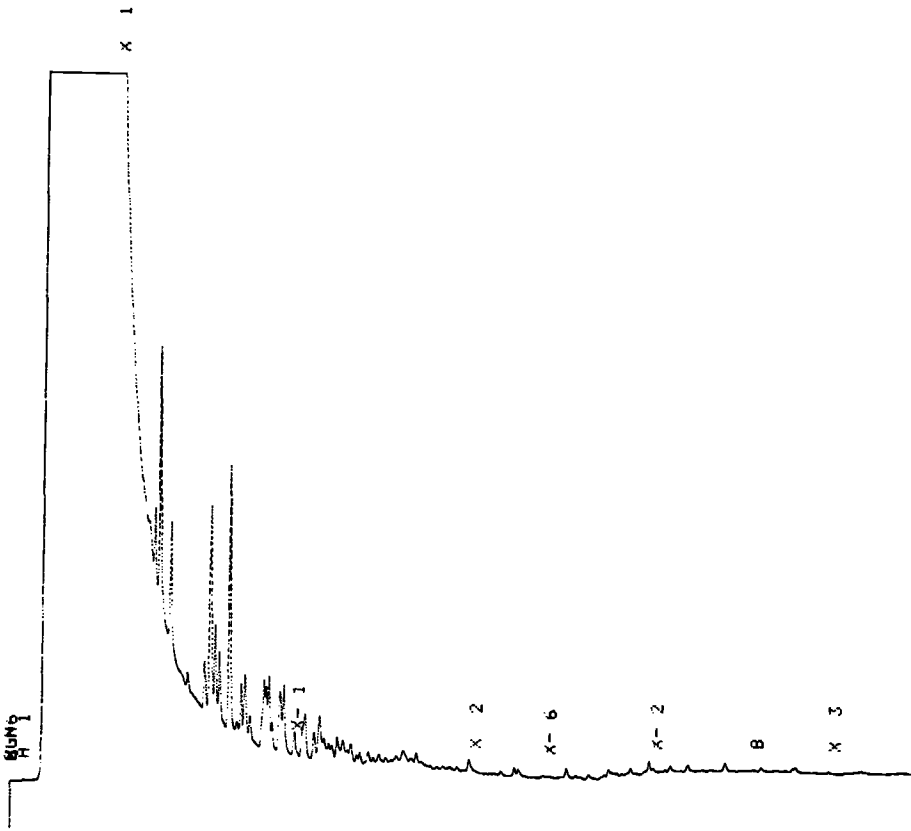


FIG. 5—Gasoline, Fraction 9.

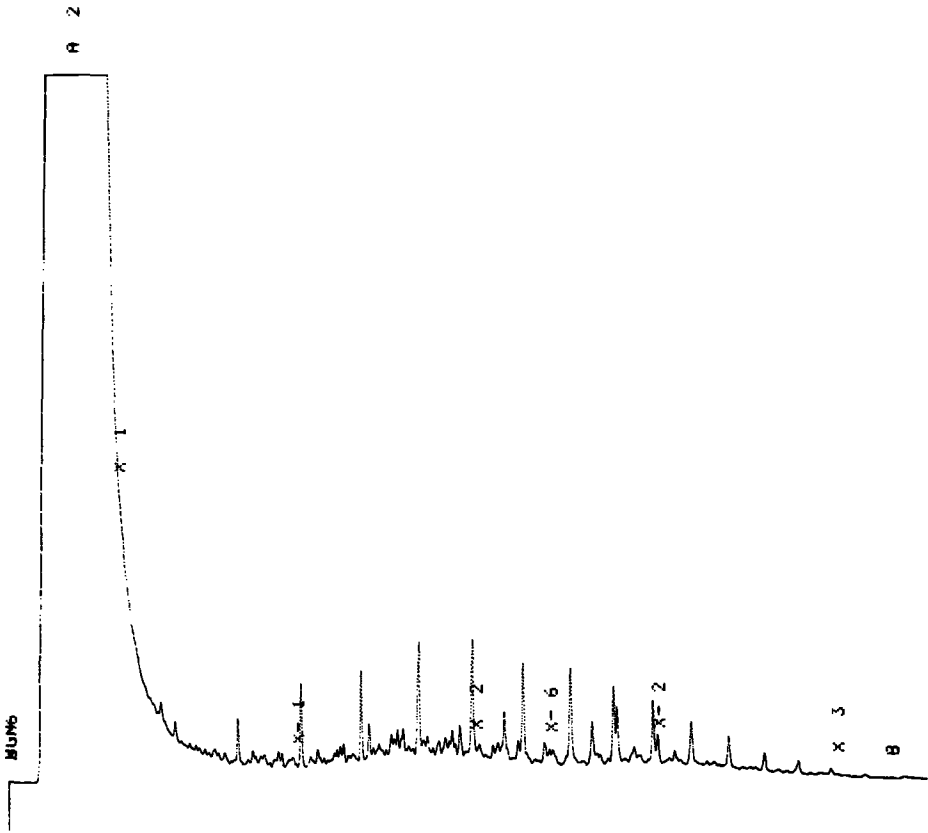


FIG. 6—Diesel, Fraction 8.

