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Detection of Petrol (Gasoline) in Fire Debris by Gas Chromatography/Mass Spectrometry/Mass Spectrometry (GC/MS/MS)*

ABSTRACT: Gas chromatography/mass spectrometry (GC/MS) is a well-known instrumental technique used for the analysis of fire debris for accelerant detection. However, matrix problems, such as pyrolysis product interference, are still encountered. These interferences often lead to inconclusive interpretation of the chromatographic results obtained.

This paper describes a method of analyzing arson accelerants using gas chromatography coupled with ion trap mass spectrometry/mass spectrometry (GC/MS/MS). Petrol was investigated as an accelerant. Analysis incorporated an ion preparation method (IPM) that manipulates the ion population in the ion trap following ionization but prior to ion analysis. Parent ions of selected mass-to-charge (m/z) values, characteristic for petrol, are stored within the ion trap. All other unwanted ions are physically removed from the trap by sophisticated electrostatic waveforms. The parent ions fill the trap and are then fragmented by means of collision-induced dissociation (CID). The resultant daughter ion spectra are obtained, which can be used for identification purposes. In this manner, ions of pyrolysis origin are removed.

KEYWORDS: forensic science, arson analysis, petrol, GC/MS, GC/MS/MS, ion preparation method (IPM), collision-induced dissociation (CID), resonant excitation, non-resonant excitation, parent ions, daughter ions, single ion monitoring (SIM)

Samples of debris from fires are routinely analyzed for traces of hydrocarbon products used as accelerants. Capillary column gas chromatography is a very effective method of characterization of the trace level volatiles isolated from fire debris (1,2). Coupled with flame ionization detection (FID), it provides a representation of the distribution of hydrocarbon components eluting from the column. Comparison with standard reference chromatograms of accelerants is used for the identification of unknown hydrocarbon distillates. The low concentrations of the analytes and the high levels of interference from pyrolysis products in many samples lead to the use of a selective detector, namely the mass spectrometer (MS), which can selectively extract the target analytes (2,3). The switch to MS, instead of FID, eliminates most of the problems caused by pyrolysis products (4). Gas chromatography/mass spectrometry (GC/MS) ion profiling is an effective technique whereby manipulation of the mass spectrometer software enables the identification of characteristic series of mass fragments indicative of hydrocarbon distillates (4,5).

However, ion profiling with mass spectrometry does not always provide sufficient selectivity to detect residues of a distillate without interference from pyrolysis products in well-burnt samples. This considerably reduces the chance of identifying the distillate. Mass spectrometry/mass spectrometry (MS/MS) not only greatly minimizes matrix interferences but enhances the signal-to-noise ratio of the characteristic ions selected to search for a hydrocarbon distillate residue (6,11,12). This results in ion profiles more easily interpreted and more confidently presented in court.

Overview

Since petrol (gasoline) is one of the more common distillate blends used by arsonists, especially in South Africa, the identification of petrol in fire debris samples was investigated. In order to overcome pyrolysis product interference and improve detection levels of the aromatic hydrocarbons in petrol residues, MS/MS was utilized as the method of detection after capillary gas chromatographic separation of petrol into its characteristic volatile hydrocarbon components.

MS/MS is a technique for isolating a single ion (precursor or parent) from a mass spectral fragmentation and causing this isolated ion to undergo a collision-induced dissociation (CID) in order to obtain the resulting product or daughter ion spectrum.

The Varian Saturn 2000 ion trap GC/MS/MS, the instrument used for the analyses (Fig. 1), takes advantage of the "tandem-in-time" concept, rather than "tandem-in-space," by using a single ion trap (Fig. 1) and a sequence of different radio frequency (RF) waveforms (10,12,13).

Detailed theory of in trap MS and MS-MS can be obtained in the literature (7–10). The MS/MS ion preparation method (IPM) intro-

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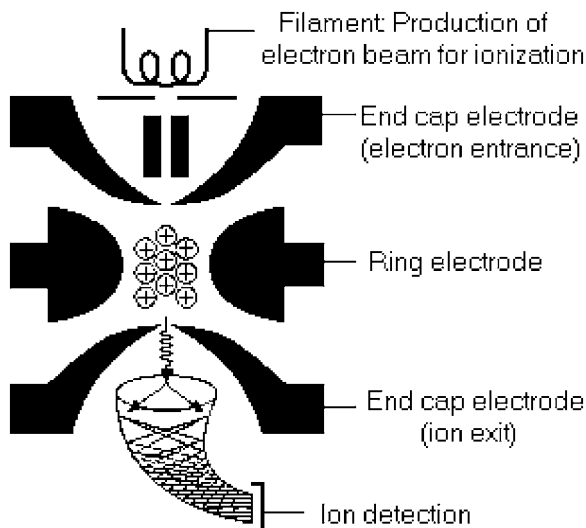
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The Ion Trap

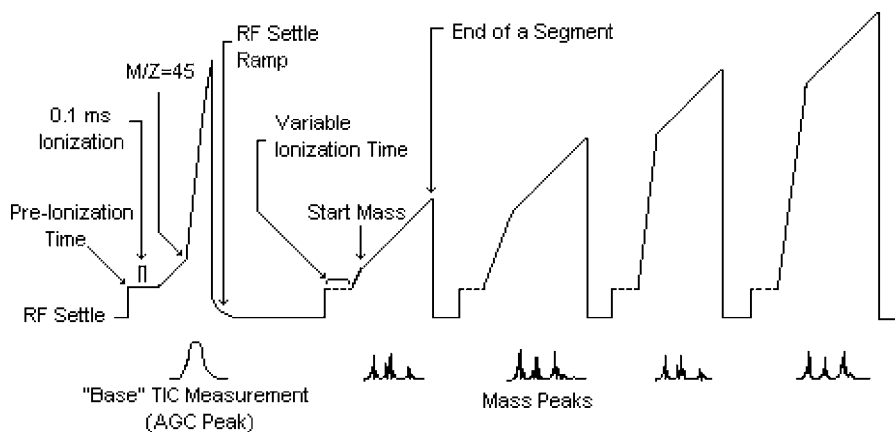
FIG. 1—Schematic representation of the ion trap.

duces intermediate scan segments (ISS—Fig. 3) into the basic RF scan function (a scan function is a representation of the timing sequence for ion trap operation—it shows the variations in time of the RF potential applied between the ring electrode and the end cap electrodes (Figs. 1, 2, and 3), as well as any supplementary waveforms applied to the end caps—Fig. 2).

There are four basic operations in Saturn ion trap tandem mass spectrometry (MS/MS) for electron ionization (10) (Fig. 4), namely ion formation and matrix ion ejection, parent ion isolation, product/daughter ion formation, and product/daughter ion mass scanning.

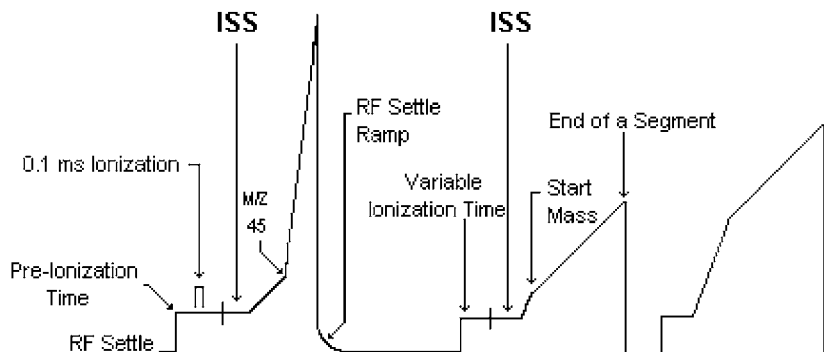
During ion formation and matrix ion ejection, a two-step rough isolation (broadband multi-frequency) waveform is applied to the end caps to resonantly eject ions below and then above the specified parent ion mass. This two-step waveform physically removes most of the low-mass ions whose space charge would otherwise affect the storage efficiency of the parent ion and most of the remaining unwanted ions from the trap (10).

Parent ion isolation uses another more accurate two-step process (fine isolation waveform), where the first step ejects the ions with masses below the parent ion mass, followed by a broadband multi-frequency waveform applied to the trap to simultaneously eject all masses above the parent ion mass (10).



The AGC Scan Function

FIG. 2—The automatic gain control (AGC) scan function.



AGC Scan Function showing location of Intermediate Scan Segments

FIG. 3—AGC scan function showing the location of the intermediate scan segments for MS/MS.

Location of Toolkit Parameters in the Saturn GC/MS Scan Function

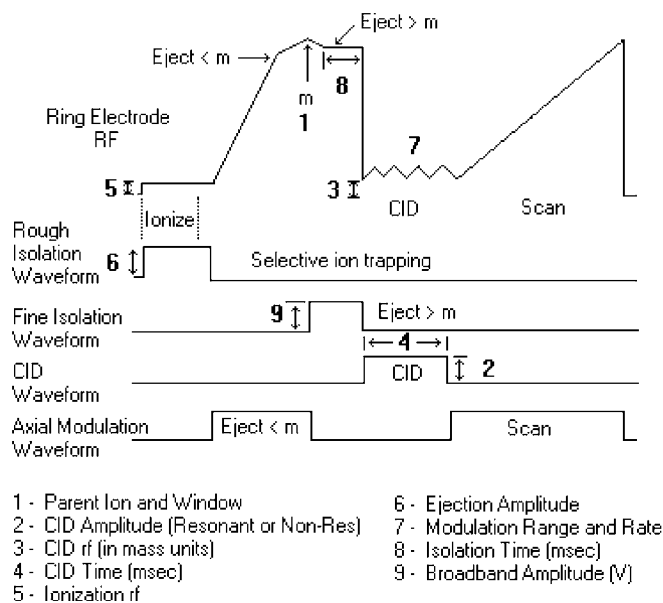


FIG. 4—Parameters in Saturn GC/MS/MS scan function.

Product or daughter ions are formed from the parent ions by collision-induced dissociation (CID). The mass-to-charge distribution that results from the CID process depends on the characteristics of the parent ion and the amount of translational kinetic energy that has been converted into internal vibrational energy. The translational kinetic energy of the parent ion can be increased using either of two methods, resonant or non-resonant excitation (10).

By applying a supplementary high-frequency “tickle” potential across the end cap electrodes, which is tuned to the fundamental secular (oscillation) frequency of the ion, the axial component of the ion motion is resonantly excited. This increases the degree of internal energy enhancement, albeit at the expense of daughter ion detection efficiency (7).

Non-resonant or “boundary activation” (7) is based on the interaction of a selected ion species with the high fields derived from the RF drive potential; this interaction leads to pronounced acceleration of the ion species, whereupon the ion is dissociated subsequent to collisions with the helium buffer gas, which causes the ions to be activated. It is, therefore, a mass-selective collisional process that does not require the careful tuning of the “tickle” voltage (7,10).

Following formation of the product or daughter ions by CID, a single RF ramp is used along with the axial modulation field (a

voltage applied at a fixed frequency and amplitude during the ramp of the RF voltage to facilitate ion ejection and improve mass resolution) to resonantly scan ions from the trap into the electron multiplier. This process generates the product or daughter ion spectrum.

Application

Petrol is a distillate blend of complex aliphatic and aromatic hydrocarbons. When analyzed by GC/MS, the characteristic ratios of the isomers for each molecular weight ion are separated and can be identified. The most important diagnostic components for petrol are the alkylated aromatic hydrocarbons. The distribution of individual components in each group of isomers (such as the C3 and C4 alkylbenzenes) is highly characteristic, and it was decided to compare only the aromatic hydrocarbons, as the extracted ion profiles of these compounds produce the most conclusive results for petrol identification by mass spectrometry. Substances such as indanes, olefins, and styrenes are present only in trace quantities and are generally not used as petrol indicators (2,3).

