*Jack Nowicki,*[1] *A.S.*

# Automated Data Analysis of Fire Debris Samples Using Gas Chromatography-Mass Spectrometry and Macro Programming

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**ABSTRACT:** A macro program written for Hewlett Packard Mass Selective Detector data stations that performs data analysis of fire debris samples is presented. The program generates a report that includes ion profiles for alkane, aromatic and polynuclear aromatic compounds, plus a list identifying the major peaks of the sample chromatogram. The algorithm that incorporates the retention index of the peak into the search of the mass spectral library is described in detail.

**KEYWORDS:** forensic science, fire, fire investigation, chemical analysis

The value of analyzing extracts of fire debris samples by gas chromatography-mass spectrometry (GC-MS) has previously been demonstrated [*1–6*]. Using the technique of selected ion profiling, the analyst can characterize the nature of the extracted hydrocarbons [*1–4*]. Selected ion profiling has been successfully applied to case samples [*3,5*]. In certain instances it may also be important to identify specific peaks in the chromatogram from their mass spectra. Keto and Wineman have suggested a technique for identifying flammable liquids by calculating the ratios of specific compounds [*6*]. These techniques make it easier for the analyst to determine whether the source of the hydrocarbons found in a sample is pyrolysis of the substrate, or a flammable liquid.

Performing the selected ion profiling and peak search functions manually on a GC-MS data station can consume a great deal of a chemist's time. For this reason, many analysts still prefer to use GC-FIC, leaving GC-MS only for the most complex samples.

The data stations on Hewlett-Packard Mass Selective Detector systems have the capability of running user-written programs called macros. By attaching the macro to a method, post-run data analysis can be performed automatically. A complete data analysis, including a printed report, can be generated without the analyst having to spend any additional time at the computer keyboard. The data analysis can be performed either directly after the conclusion of the GC run during the oven cool-down period, or can be batched with other samples injected during the day and printed out overnight.

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[1]Forensic Scientist, Illinois State Police, Suburban Chicago Laboratory, Maywood, IL.

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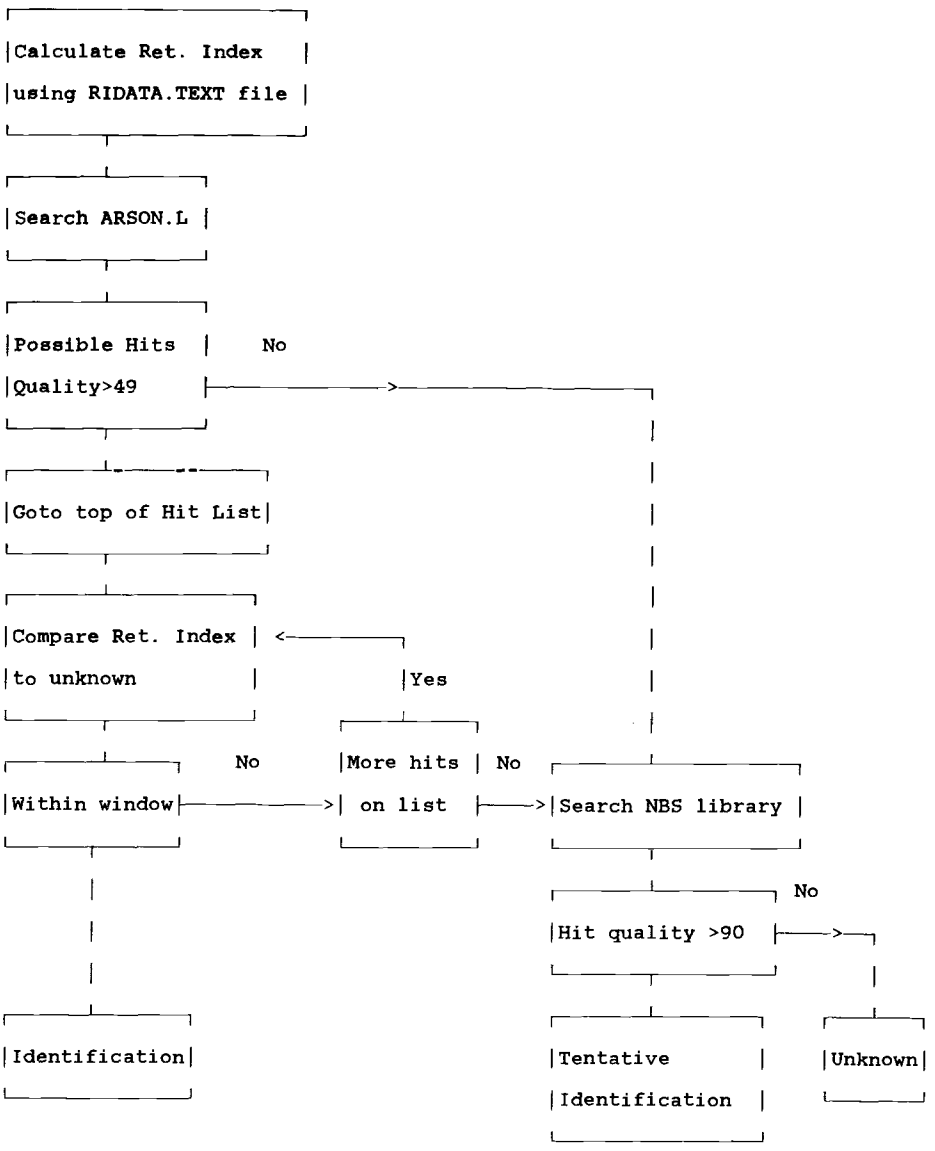