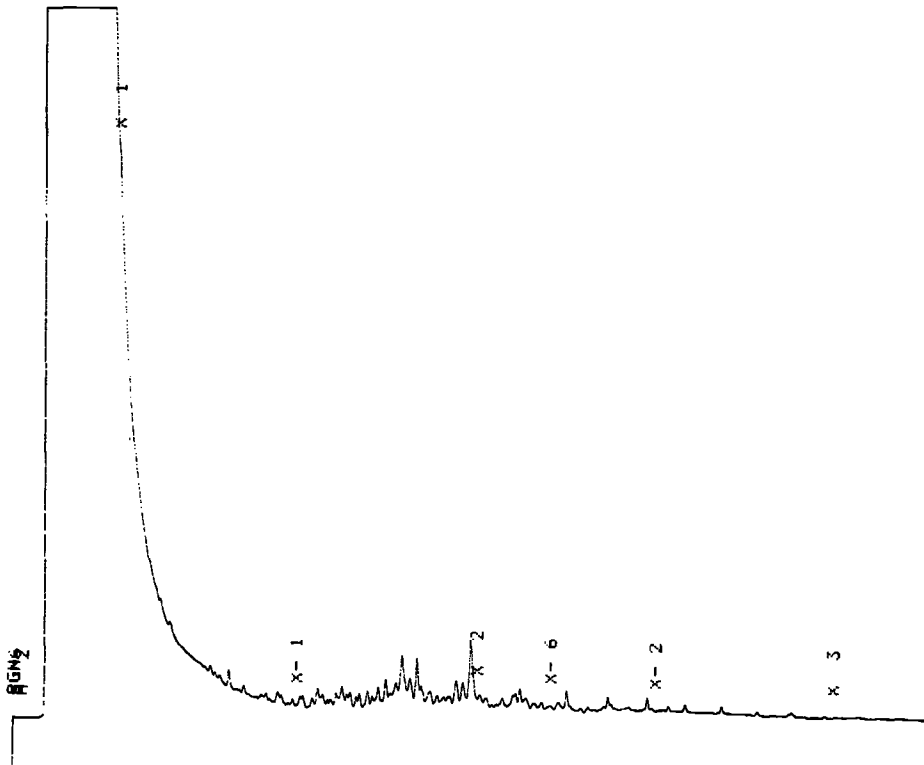


FIG. 7—Diesel, Fraction 12.

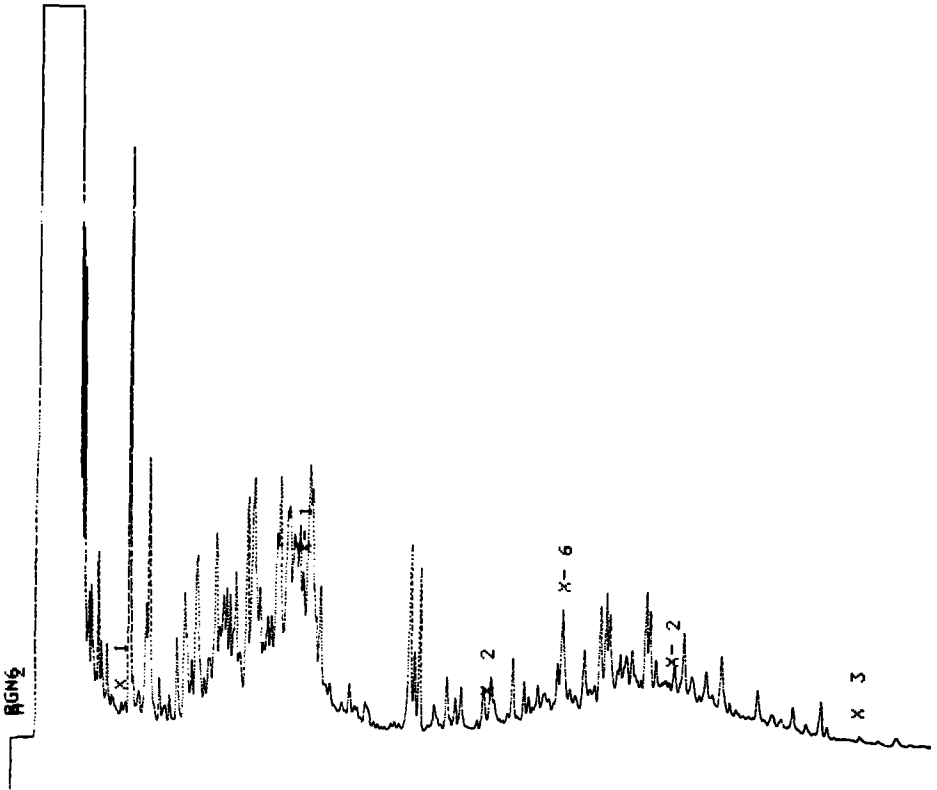


FIG. 8—Pyrolyzate residue.