Mass-to-charge ratio (m/z) 91 was initially selected as the parent ion mass and was isolated throughout the chromatographic run to obtain the MS/MS daughter ion chromatogram for the petrol distillate using resonant excitation (6). The same analysis was then performed on fire debris samples. Results were successful, although isolating m/z 91 was too similar to SIM (selected ion monitoring) and did not provide sufficient diagnostic daughter ions to enhance or improve the MS method of ion profiling. It did, however, remove pyrolysis product interference by enhancing the m/z 91 aromatic isomers present in petrol (6,11,12). This ion was also not part of the pyrolysis daughter ion after CID.

This prompted the decision to use the automated method development (AMD) software feature with non-resonant excitation to determine the CID voltage (non-resonant excitation amplitude for each selected characteristic aromatic hydrocarbon mass—refer to Table 1). This allows the CID voltage to be incremented on a scan-by-scan basis. The Mathieu “ q ” parameter is used to determine the stability of the parent ion trajectory (7,10, 12), and the “ q ” value of 0.4 provides an optimum yield of ions and determines the CID excitation storage RF value (m/z) according to the selected ion mass. These values are depicted in Table 2. Standards for the common aromatic compounds in petrol were injected for this purpose. Ten different sets of MS/MS conditions for parent ions can be achieved involving an MS scan routine obtained over the time a chromatographic peak elutes from the GC column for a single mass spectrum. The conditions leading to the most favorable daughter ion mass spectra can then be found in less time than the method of using slightly different conditions for obtaining MS/MS over ten dif-

TABLE 1—Using m/z 91 as an example of initial conditions required for CID voltage determination.

Parent Ion Mass	Mass Window	CID Voltage	RF Excitation Storage Level	CID Time (ms)	CID Amplitude (V)	Waveform Type
91	3	25	48.0	20	20.00	Nonres
91	3	30	48.0	20	20.00	Nonres
91	3	35	48.0	20	20.00	Nonres
91	3	40	48.0	20	20.00	Nonres
91	3	45	48.0	20	20.00	Nonres
91	3	50	48.0	20	20.00	Nonres
91	3	55	48.0	20	20.00	Nonres
91	3	60	48.0	20	20.00	Nonres
91	3	65	48.0	20	20.00	Nonres
91	3	70	48.0	20	20.00	Nonres

TABLE 2—CID voltages for each selected mass.

Segment No.	Segment Time (min)	Ion Mode	Mass	Mass Window	CID Voltage	RF Excitation Storage Level	Parent Ion
1	0:00–3:00	EI
2	3:00–3:40	EI
3	3:40–6:00	MS/MS	78	1	67	48.0	Benzene
4	6:00–10:00	MS/MS	91	1	61	48.0	C1-Benzenes
5	10:00–12:89	MS/MS	106	1	55	48.0	C2-Benzenes
6	12:89–14:14	MS/MS	120 (105)	1	50	52.7	Isopropyl-benzene +
7	14:14–15:66	MS/MS	120	1	47	52.7	Propylbenzene
8	15:66–15:95	MS/MS	117	1	55	51.4	C3-Benzenes
9	15:95–16:82	MS/MS	134	1	47	58.9	Indane
10	16:82–17:10	MS/MS	148	1	50	65.1	C4-Benzenes
11	17:10–17:42	MS/MS	134	1	47	58.9	C5-Benzenes
12	17:42–18:24	MS/MS	148	1	50	65.1	C4-Benzenes
13	18:24–18:60	MS/MS	162	1	52	71.3	C5-Benzenes
14	18:60–19:70	MS/MS	128	1	65	56.2	C6-Benzenes
15	19:70–20:80	MS/MS	142	1	69	62.4	Naphthalene
16	20:80–22:20	MS/MS	156	1	67	68.6	C1-Naphthalenes
17	22:20–24:70	MS/MS	170	1	69	74.8	C2-Naphthalenes
18	24:70–29:00	EI	C3-Naphthalenes

ferent chromatographic runs. Table 1 provides an example of initial conditions required for obtaining MS/MS spectra using m/z 91 as an example.

These results then gave the optimum conditions for obtaining MS/MS spectra. The resultant daughter ion spectra were comparable, although not identical, with standard MS spectra of the characteristic aromatic hydrocarbon compounds analyzed. In this manner, isomers of varying molecular weights can be scanned at their specific retention times without interference from pyrolysis products in the mass chromatogram.

GC/MS analysis allows for the identification of the characteristic ions for the alkanes, cycloalkanes, aromatics, condensed ring aromatics, and other general isomers specific to petrol. It must be emphasized that the sensitivity of the MS/MS technique also allows identification of residues of aromatic blend solvents used for coatings, paints, varnishes, adhesives, and insecticides. These specialty solvents can differ from evaporated petrol only in their ratios of aromatics to aliphatics (alkanes), and therefore the GC/MS analysis must form part of the MS/MS analysis for a total overview of the characteristic hydrocarbons actually present, especially to ensure a positive or negative identification of the presence of an ignitable liquid. In this way we try to prevent false negatives.

Intercomparison of MS/MS daughter ion spectra between different laboratories could prove beneficial and collaborative if the criteria required to generate the MS/MS data can be standardized, although it must be remembered that it is the comparability of the sample data to the same laboratory's reference sample analysis also done by GC/MS/MS that is important. GC/MS positives are not based on the comparability to another laboratory's data; thus, it is not important to GC/MS/MS data either.

Different parent ions can be selected to represent the characteristic aromatic hydrocarbons under analysis from laboratory to laboratory, depending on the information required per analysis, but if a basic MS/MS method were to be set forth as an ASTM standard guide (15), this could then ensure continuity.

Experimental

Standard aromatic hydrocarbon compounds, as well as standard petrol distillates dissolved in Riedel deHaen[®] analytical reagent

grade carbon disulphide, were used to determine the MS/MS conditions required for reproducible spectra before applying the method to samples of fire debris containing trace levels of petrol distillate residues.

Samples of fire debris (actual cases pending court procedure, since the MS/MS method is to show its validity in actual unknowns after having been compared against simulated debris samples spiked with petrol, which is not discussed in this article) were placed in Kapak[®] evidence bags; a Traceair[®] organic vapor monitor adsorbent charcoal strip was placed with the sample in the evidence bags before sealing them and placing them in a preheated oven at 60°C overnight for approximately 16 h (14). After the selected time had elapsed, the evidence bags were opened and the charcoal adsorbent strips were removed and placed in 4 mL glass screw cap sample vials. To elute the trapped hydrocarbon compounds, 0.5 mL AR carbon disulphide was added. The resultant extracts were then analyzed in the same manner as the standards by means of a Varian 3400CX gas chromatograph coupled with a Varian Saturn 2000 ion trap mass spectrometer/mass spectrometer.

GC Conditions:

Column: Chrompack WCOT fused silica 30 m by 0.25 mm capillary column with CP Sil 8CB DF = 0.25 μ m film coating
 Temperature Program: 30°C for 6 min, 30 to 70°C @ 7°C/min, 70°C to 230°C @ 10°C/min, 230°C for 13 min
 Injector Temperature: 180°C

MS and AMD Conditions:

Scan Range: 40 to 300 amu
 (atomic mass units)
 Scan Rate: 0.650 s (1 μ Scan per scan)
 Background Mass: 35 amu
 Trap Temperature: 120°C
 Manifold Temperature: 45°C (manifold has separate heater)
 Transfer Line Temperature: 200°C
 Emission Current: 50 μ A (microamps)

AGC PreScan Ionization Time:	100 μ s (microseconds) for MS
AGC PreScan Ionization Time	1500 μ s for AMD
Target TIC:	10 000 counts
<i>MS/MS Conditions:</i>	
Scan Range:	40 to 300 amu (atomic mass units)
Scan Rate:	0.910 s (3 μ scans per scan)
Background Mass:	35 amu
Trap Temperature:	120°C
Manifold Temperature:	45°C
Transfer Line Temperature:	200°C
Emission Current:	10 μ A (microamps)
AGC PreScan Ionization Time:	100 μ s (microseconds) for MS
AGC PreScan Ionization Time:	1500 μ s for MS/MS
Target TIC:	10 000 counts

The CID excitation time was maintained at 20 ms, and the amplitude range was maintained at 20.00 V. These values can be customized as required, but were left at their default values for the purpose of this analysis. Segment 1 refers to a delay of 3:00 min before actual scanning begins. Segment 2 refers to the EI mode for normal MS scanning for 3:00 to 3:40 min, and Segment 3 begins the MS/MS scan for benzene from 3:40 to 6:00 min. The segment times will vary depending on gas flow rate. The last segment, Segment 18, reverts back to EI mode for normal MS scanning.

All standards and samples were injected manually, which leads to slight differences in retention time, and, since the detected hydrocarbon residues from arson debris are not usually quantified, emphasis has not been placed on quantification, but rather the actual detection of trace amounts of accelerant in pyrolysis debris.

A mass spectrum is a graphical representation of the ion intensities versus the mass-to-charge ratio (x-axis scans). When looking at the chromatograms, the ion intensities along the y-axis can be read in “kCounts” (kilo counts) or “MCounts” (mega counts), which are 1000X more concentrated than “kCounts”. If only “Counts” are indicated, then these are 1000X less concentrated than “kCounts” and are actually bordering on the signal-to-noise ratio of the instrument.

Results

The chromatograms selected for discussion are from a petrol standard (Figs. 5a and 5b) and actual cases pending court procedure. The following debris samples were used for examples from these case studies: pieces of chopped floor screed (or grano: a sand and cement finishing/topping/surface layer or sub-leveling layer on concrete floors prior to carpeting—usually 25 to 35 mm thick creating a smooth surface) taken from the concrete floor of a wood product factory about one month after the fire. The area was indicated by an arson canine (Figs. 5c to 5g). A section of pine floor planking was taken in an area of “pool-mark” charring and pour patterns, as well as where the planking had burnt through at the “tongue-and-groove joint” (Figs. 6a to 6g). Debris was sampled from the floor of a shoe store warehouse, containing polymers and glues (Figs. 7a to 7d) and again in an area where pour patterns were evident on the burned carpeting. The gymnasium floor-covering debris was sampled in an area with unusual char patterns from a gymnasium that burned (Figs. 8a and 8b). The carpeting and bedding debris sample came from a privately owned house (Figs. 9a and 9b), again where there was evidence of accelerated char patterns. The carpet that was used for background had a nylon pile with an urethane/polyester type backing, which was burned using an LPG gas flame (Figs. 10a and 10b).