FIG. 1—*Flow chart of the peak identification steps of the ARSONMAC macro.*

This article describes a macro written by the author routinely used on fire debris samples analyzed in this laboratory.

## Equipment

Samples were analyzed on a Hewlett-Packard 5890 Gas Chromatograph equipped with a Model 5970 Mass Selective Detector. The gas chromatographic conditions are as follows:

Column: 25 m by 0.2 mm HP-1 (methyl silicone), 0.5 μm film thickness
Injector temperature: 250°C

```
Data file: /chem/arson/CRYSTAL.d
File type: GC / MS DATA FILE

Name Info: AMOCO ULTIMATE GASOLINE
Misc Info:
Operator : RICHARD A. PAULAS

Date     :  4 Dec 92    5:29 pm
Instrment: MS_5970
Inlet    : GC

Sequence index :    0
Als bottle num :    0
Replicate num  :    1
```

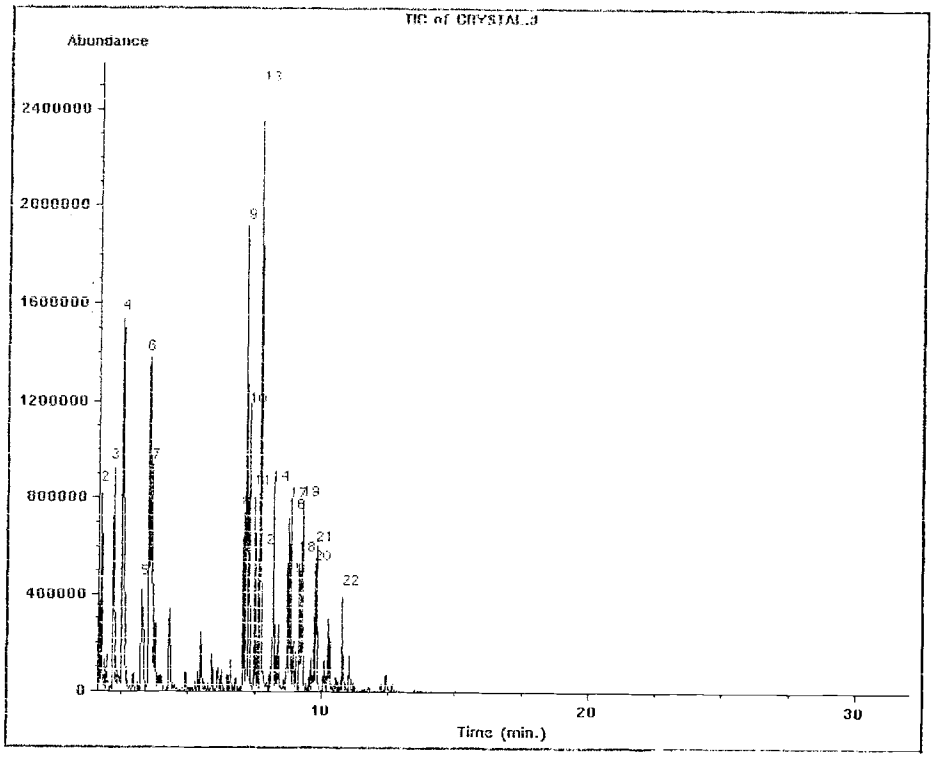


FIG. 2—*Report in Amoco Ultimate gasoline using ARSONMAC macro, consisting of* (a) *total ion chromatogram,* (b) *identification of major peaks, and* (c) *selected ion profiles of alkane, aromatic, and polynuclear aromatic compounds.*

Transfer line temperature: 280°C
Oven temperature: 40°C initially for 2 min ramp 10°/min to 250°C hold at 250° for 10 min
Carrier gas: helium at 12 psi (85 kPa) resulting in a linear velocity of 25 cm/sec
Split ratio: 35:1

Data was processed on a UNIX based data station running Version A.01.04 software.

## Program Description

The arson analysis program will print out the following information:

1. Sample header information (case number, analyst name, etc.)

AMOCO ULTIMATE GASOLINE

| PEAK# | RET TIME | RI | QUALITY | COMPOUND |
|---|---|---|---|---|