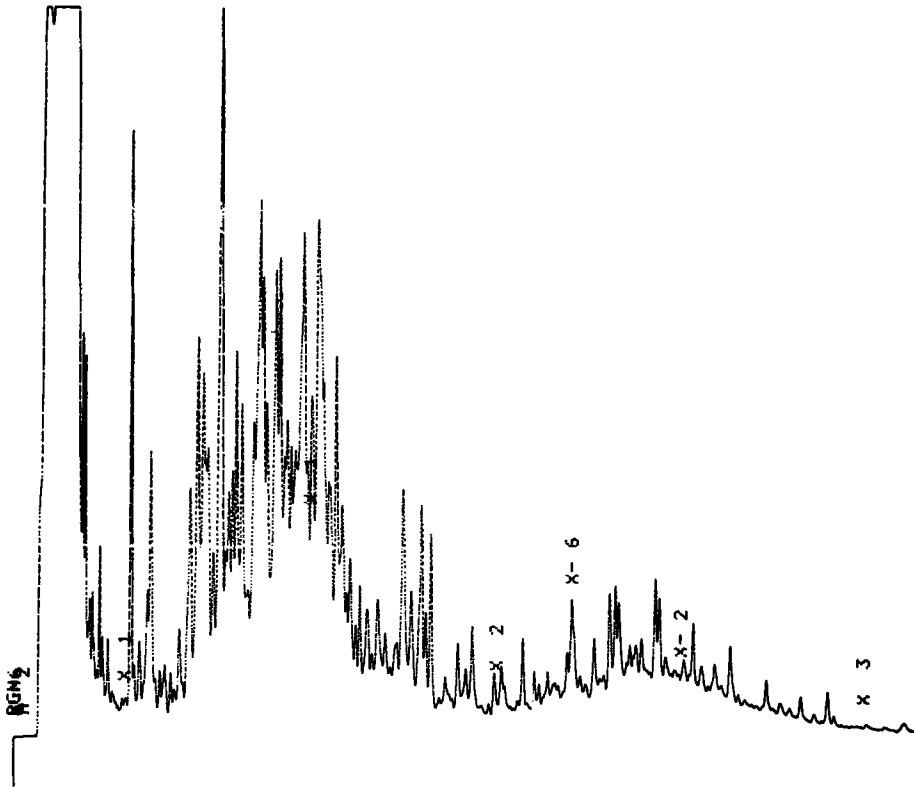


FIG. 9—Spiked pyrolyzate residue.