Figures 5a and 5b show the total chromatographic ion profile (total mass chromatogram) and typical selected (extracted) ion pro-

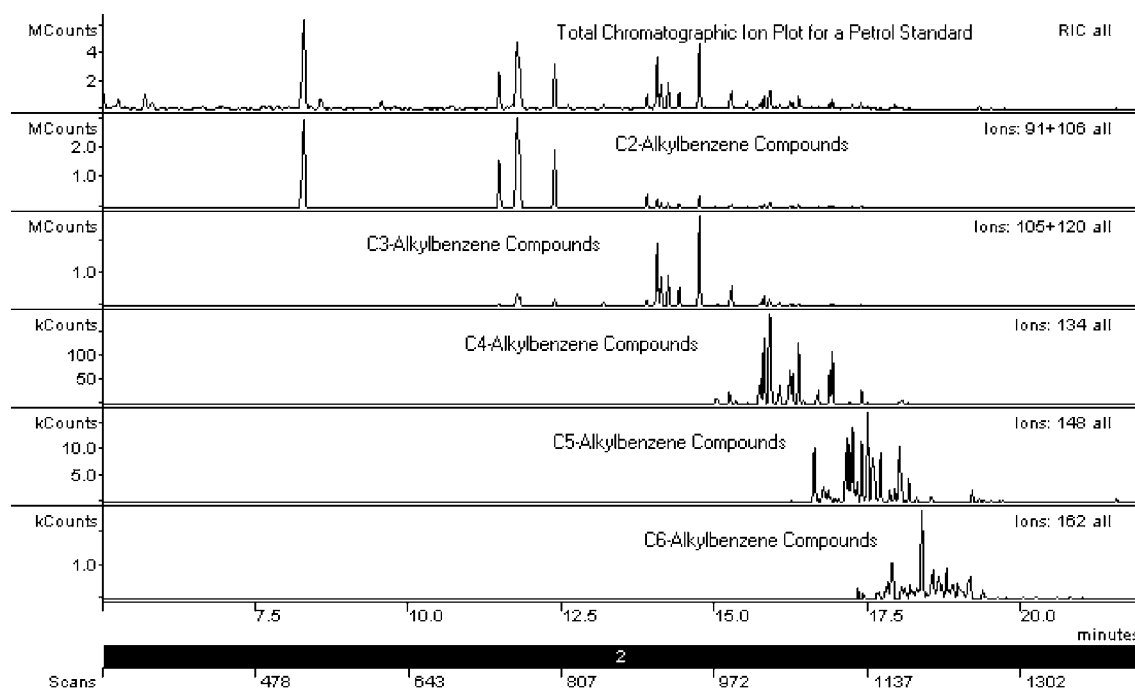


FIG. 5a—Total chromatographic ion profile (profile) for a petrol standard by GC/MS. The reconstructed ion profiles (profiles) for the aromatic hydrocarbons and their isomers are depicted below the total ion profile (profile).

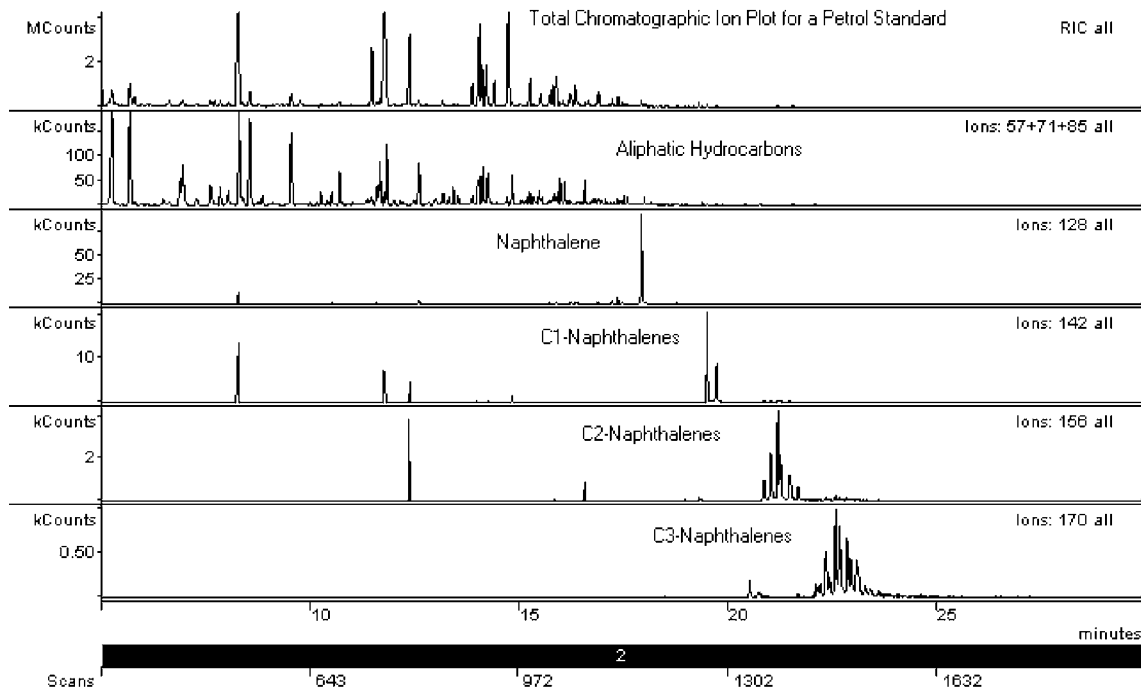


FIG. 5b—Total chromatographic ion profile for a petrol standard by GC/MS. The reconstructed ion profiles for the aliphatic hydrocarbons, naphthalene, and the alkyl naphthalenes and their isomers are depicted below the total ion profile.

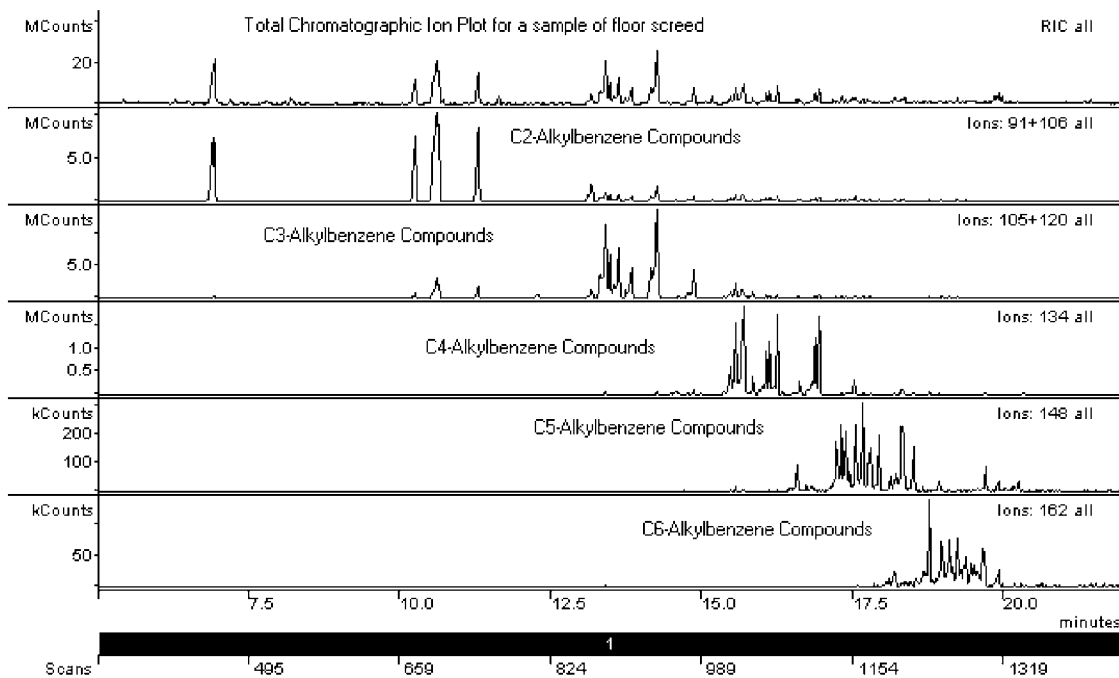


FIG. 5c—Total chromatographic ion profile for a debris sample of floor screed by GC/MS. The reconstructed ion profiles for the aromatic hydrocarbons and their isomers are depicted below the total ion profile.

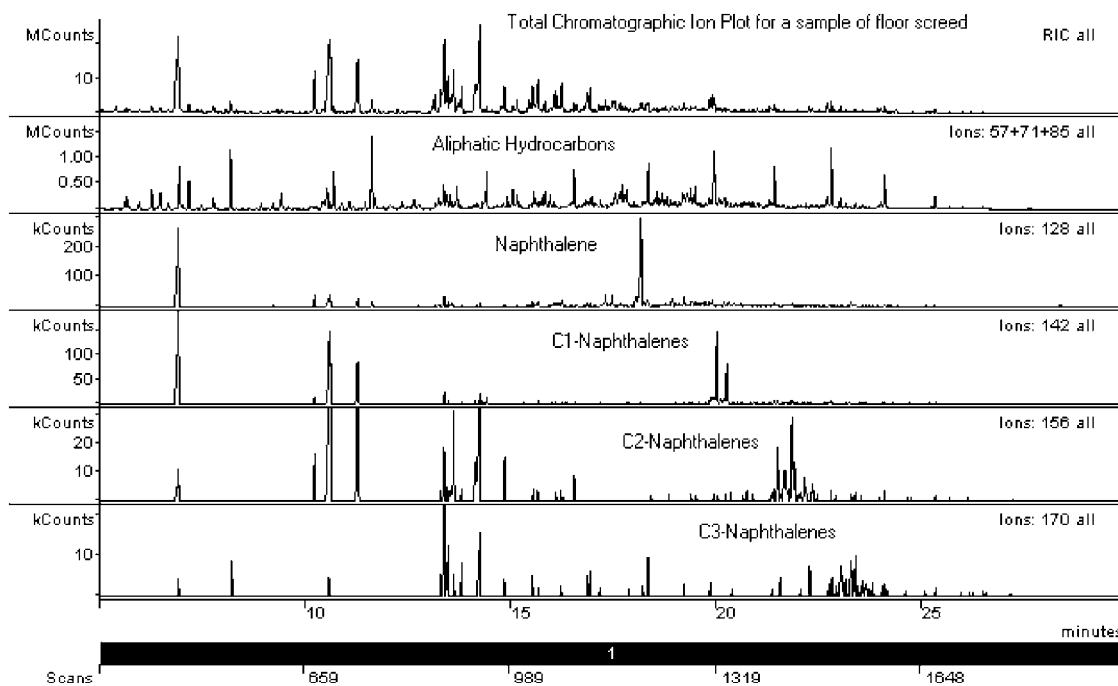


FIG. 5d—Total chromatographic ion profile for a debris sample of floor screed by GC/MS. The reconstructed ion profiles for the aliphatic hydrocarbons, naphthalene, and the alkyl naphthalenes and their isomers are depicted below the total ion profile.

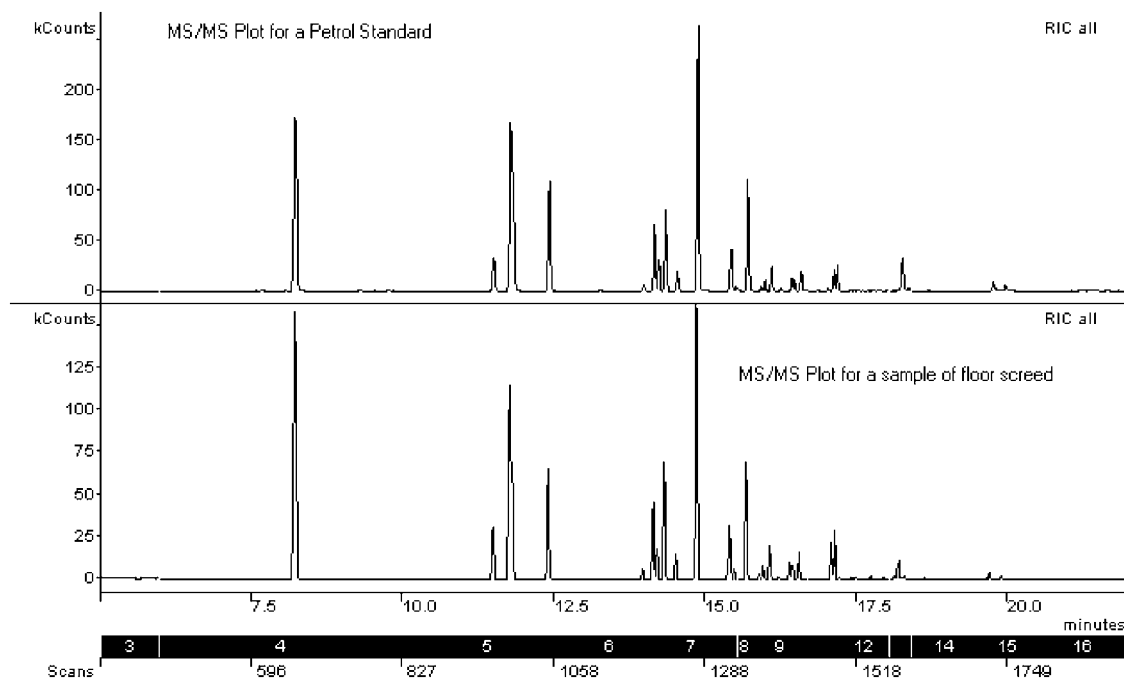


FIG. 5e—The product ion MS/MS profile (profile) for a petrol standard, with the product ion MS/MS profile for the debris sample of floor screed below.