| 1 | 1.663 | 624 | 87 | Cyclopentane, methyl- |
| 2 | 1.756 | 633 | 91 | Pentane, 2,4-dimethyl |
| 3 | 2.191 | 670 | 91 | Pentane, 2,3-dimethyl- |
| 4 | 2.516 | 693 | 99 | *Butane, 2-azido-2,3,3-trimethyl- (9C |
| 5 | 3.260 | 742 | 96 | *Hexane, 2,5-dimethyl- (8CI9CI) |
| 6 | 3.533 | 758 | 94 | *Pentane, 2,3,4-trimethyl- (8CI9CI) |
| 7 | 3.612 | 762 | 97 | *Pentane, 2,3,3-trimethyl- (8CI9CI) |
| 8 | 7.067 | 948 | 91 | Benzene, propyl- |
| 9 | 7.146 | 953 | 95 | Benzene, 1-ethyl-4-methyl- |
| 10 | 7.268 | 960 | 94 | Benzene, 1-ethyl-4-methyl- |
| 11 | 7.491 | 972 | 91 | Benzene, 1-ethyl-2-methyl- |
| 12 | 7.609 | 978 | 98 | *Hexane, 2,2,5,5-tetramethyl- (8CI9CI |
| 13 | 7.673 | 981 | 95 | Benzene, 1,2,4-trimethyl- |
| 14 | 8.181 | 1009 | 95 | Benzene, 1,2,3-trimethyl- |
| 15 | 8.718 | 1043 | 95 | Benzene, 1,3-diethyl- |
| 16 | 8.745 | 1045 | 91 | Benzene, 1-methyl-3-propyl- |
| 17 | 8.837 | 1051 | 90 | Benzene, 1-ethyl-3,5-dimethyl- |
| 18 | 9.162 | 1070 | 94 | Benzene, 2-ethyl-1,4-dimethyl- |
| 19 | 9.267 | 1076 | 94 | Benzene, 1-methyl-2-(1-methylethyl)- |
| 20 | 9.752 | 1104 | 96 | Benzene, 1,2,3,4-tetramethyl- |
| 21 | 9.818 | 1109 | 96 | Benzene, 1,2,3,4-tetramethyl- |
| 22 | 10.782 | 1173 | 95 | Naphthalene |

FIG. 2—*Continued.*

2. Total ion chromatogram
3. Identification of major peaks
4. Selected ion profiles for alkane, aromatic, and polynuclear aromatic compounds [*1,2*]

Steps 1, 2 and 4 are straight-forward and can be understood by examining the program listing. The third section of the program, identifying the major peaks, is more complex and requires a detailed explanation.