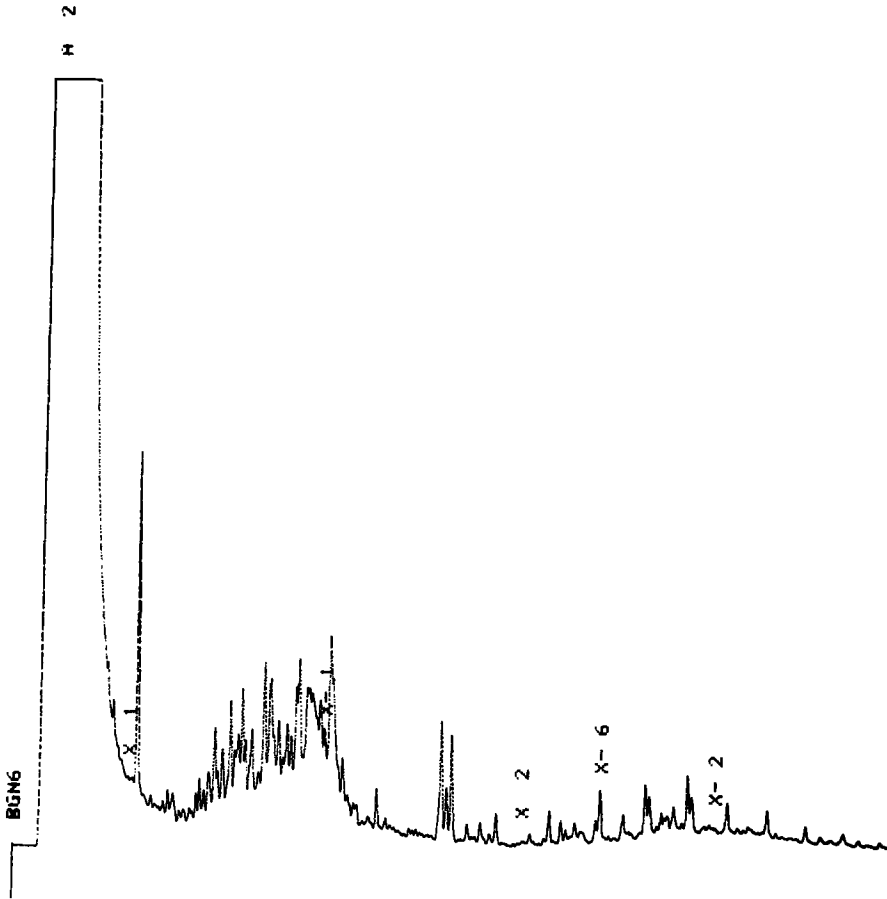


FIG. 10—AHC fraction (2/6) of spiked sample.

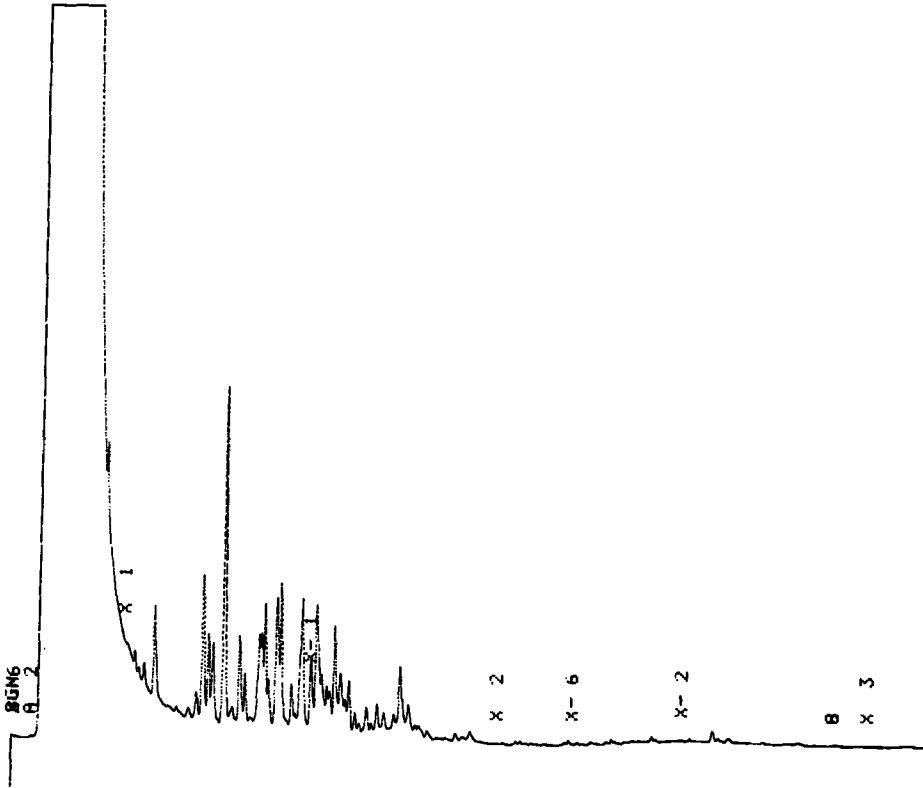


FIG. 11—ARHC fraction of spiked sample.

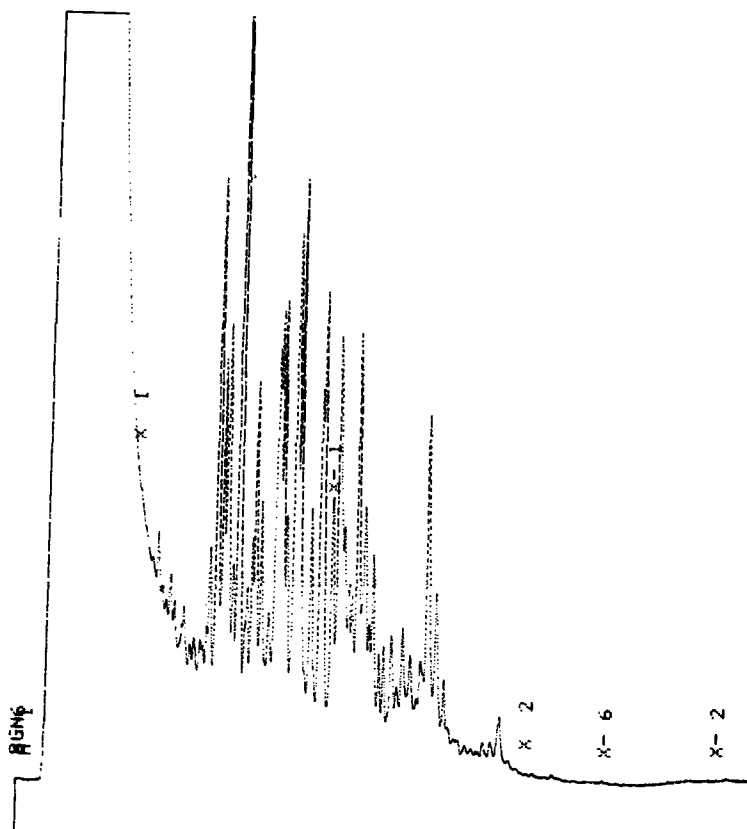


FIG. 12—Eighty-seven percent evaporated gasoline.