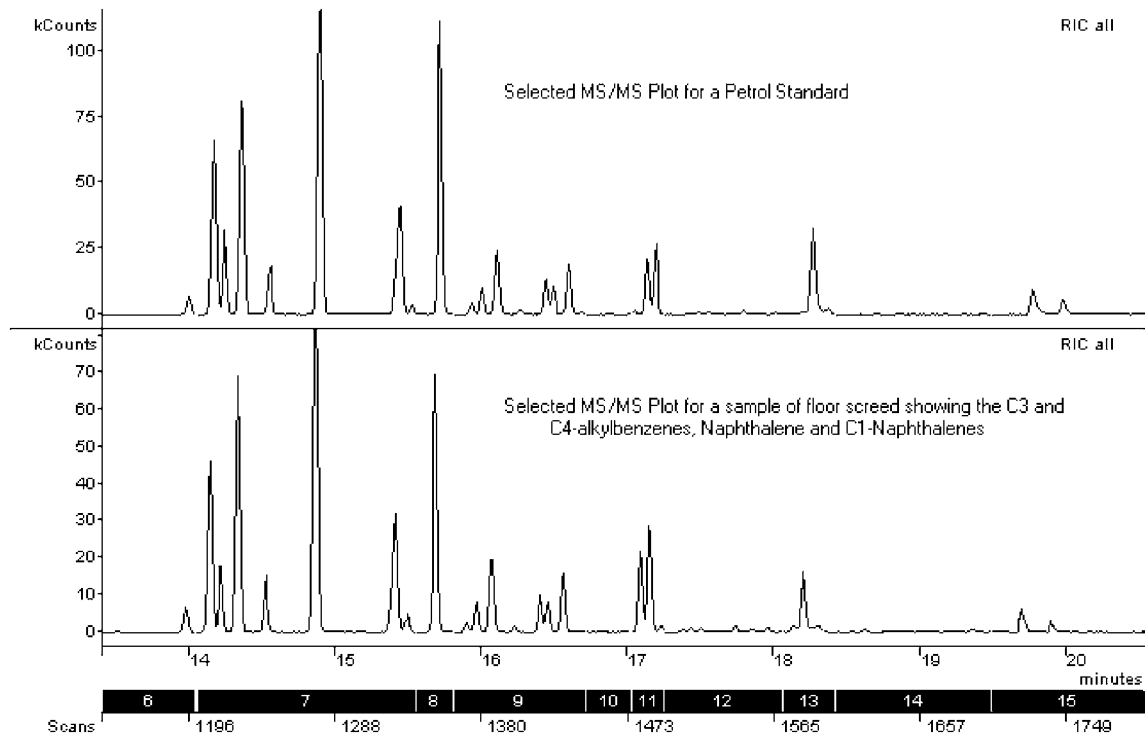


FIG. 5f—The selected time segment product ion MS/MS profile for a petrol standard with the selected product ion MS/MS profile for the debris sample of floor screed below, to illustrate more clearly the C3 and C4-alkylbenzenes, naphthalene, and the C1-naphthalenes.

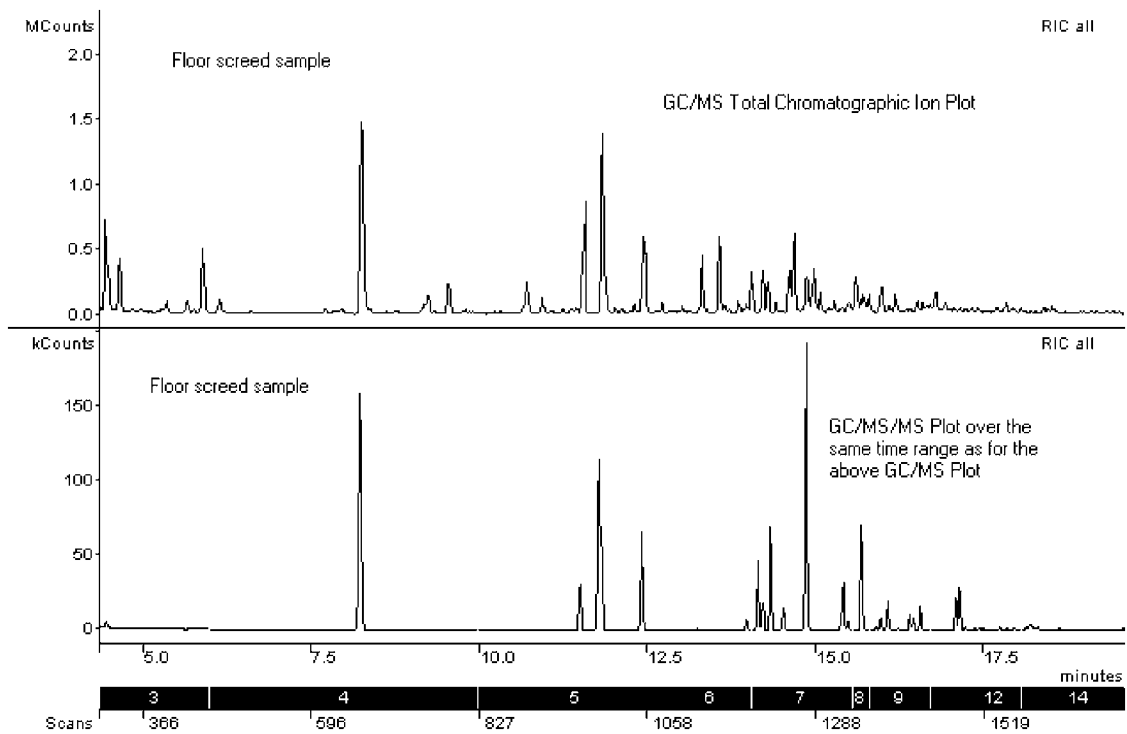


FIG. 5g—The GC/MS total chromatographic ion profile for the sample of floor screed with the product ion GC/MS/MS profile below. The MS/MS profile is clearly less “cluttered” than the MS total ion profile.

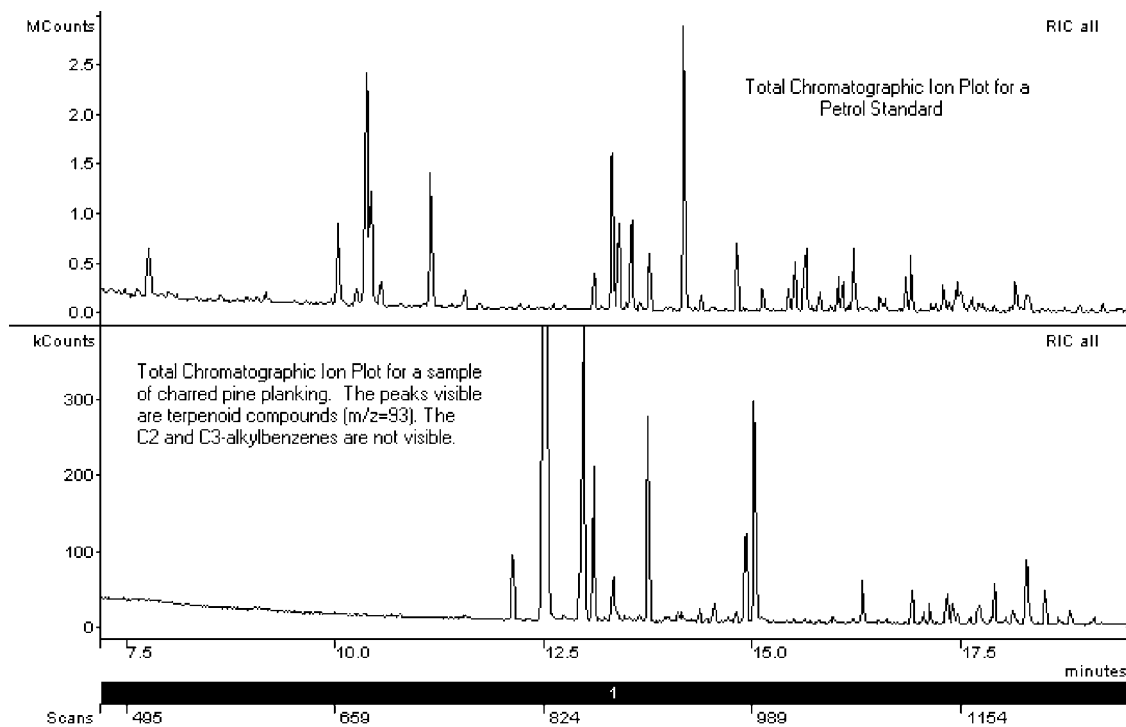


FIG. 6a—Total chromatographic ion profile for a petrol standard by GC/MS with the total chromatographic ion profile for a debris sample of charred pine floor planking below. The terpenoid compounds visible in the pine floor planking sample obscure the aromatic compounds.

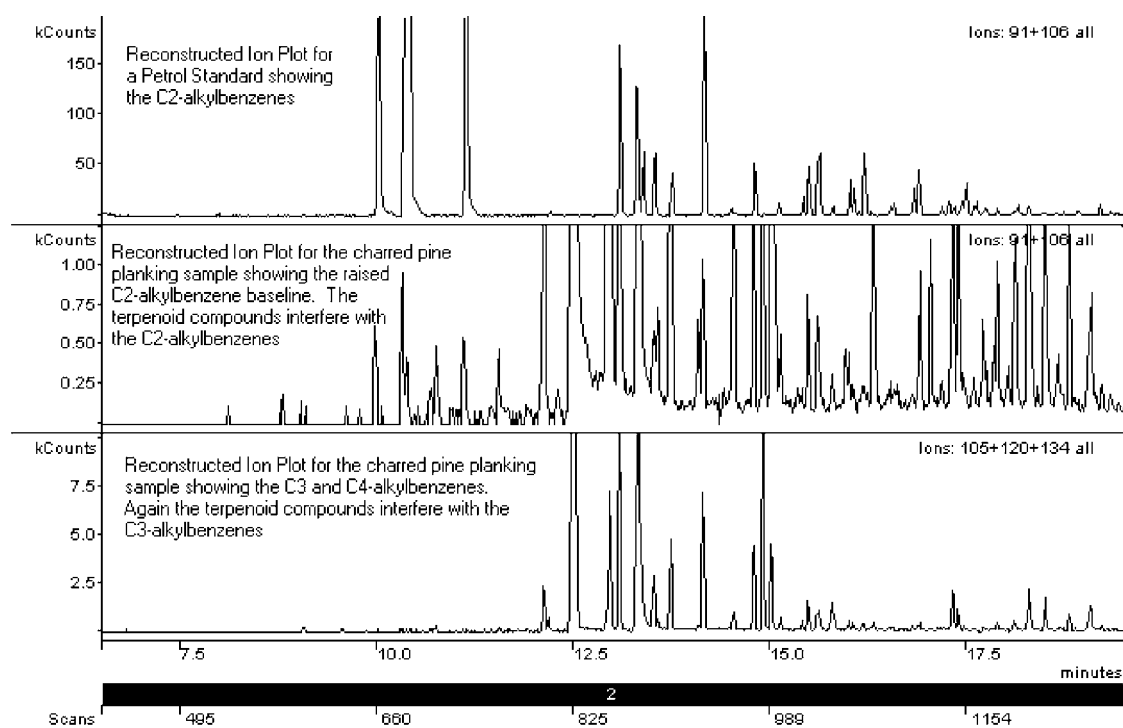


FIG. 6b—Reconstructed ion profile for a petrol standard showing the C2-alkylbenzenes by GC/MS. The reconstructed ion profiles for the C2 and C3-alkylbenzenes for the charred pine floor-plank sample are depicted below the selected ion profile for petrol. The C2-alkylbenzene baseline for the pine floor-plank sample has been enhanced to illustrate how the terpenoid compounds obscure the C2 and C3-alkylbenzenes.