Hewlett-Packard data stations are equipped with extensive spectral libraries (the Wiley library on UNIX systems) and use Probability Based Matching (PBM) search algorithms. By itself, a PBM search is not capable of discriminating among the mass spectra of many hydrocarbon isomers. For example, a PBM search will not reliably distinguish between 1,2-, 1,3-, and 1,4-dimethyl benzene (the xylene isomers), or between 1,2,4- and 1,3,5-trimethyl benzene (major components of gasoline). To accurately identify a peak in a hydrocarbon mixture, it is necessary to do more than just accept the reported best fit from a library search.

Many of these problem isomers can be distinguished by their retention times (calculated as a Kovats Index). Thus, a more reliable peak identification will be made by incorporating a retention index filter into the library search procedure. Hewlett-Packard data stations allow for spectral libraries to be created in which the retention index of a compound is saved along with its mass spectra.

## Initial Steps

Before the programs can be run, one text file and one user library must be created on the data station:

### *RIDATA Text File*

To calculate the Kovats Index of a peak in the sample Total Ion Chromatogram (TIC), a reference table containing retention times of the n-alkane series must be created. The

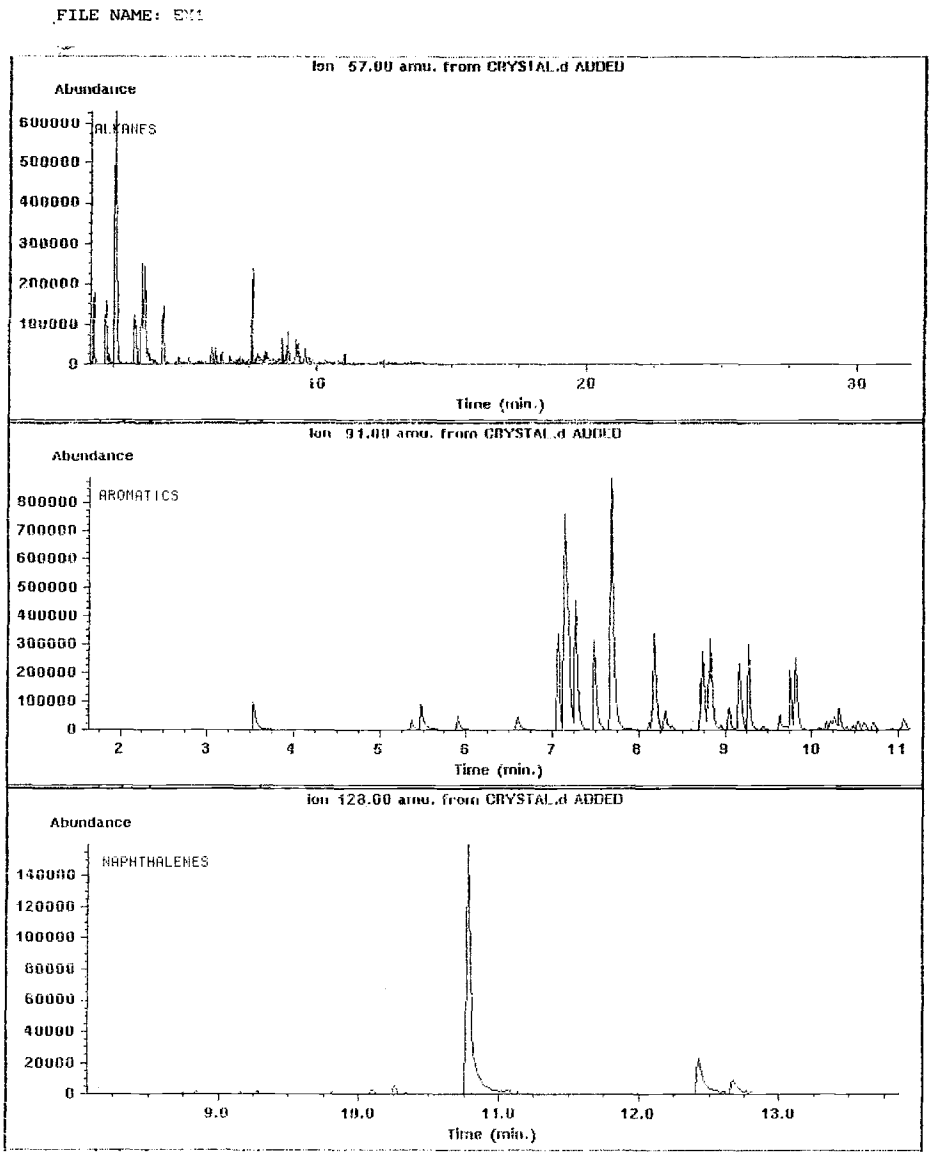


FIG. 2—*Continued.*

RIDATA file used in these programs is a list of retention times of the n-alkanes from pentane (C5) to eicosane (C20).

*ARSON.L Library*

This is a user created library of compounds commonly encountered in fire debris samples. It can be created as a subset of the Wiley library, and supplemented by adding additional compounds. When a compound is placed in the library, the retention index

```
Data file: /chem/arson/CARPET.d
File type: GC / MS DATA FILE

Name Info: BURNT CARPET
Misc Info:
Operator : S.N. SANDERS

Date     :  7 Dec 92   2:34 pm
Instrment: MS_5970
Inlet    : GC

Sequence index :    0
Als bottle num :    0
Replicate num  :    1
```

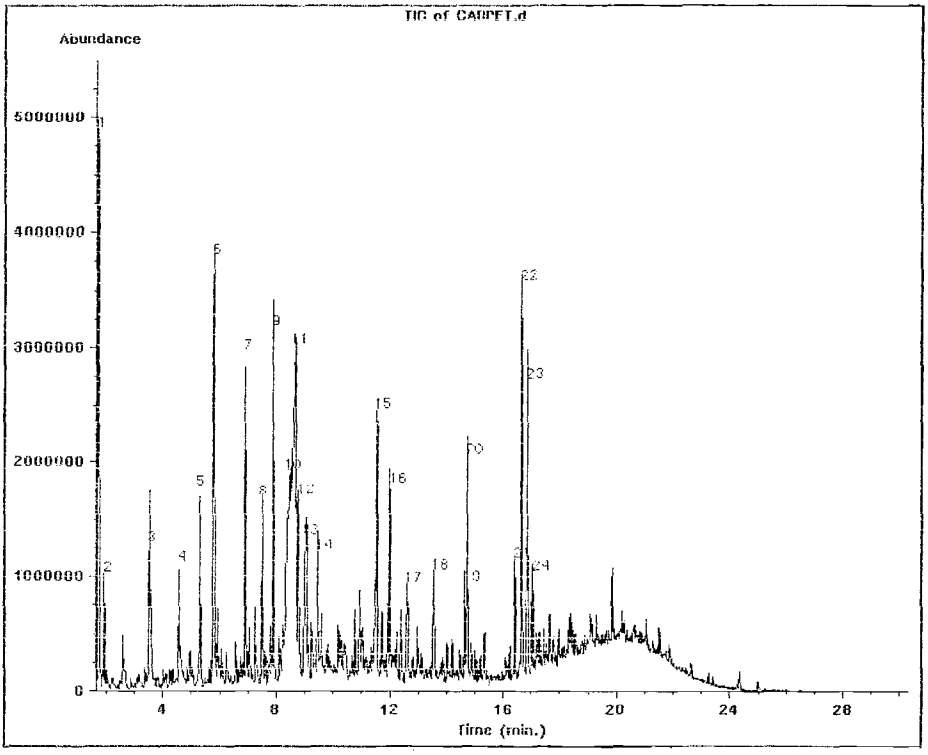


FIG. 3—*Report on burned carpet with no accelerant added using ARSONMAC macro, consisting of* (a) *total ion chromatogram,* (b) *identification of major peaks, and* (c) *selected ion profiles of alkane, aromatic, and polynuclear aromatic compounds.*

must also be included. Retention indices of many compounds commonly encountered in fire debris, analyzed under these chromatographic conditions, have previously been published [*4*].