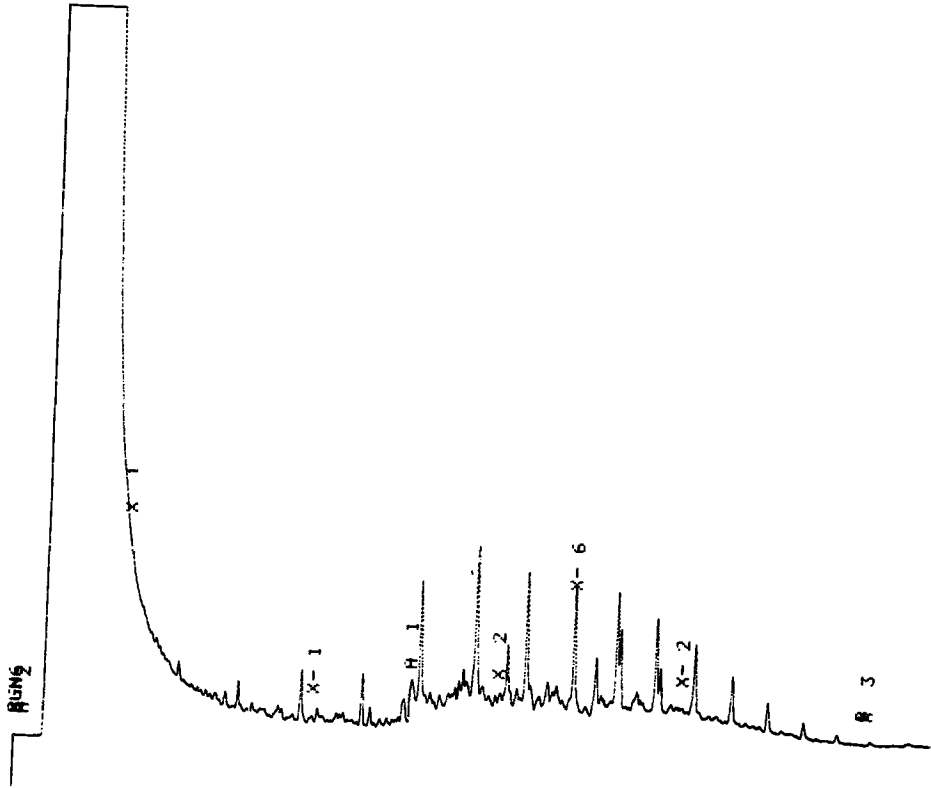


FIG. 13—Diesel fuel.