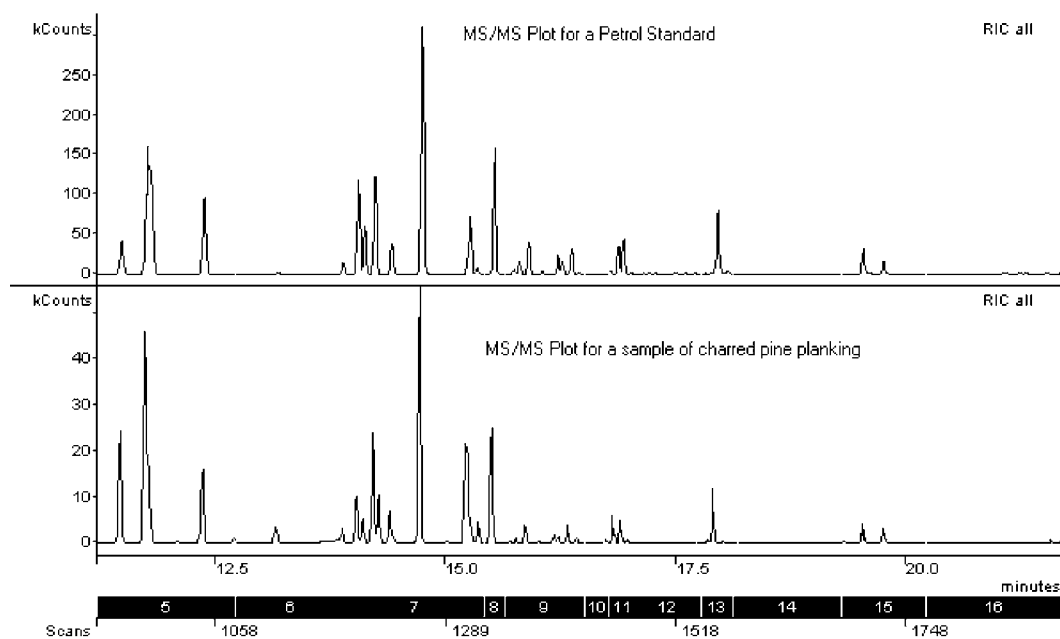


FIG. 6c—The product ion MS/MS profile for a petrol standard with the product ion MS/MS profile for the debris sample of charred pine floor planking below.

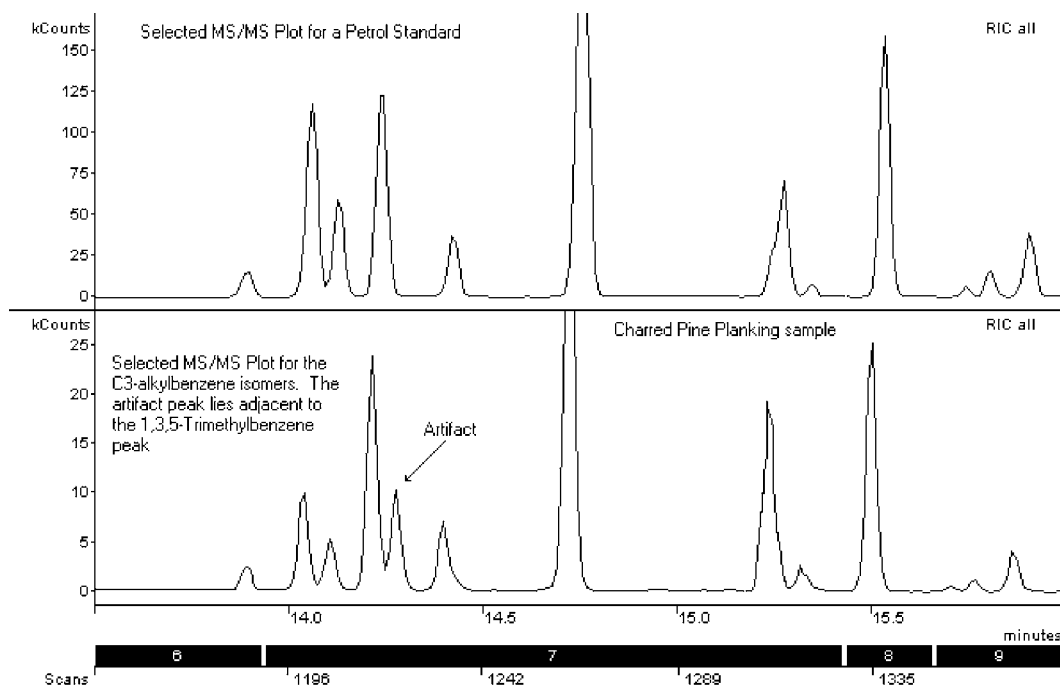


FIG. 6d—Selected time segment product ion MS/MS profile for a petrol standard with the selected time segment product ion MS/MS profile for the debris sample of charred pine floor planking below showing the C3-alkylbenzenes with an artifact peak lying adjacent to the 1,3,5-trimethylbenzene peak.

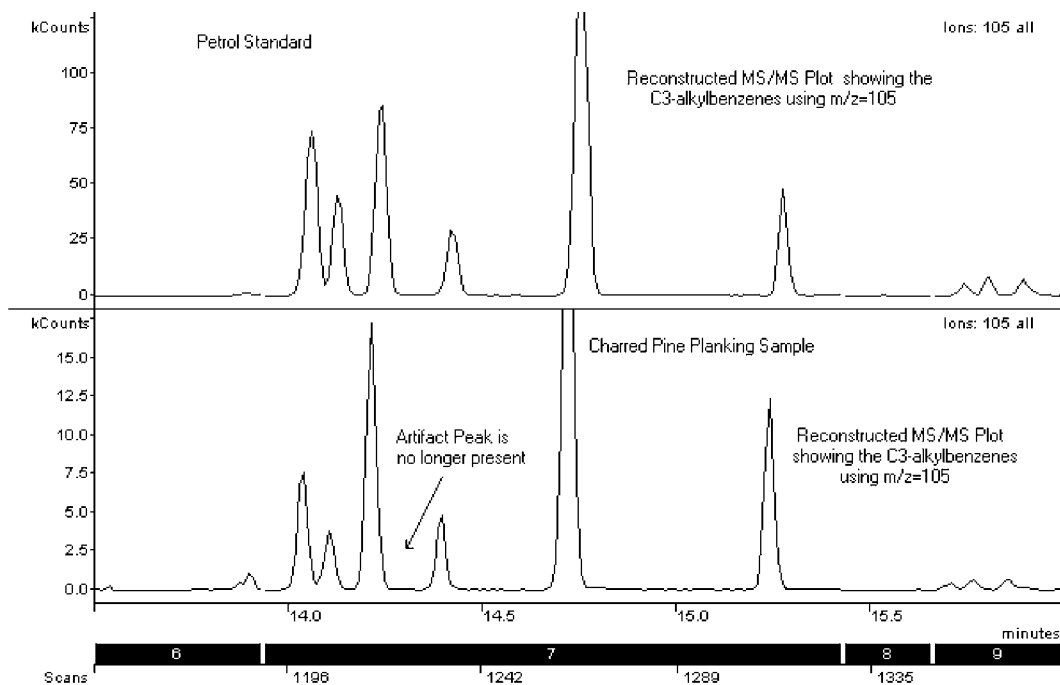


FIG. 6e—Reconstructed product ion MS/MS profile for a petrol standard using $m/z = 105$ with the reconstructed product ion MS/MS profile ($m/z = 105$) for the debris sample of charred pine floor planking below showing the C3-alkylbenzenes with the artifact peak removed.

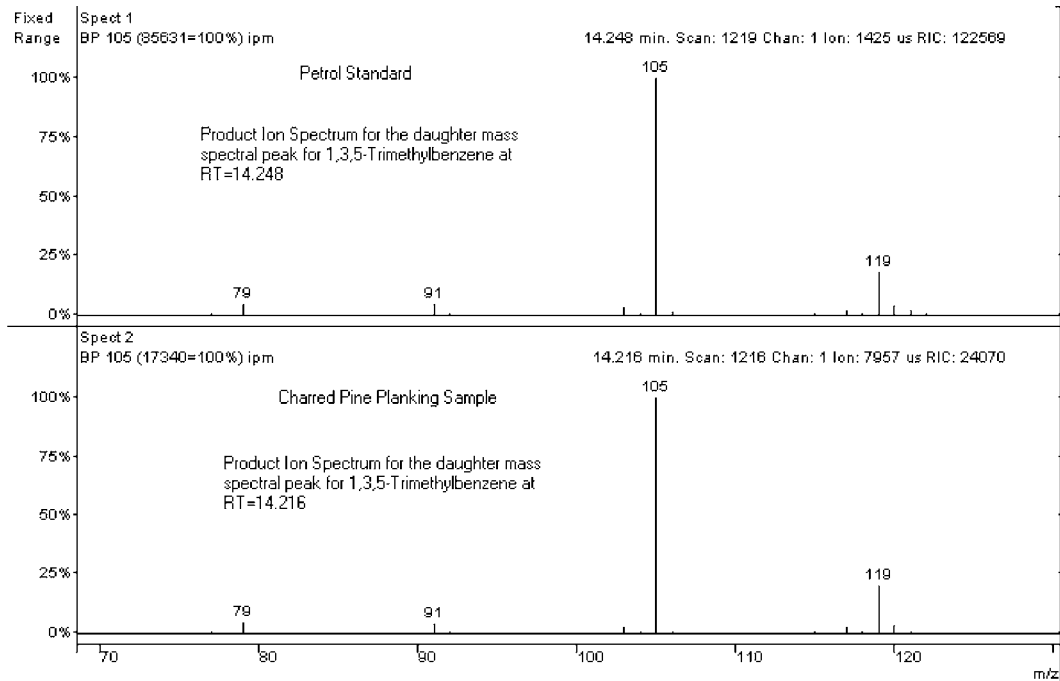


FIG. 6f—Product ion spectrum for the daughter mass spectral peak for 1,3,5-trimethylbenzene for a petrol standard. The same 1,3,5-trimethylbenzene daughter mass spectral peak was selected for the charred pine floor-planking sample and the product ion spectrum obtained is depicted below.