## Peak Identification

A flow chart depicting the peak identification steps of the program is given in Fig. 1. The following steps are run as a loop for each major peak in the total ion chromatogram.

First, the retention index of the peak is calculated using the peak's retention time and the data from the RIDATA file. Next, a spectral search against the ARSON.L library is made, which creates an internal list of possible matches, ranked by the quality of fit.

BURNT CARPET

| PEAK# | RET TIME | RI | QUALITY | COMPOUND |
|---|---|---|---|---|
| 1 | 1.704 | 628 | 97 | *Cyclopropane, (1-methylethyl)- (9CI) |
| 2 | 1.927 | 649 | 94 | Benzene |
| 3 | 3.513 | 757 | 94 | Toluene |
| 4 | 4.550 | 809 | 0 | UNKNOWN |
| 5 | 5.286 | 851 | 94 | Benzene, ethyl- |
| 6 | 5.771 | 875 | 96 | STYRENE |
| 7 | 6.880 | 935 | 92 | *Benzaldehyde (8CI9CI) |
| 8 | 7.489 | 970 | 96 | *Benzene, 1-propenyl- (9CI) |
| 9 | 7.872 | 990 | 99 | *Benzene, (chloromethyl)- (VAN9CI) |
| 10 | 8.485 | 1028 | 94 | *Hexanedinitrile (9CI) |
| 11 | 8.671 | 1040 | 92 | *Hexanedinitrile (9CI) |
| 12 | 8.764 | 1046 | 97 | *1,2-Propanedione, 1-phenyl- (8CI9CI) |
| 13 | 9.043 | 1063 | 0 | UNKNOWN |
| 14 | 9.453 | 1087 | 0 | UNKNOWN |
| 15 | 11.533 | 1227 | 0 | UNKNOWN |
| 16 | 11.989 | 1260 | 0 | UNKNOWN |
| 17 | 12.614 | 1304 | 0 | UNKNOWN |
| 18 | 13.536 | 1375 | 96 | 1,1-Biphenyl |
| 19 | 14.631 | 1463 | 90 | *Tetradecane, 1-chloro- (8CI9CI) |
| 20 | 14.724 | 1470 | 100 | *3-Tetradecene, (Z)- (9CI) |
| 21 | 16.419 | 1615 | 99 | *Butyric acid, thio-, S-pentyl ester |
| 22 | 16.633 | 1634 | 95 | *Phosphoric acid, tributyl ester (8CI |
| 23 | 16.847 | 1653 | 99 | *Benzene, 1,1'-(1,3-propanediyl)bis- |
| 24 | 17.049 | 1671 | 99 | *1-Heptadecanol (8CI9CI) |

FIG. 3—*Continued.*

Starting at the top of this "hit list," the retention index of the unknown peak is compared to the retention index of the possible match. If their retention indices are comparable (within three units), an identification is made and the program moves on to the next peak in the TIC. If the retention index of the unknown falls outside this range, the program compares it to the next ranked compound on the list. This process continues until either the compound is identified, or the match quality with the hit list falls below 90.

If the hit list has been exhausted and no identification has been made, the program will then search the unknown against the full Wiley library. If a hit with a match quality above 50 is obtained, the program will mark this peak as a possible identification and will be printed out with an asterisk. If no match is found at this point, the peak is considered "Unknown."

## Program Listings

Examples of the output from this program are given in Figs. 2 and 3. Figure 2 represents a sample of Amoco Premium Unleaded, the new "crystal-clear" gasoline. Figure 3 represents a sample of burnt carpet with no accelerant present.