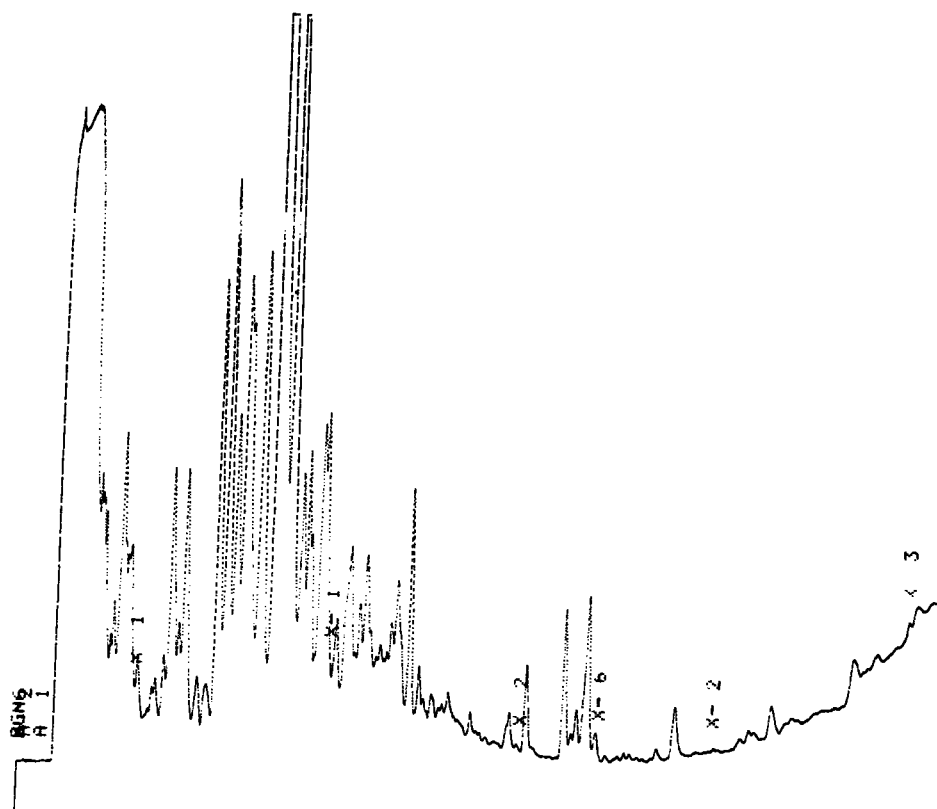


FIG. 14—Adsorption elution extract Sample 5.

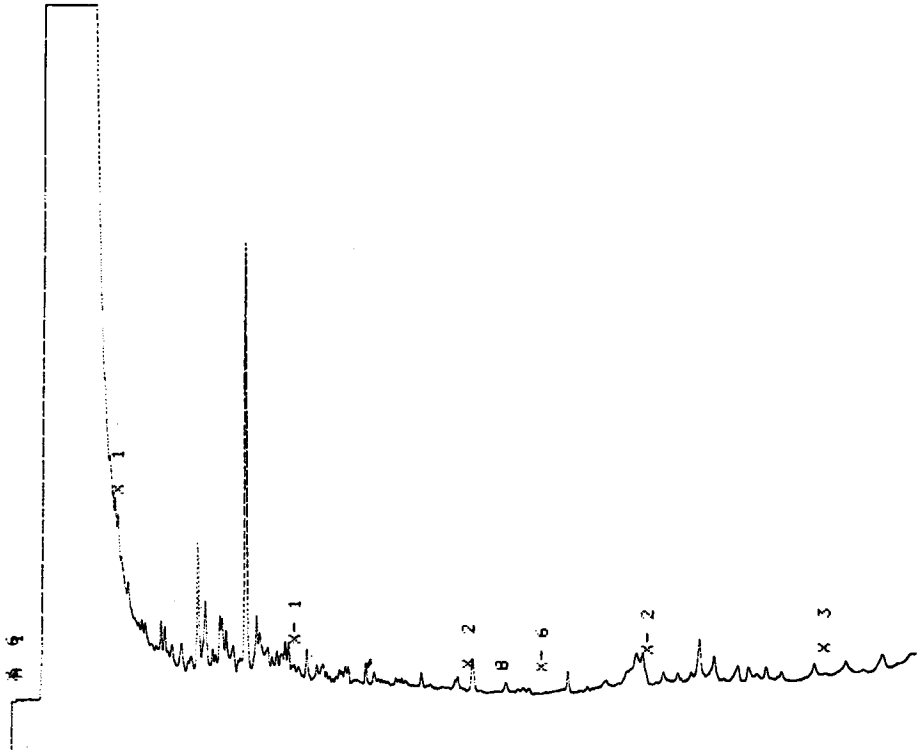


FIG. 15—AHC fraction of Sample 5.