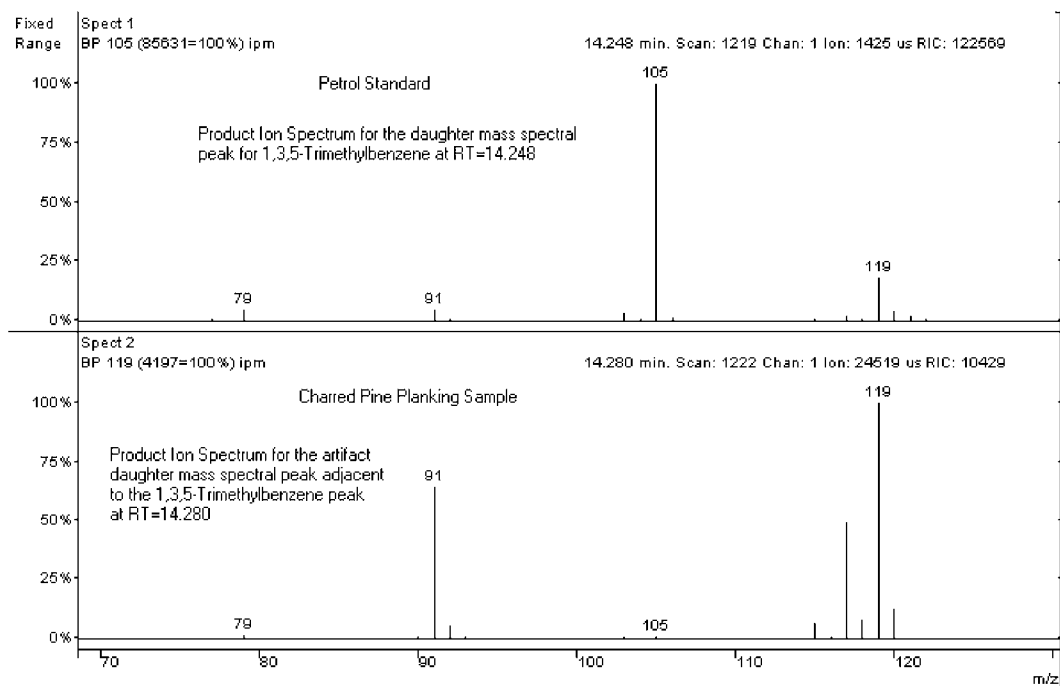


FIG. 6g—Product ion spectrum for the daughter mass spectral peak for 1,3,5-trimethylbenzene for a petrol standard. The artifact peak adjacent to the 1,3,5-trimethylbenzene daughter mass spectral peak was selected for the charred pine planking sample and the product ion spectrum obtained is depicted below.

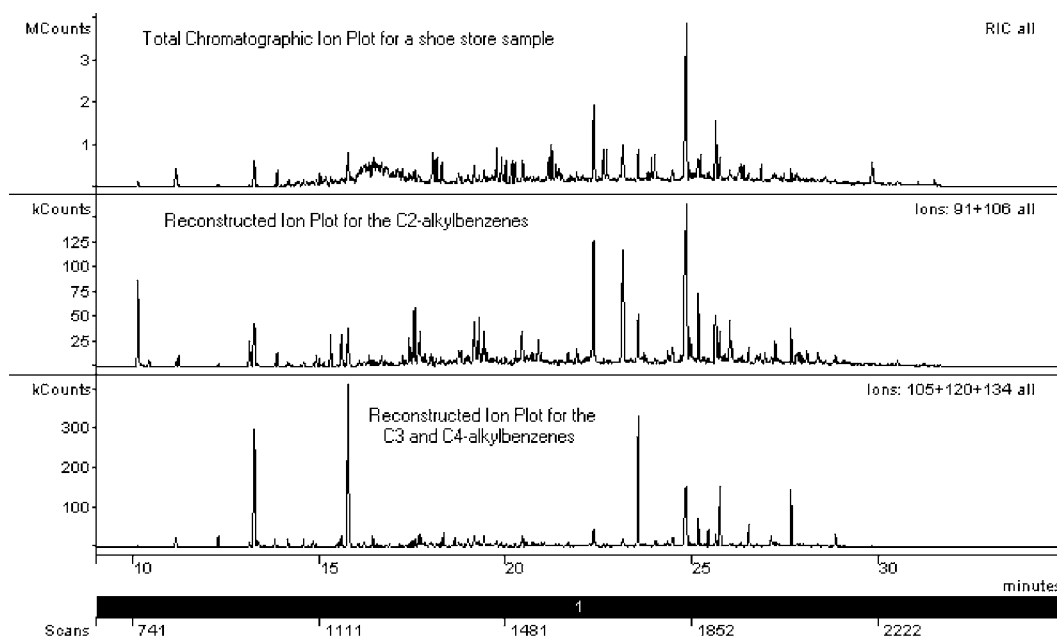


FIG. 7a—Total chromatographic ion profile for a debris sample of shoes and carpeting from a shoe store. The reconstructed ion profiles for the C2 to C4-alkylbenzenes are depicted below the total ion profile.

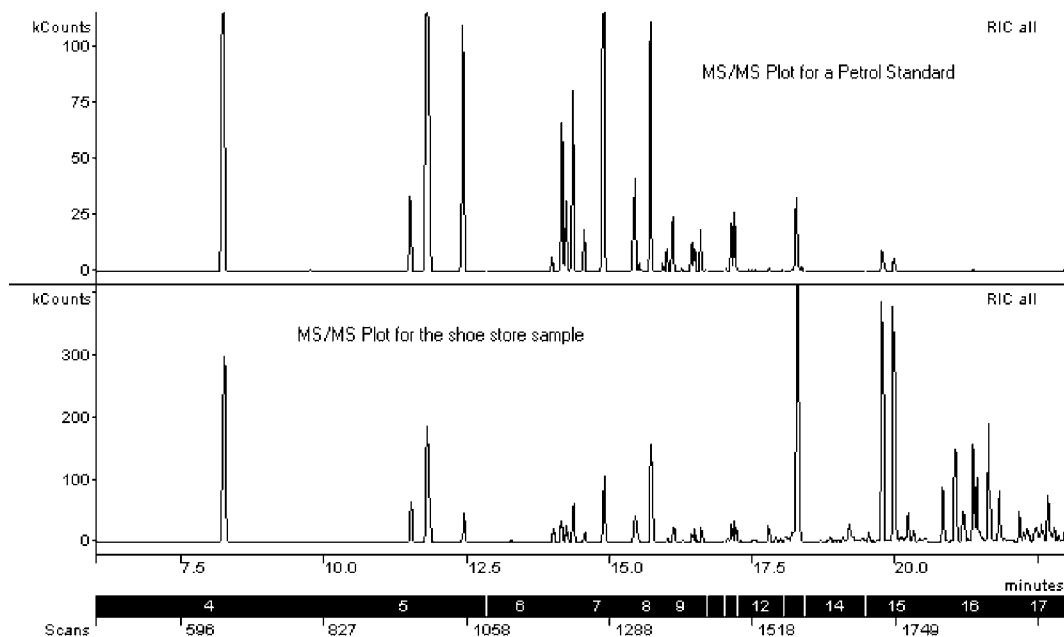


FIG. 7b—The product ion MS/MS profile for a petrol standard by GC/MS with the product ion MS/MS profile for the debris sample of shoes and carpeting from a shoe store below.

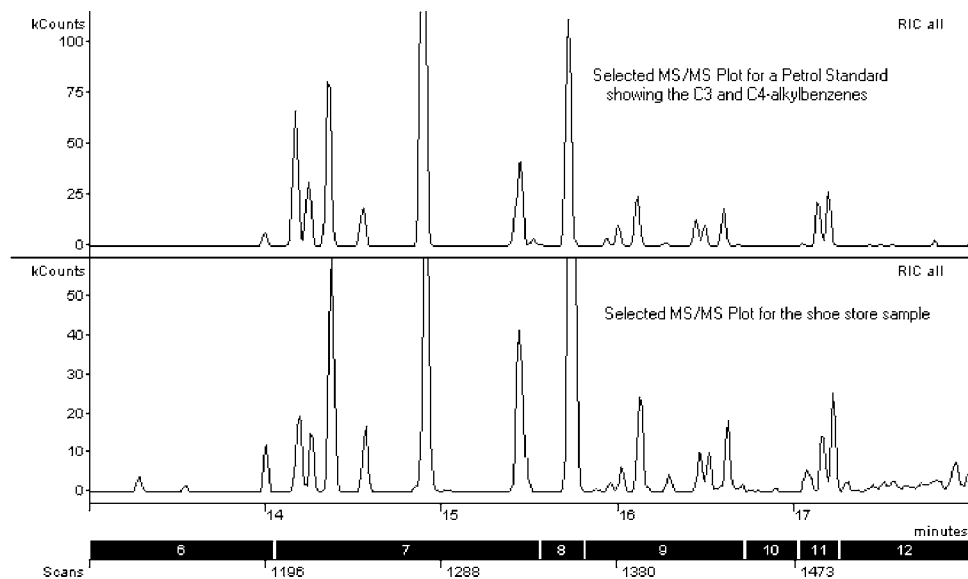


FIG. 7c—Selected time segment product ion MS/MS profile for a petrol standard, with the selected time segment product ion MS/MS profile for a debris sample of shoes and carpeting from a shoe store below, showing the C3 and C4-alkylbenzenes.

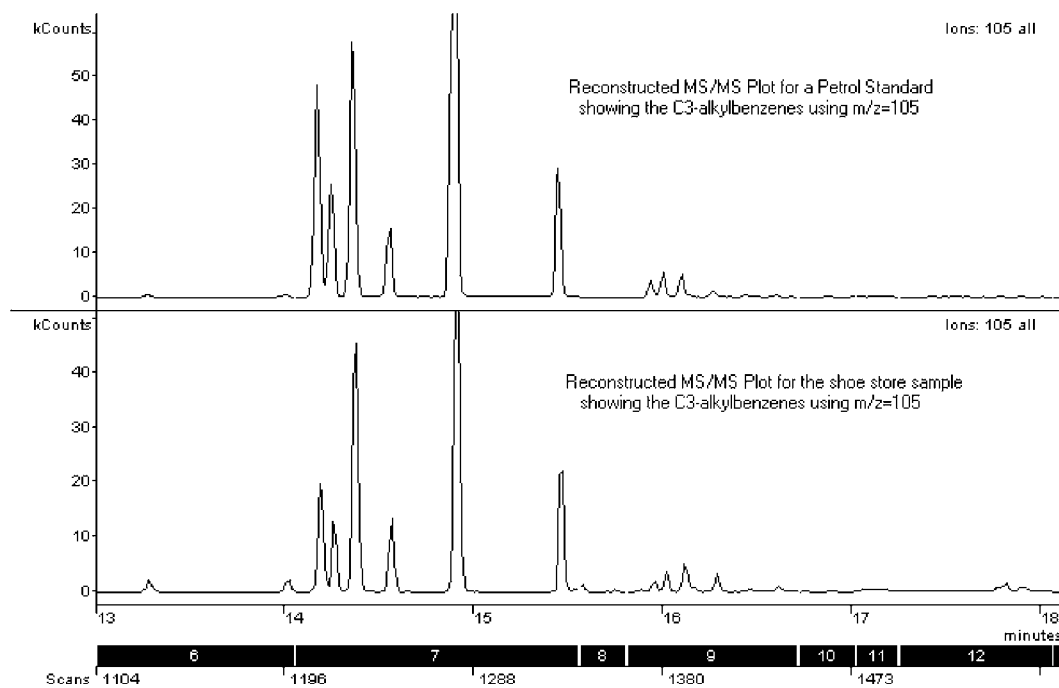


FIG. 7d—Reconstructed product ion MS/MS profile for a petrol standard using $m/z = 105$ with the reconstructed product ion MS/MS profile ($m/z = 105$) for the debris sample of shoes and carpeting from a shoe store below, showing the C3-alkylbenzenes more clearly.