## Further Information

A complete program listing compatible with UNIX or PASCAL data stations may be obtained by contacting the author. A fully commented copy of the program will appear in a future issue of this Journal.

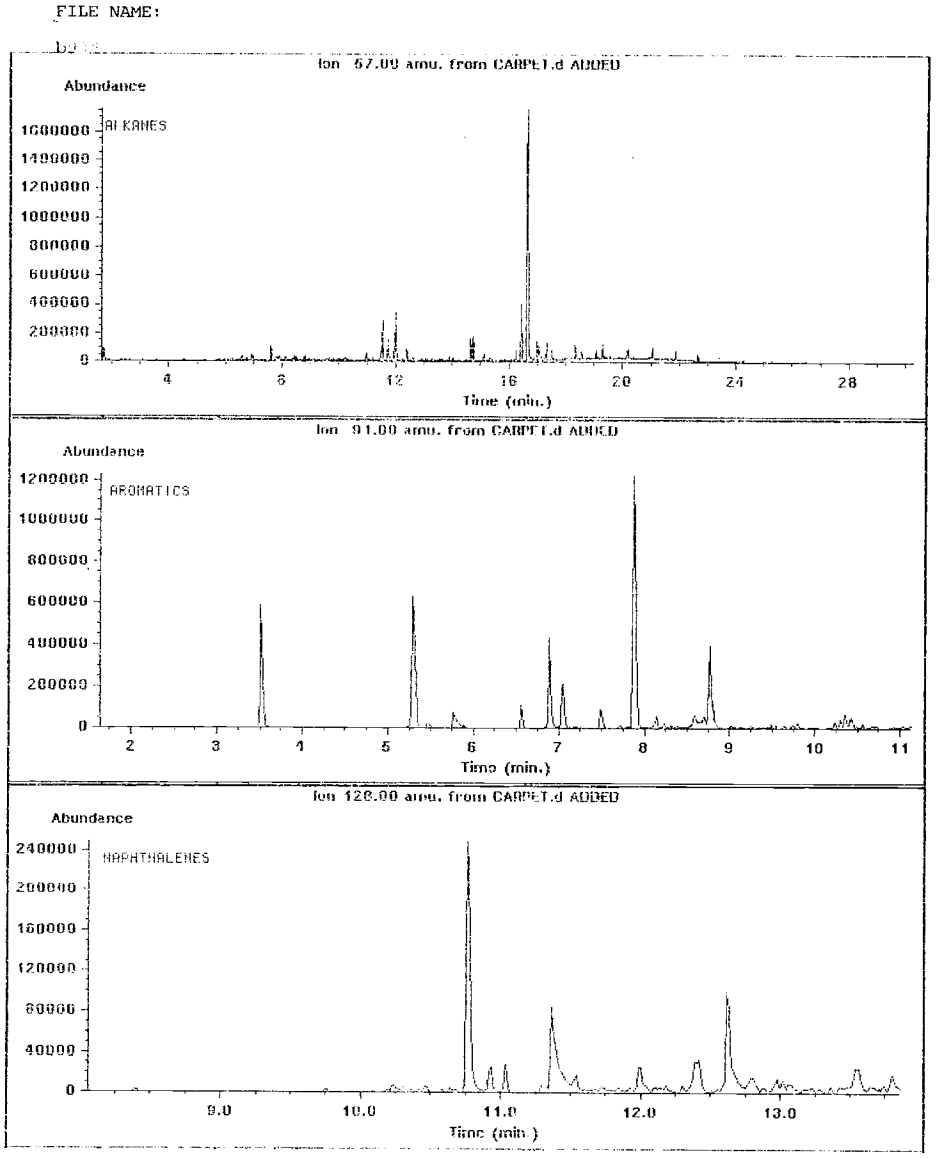


FIG. 3—*Continued.*

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Address requests for reprints or additional information to
Jack Nowicki
Illinois State Police
1401 S. Maybrook Drive
Maywood, IL 60153