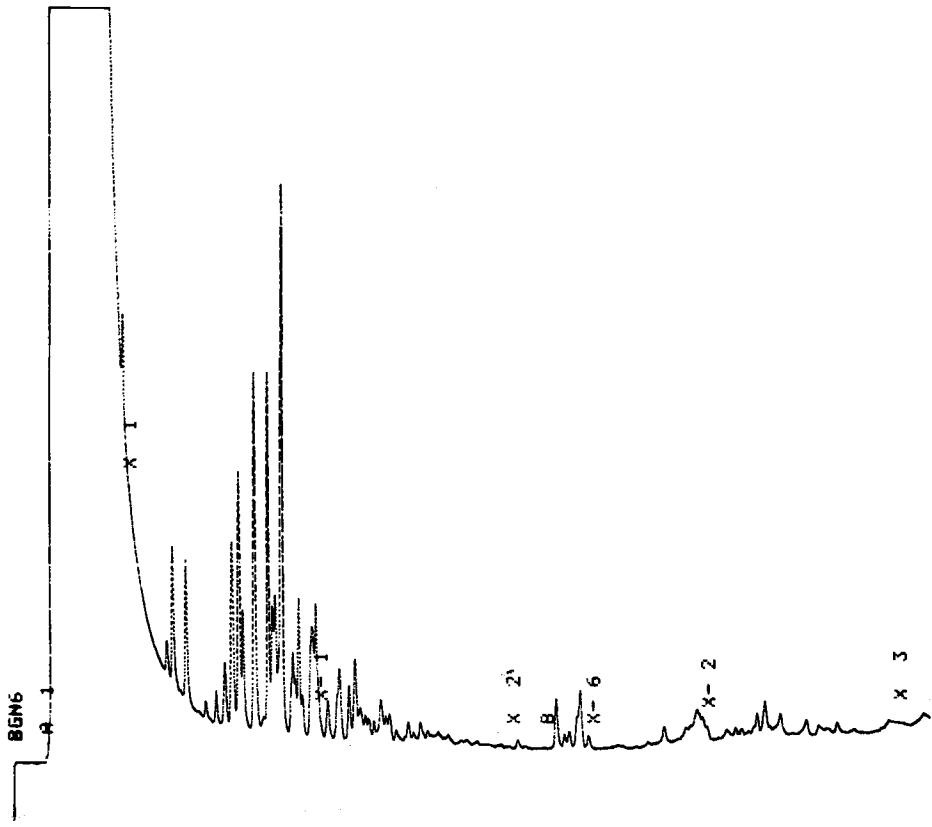


FIG. 16—ARHC fraction of Sample 5.

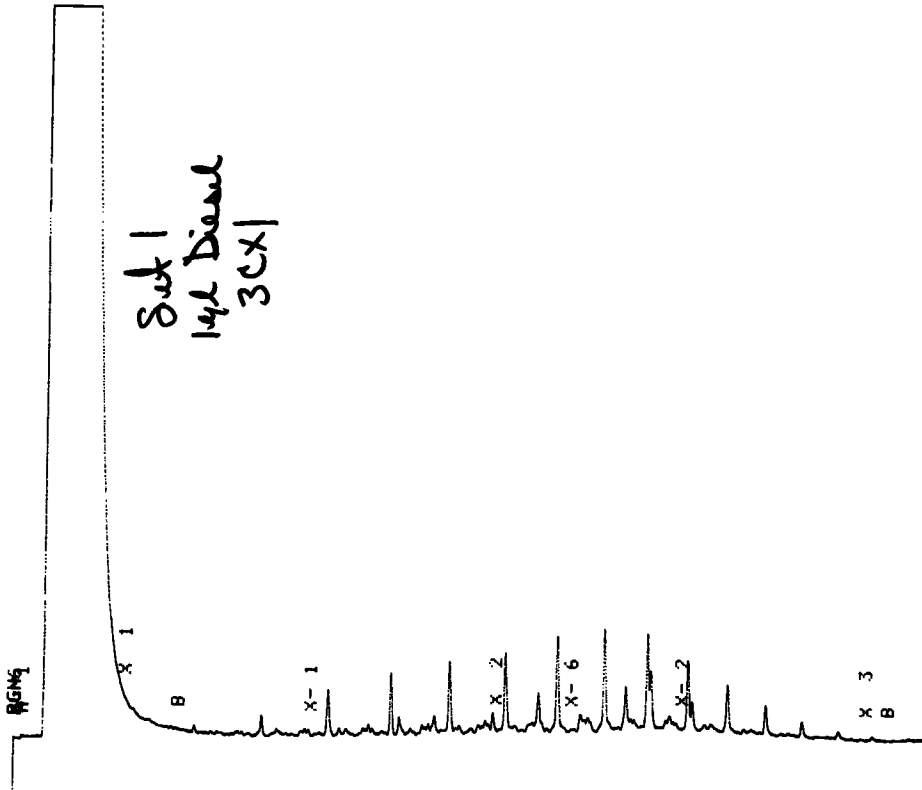


FIG. 17—Fraction 1, diesel on Prepsep.

free of interferences. If the pyrolyzate is primarily aromatic, little contamination would appear in the separated AHC.

The spiked pyrolyzate sample represents a real world sample. Referring to the chromatograms resulting from fractionating the spiked pyrolysis standard, Figs. 8 through 11, one can see the ARHC of evaporated gasoline quite evident in Fig. 11. Figure 12 shows the evaporated gasoline used as the spike. (It is also evident that a heavy petroleum distillate was present in the original carpet sample used when Fig. 10 is compared to standard diesel in Fig. 13.) A comparison of Fig. 10 and the chromatogram of the original pyrolyzate, Fig. 8, shows remarkable similarity. This indicates that the pyrolyzate eluting the cartridge by Fraction 5% and is most likely high in AHC. This is consistent with the pyrolysis of polyurethane and nylon.

Figures 14 thru 16 show fractionation of a case sample. The debris consisted of wood scrapings from a windowsill. Of the seven samples submitted in this case only one had an identifiable chromatogram (gasoline). Sample 5 showed some components present that were similar to gasoline. This arson debris extract was fractionated as previously described and yielded the chromatogram in Fig. 16. This allowed an identification of the accelerant gasoline inside the structure along with the gasoline found in a soil sample from the scene.