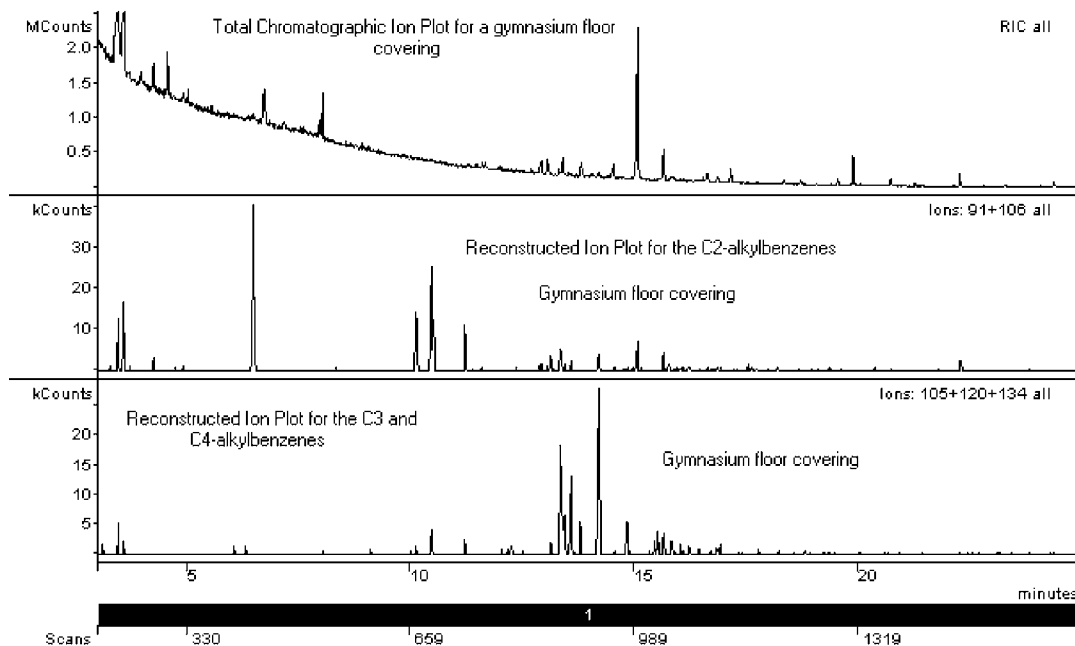


FIG. 8a—Total chromatographic ion profile for a debris sample of gymnasium floor covering by GC/MS. The reconstructed ion profiles for the C2 to C4-alkylbenzenes are depicted below the total ion profile.

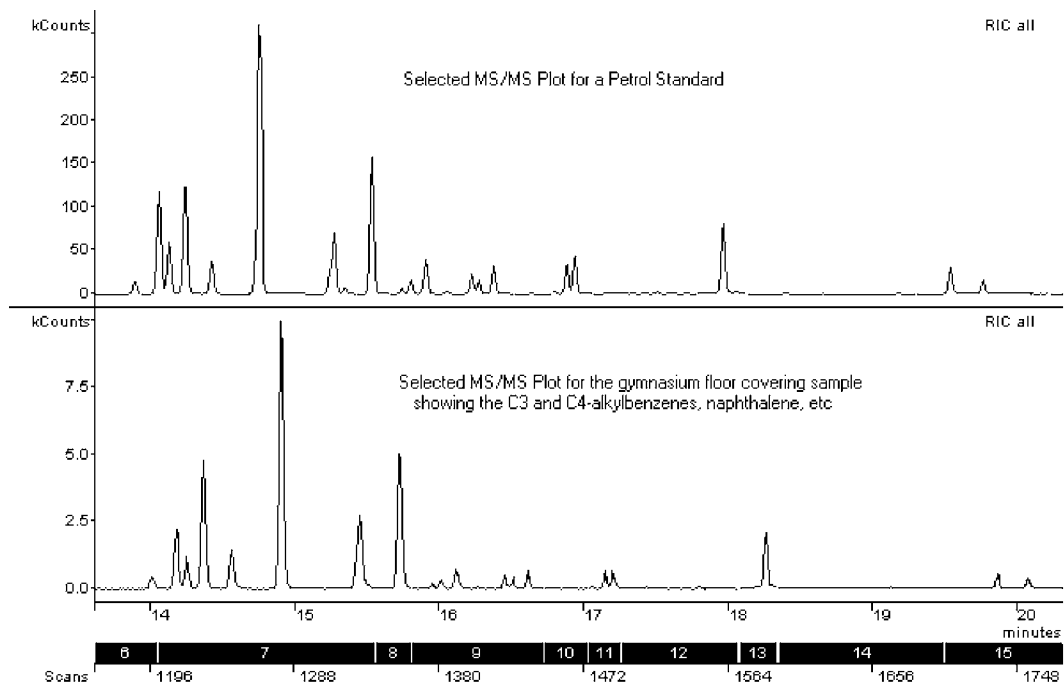


FIG. 8b—The product ion MS/MS profile for a petrol standard, with the product ion MS/MS profile for the debris sample of gymnasium floor covering below.

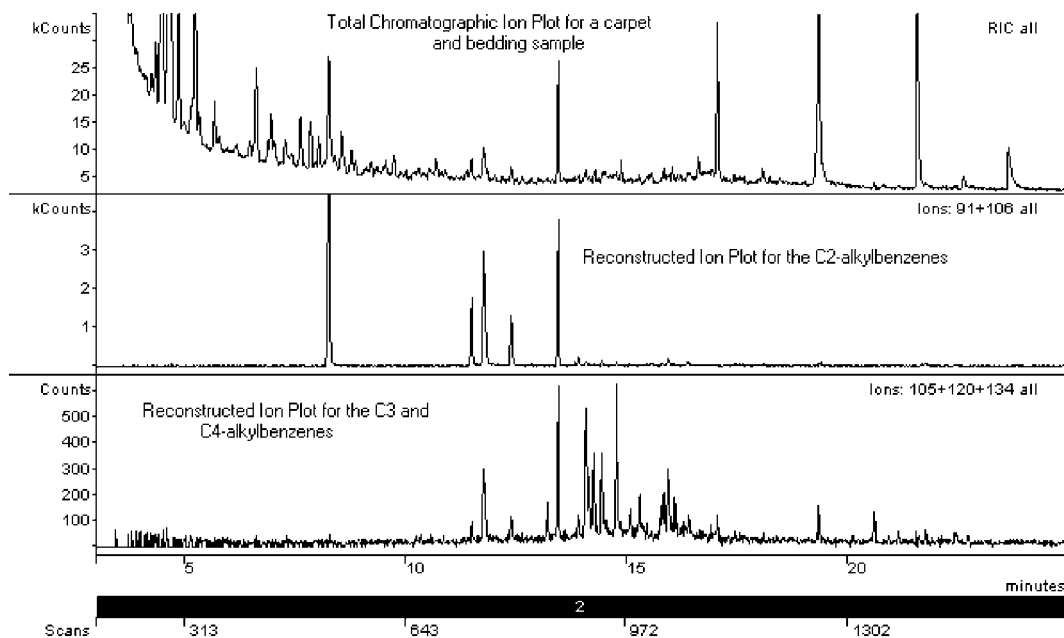


FIG. 9a—Total chromatographic ion profile for a debris sample of carpeting and bedding by GC/MS. The selected ion profiles for the C2 to C4-alkylbenzenes are depicted below the total ion profile.

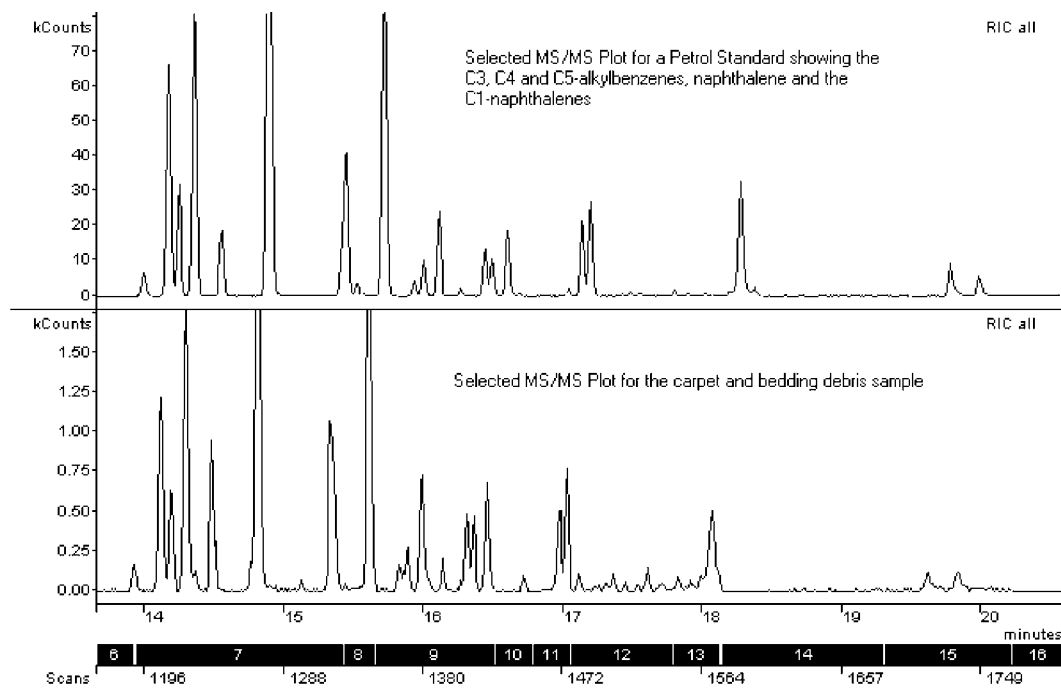


FIG. 9b—The product ion MS/MS profile for a petrol standard, with the product ion MS/MS profile for the debris sample of carpeting and bedding below.

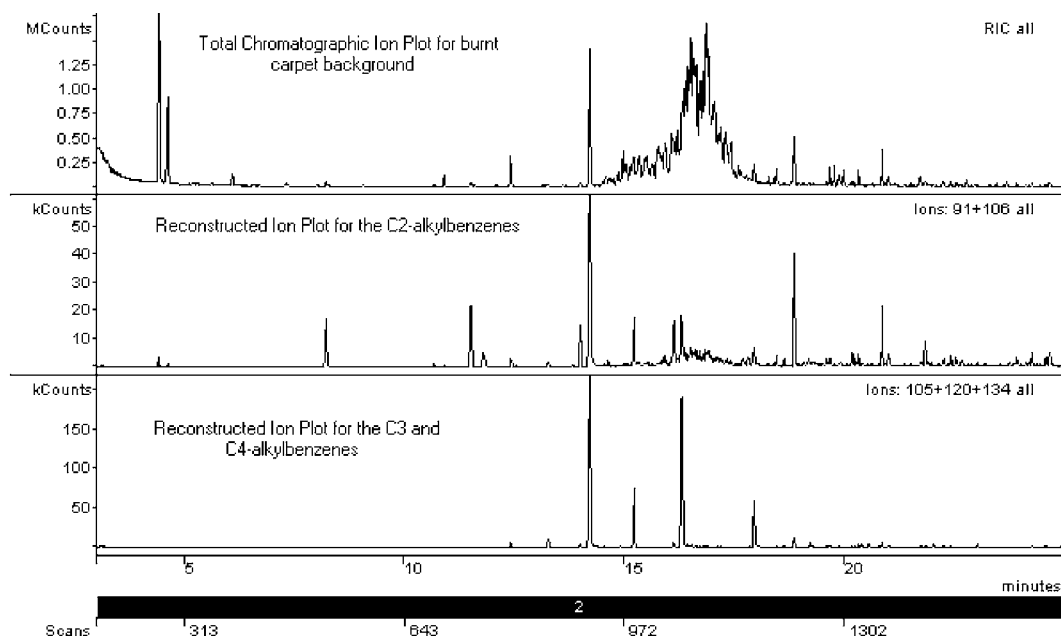


FIG. 10a—Total chromatographic ion profile for a burnt carpet background sample by GC/MS. The selected ion profiles for the C2 to C4-alkylbenzenes are depicted below the total ion profile.