The fractioning technique has been applied to diesel fuel, evaporated gasoline, fresh gasoline, and blank pyrolysis samples in this lab using both Sep-Pak and Fisher: Prepsep materials. The separations obtained produce consistent GC patterns but the elution volumes for compound families (AHC or ARHC) are product dependent. Figures 17 and 18 represent diesel fractionated on Fisher: Prepsep. The fractions that hold the AHC and ARHC are different

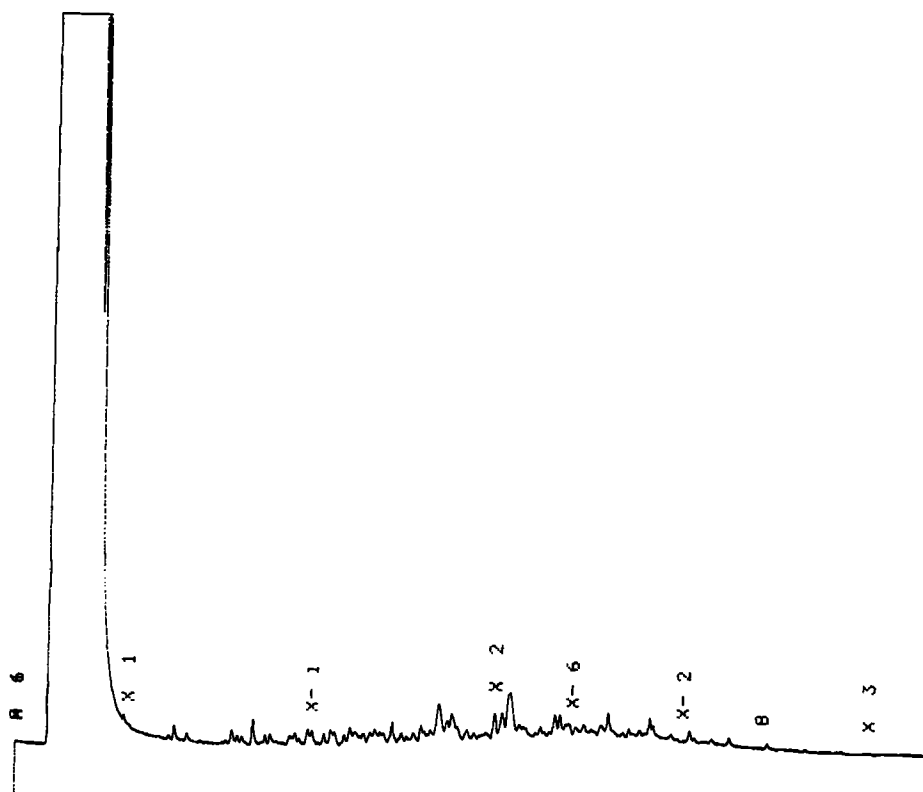


FIG. 18—Fraction 5, diesel on Prepsep.

than those for the Sep-Pak product (Figs. 8 and 12). Although delivery rate was not examined in this study, flow through the column should affect resolution and elution volume.

Summary

The added benefit of deriving two reproducible chromatograms from one accelerant liquid amplifies the criminalist's potential for identifying that accelerant. By coupling the fact of easy elimination of relatively polar pyrolyzate materials (that is, oxygenated compounds) with subsequent grouping of other pyrolyzates into families, many complex chromatograms become simple pattern matching identification procedures. In this procedure, expense and time resources are kept to an absolute minimum. Additionally, explanation of the methods employed in the analysis for the nontechnical juror is simplified.

Studies are continuing on improving the fractionation so that ARHC can be resolved into single and fused ring groups. Changes in the chromatograms of fractioned pyrolyzate samples can sometimes be seen in adjacent fractions. Because of this, an improvement in overall resolution by standard SPE manipulations is expected.

References

- [1] Kelly, R. L. and Martz, R. M., "Accelerant Identification in Fire Debris by Gas Chromatography/Mass Spectrometry Techniques," *Journal of Forensic Sciences*, Vol. 29, No. 3, July 1984, pp. 714-722.

- [2] Smith, R. M., "Arson Analysis by Mass Chromatography," *Analytical Chemistry*, Vol. 4, No. 13, Nov. 1982, pp. 1399A-1409A.
- [3] Howard, J. and McKague, A. B., "A Fire Investigation Involving Combustion of Carpet Material," *Journal of Forensic Sciences*, Vol. 29, No. 3, July 1984, pp. 919-922.
- [4] Aldridge, T. A., "A Thin Layer Chromatographic Clean-Up for Arson Distillates," *Arson Analysis Newsletter*, Vol. 5, No. 3, May 1981, pp. 39-42.
- [5] "Solid Phase Extraction: Sample Preparation," J. T. Baker Chemical Co., Research Products Division, 222 Red School Lane, Phillipsburg, NJ 08865.
- [6] Sanders, W. N. and Maynard, J. C., "Capillary Gas Chromatographic Method for Determining the C3-C12 Hydrocarbons in Full-Range Motor Gasolines," Shell Oil Co., Research Laboratory, Wood River, IL 62095.

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