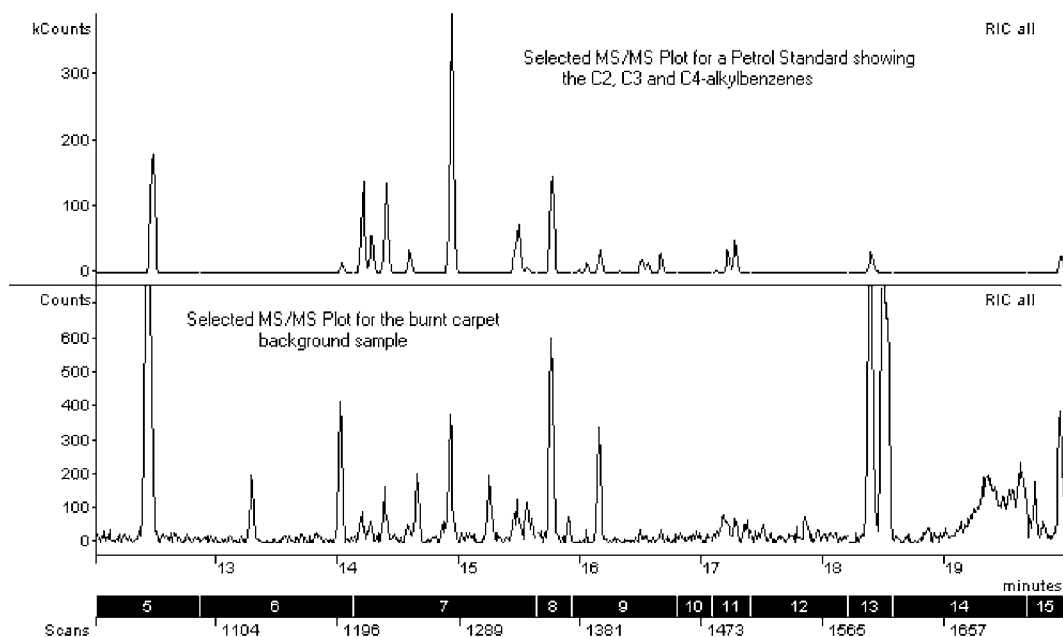


FIG. 10b—Selected time segment ion MS/MS profile for a petrol standard with the product ion MS/MS profile for the burnt carpet background sample below, showing the C3 and C4-alkylbenzenes.

files below each total profile for a petrol standard as used by this laboratory when initially examining arson chromatograms. Benzene is not usually indicated since the carbon disulphide solvent contains benzene contaminants and, unless benzene is suspected, is usually not examined when petrol is suspected. The aliphatic (alkanes and cycloalkanes) hydrocarbons are examined, as well as the alkylbenzene compounds (aromatics) and alkylnaphthalene compounds (condensed ring aromatics).

Figures 5c and 5d show the same total chromatographic ion profile (mass chromatogram) and selected ion profiles for a sample of floor screed containing a reasonable amount of petrol residue and a minor amount of pyrolysis products. From these extracted GC/MS ion profiles, the aliphatic and aromatic hydrocarbons present can be easily detected and favorably compared with a GC/MS chromatographic ion profile for a petrol standard, thus giving a positive result. The presence of paraffin can also be seen from the m/e 57 selected ion profile.

Figure 5e is the product ion profile (daughter ion mass chromatogram) for the floor screed sample mass chromatogram obtained in Figs. 5c and 5d. In this figure it can be seen that the pyrolysis products have been removed by MS/MS in the sample and the resultant product (daughter) ion profile compares well with that of the product ion profile for a petrol standard. This is, however, a good example, where the petrol residue was easily detected and MS/MS would not really be necessary. Cases where pyrolysis products have interfered with the MS chromatograms, even after examination of the extracted ion profiles, will show that MS/MS has the capability of effectively minimizing, if not entirely removing, the pyrolysis interferences.

By reconstructing the daughter ion chromatogram over a specific retention time period (Fig. 5f), the C3 and C4-alkylbenzene compounds of the floor screed sample can be clearly compared with the petrol standard. Naphthalene and the C1-naphthalenes are also clearly visible.

Direct comparison of the GC/MS total chromatographic ion profile with the product (daughter) ion MS/MS profile (Fig. 5g) gives a clear indication that the MS/MS chromatographic profile pro-

vides a more definitive and less “cluttered” chromatogram than the GC/MS chromatographic profile, where pyrolysis products obscure the characteristic isomers.

The total chromatographic ion profile for a sample of pine floor planking is shown in Fig. 6a with the total chromatographic ion profile for a petrol standard above. Figure 6b depicts selected ion profiles for the pine floor-planking sample. In these selected profiles it can be seen by the enhanced baseline that terpenoid compounds are the main pyrolysis interference. In Fig. 6c the product ion profile compares well with petrol, and upon closer examination the trimethylbenzene compounds are clearly present, proving that petrol is part of the sample. The “pool-mark” charring and pour patterns verify that not only pine planking could be present.

Figure 6d shows the selected time segment product (daughter) MS/MS ion profile for the C3-alkylbenzene compounds. When compared with a petrol standard, there is an artifact peak present as a shoulder peak adjacent to the mesitylene peak (1,3,5-trimethylbenzene). By reconstructing the product ion MS/MS profile (chromatogram) over the time range of the segment (Segment 7) using $m/e = 105$, the artifact peak is removed from the chromatographic product (daughter) ion MS/MS profile of the charred pine planking sample. The real benefit of MS/MS is the “selectivity” gain achieved through reconstruction of the 105 ion.

Figures 6f and 6g show the actual product (daughter) ion spectrum for the mesitylene peak in a typical petrol standard as compared with the product (daughter) ion spectrum of mesitylene in the charred pine planking sample and the product (daughter) ion spectrum of the adjacent artifact peak. The spectra clearly differ (Fig. 6g). The added selectivity of the product (daughter) ion spectra, allows for added confidence in the chromatographic result.

Figure 7a shows the total chromatographic ion profile and selected ion profiles for a shoe store floor sample, including carpeting and shoe debris. The product ion MS/MS profile for this sample is shown in Fig. 7b. Note that the naphthalene compounds are very concentrated.

A closer comparison of the C3, C4, and C5-alkylbenzene compounds in Fig. 7c indicated the presence of petrol, which was not

clearly indicated in the GC/MS selected ion profiles, due to additional C3-alkylbenzene and naphthalene compounds present as a result of solvents incident in the shoe store. Figure 7d is a reconstructed selected time segment product (daughter) ion MS/MS profile for $m/e=105$. Based on the analyses (GC/MS and GC/MS/MS) the sample was determined to be positive, and therefore petrol was indicated in the sample.

Figure 8a shows the chromatograms for a sample of gymnasium floor covering. The chromatogram is weak, and therefore MS/MS was performed in order to enhance the possible presence of a petrol residue, which can be seen in Fig. 8b, where the sample product (daughter) ion MS/MS profile compares well with those for a petrol standard, and, thus, again based on both analyses, petrol was present in the sample.

Figure 9a is a sample of carpeting and bedding. The selected ion profiles by GC/MS give an indication of a weak petrol residue, but the result is uncertain. The product ion MS/MS profile for this sample clearly indicated the residual petrol presence (Fig. 9b).

Since carpet background is often the most common source of pyrolysis interference, Fig. 10a shows the total chromatographic ion profile and selected ion profiles for a typical nylon carpet pile with an urethane/polyester type backing. The product (daughter) ion MS/MS profile is given in Fig. 10b, where close examination of the C3-alkylbenzene compounds shows that they are not comparable with the C3-alkylbenzene compounds found in petrol.

Finally, Figs. 11a, 11b, 11c, 11d, 11e, and 11f are the mass spectra for some of the characteristic aromatic masses selected for GC/MS and compared with the GC/MS/MS product (daughter) ion spectra of the same characteristic aromatic masses. Depending on the CID voltage selected, the product ion MS/MS spectra obtained are reasonably comparable with the conventional mass spectra, and it can be seen that a library of product (daughter) ion spectra can be created against which searches can be performed. The examples in the figures are toluene, ethyl benzene, 1,2,4-trimethylbenzene, C4-alkylbenzenes, naphthalene and the C1-naphthalenes.

Discussion

The use of MS/MS as a means of detection and clarification of petrol residues has been shown to be an enhancement on the use of MS ion profiling methods and an improvement in the elimination of pyrolysis interference. All the information required for positive identification of petrol in a sample of fire debris containing large amounts of pyrolysis products can now be obtained in a conventional MS chromatographic run, followed by an MS/MS chromatographic run.

Aromatic compounds fragment very readily and give very intense daughter ions. The degree to which the selected parent ion is fragmented depends on the amount of information to be derived from the product (daughter) ion spectrum or reconstructed parent/daughter ion spectrum. If a "softer" excitation amplitude is used, the parent ion will fragment less and the resultant product (daughter) ion spectrum will more closely resemble the GC/MS mass spectrum of that ion. If a completely different product (daughter) ion spectrum is desired, a "harsher" excitation amplitude is necessary in order to almost totally remove the parent ion and produce a unique product (daughter) mass spectrum. MS/MS is very specific and the method of fragmentation in this study is "tuned" to the detection of the characteristic aromatic hydrocarbons found in petrol.

Selecting one parent ion per segment does allow for a more sensitive chromatogram and is similar to SIM, an enhancement over GC/MS, but it also allows more sensitivity for any pyrolysates that have the same ion. The advantage lies in the reconstruction of both the selected parent ion and any daughter ions of interest. Reconstructing the product (daughter) ion chromatogram gives a totally different profile, which serves as new information for the sample case and can also be compared to the daughter ion chromatogram of the petrol standard.

GC/MS/MS, used in conjunction with GC/MS, provides a second confirmatory analysis and can simplify complex or trace re-

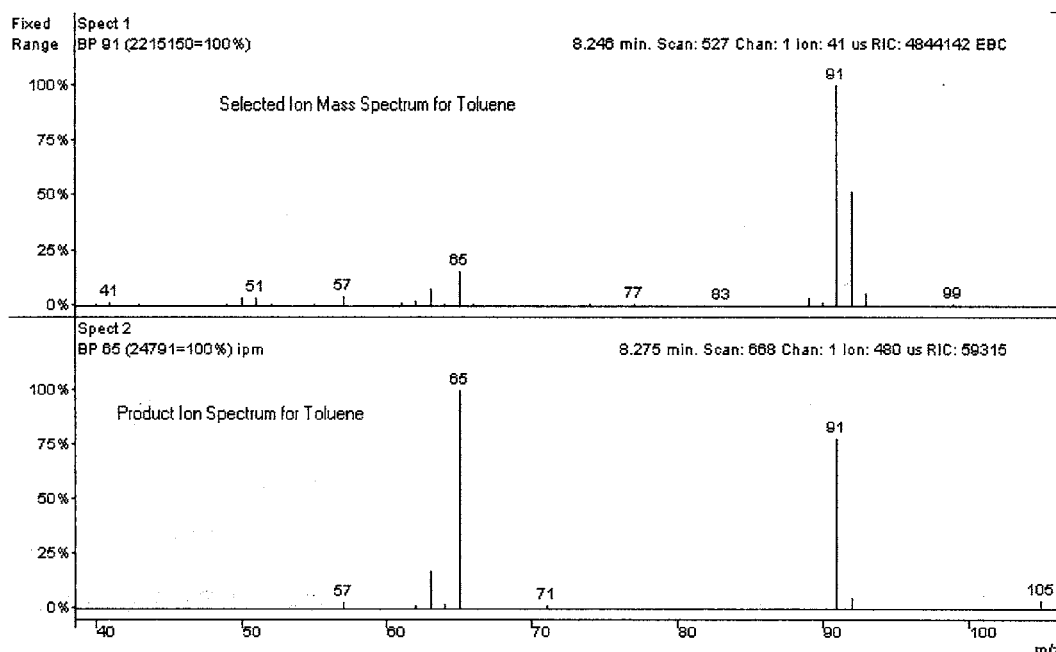


FIG. 11a—Background subtracted GC/MS mass spectrum for toluene above, with the product ion MS/MS spectrum for toluene below.

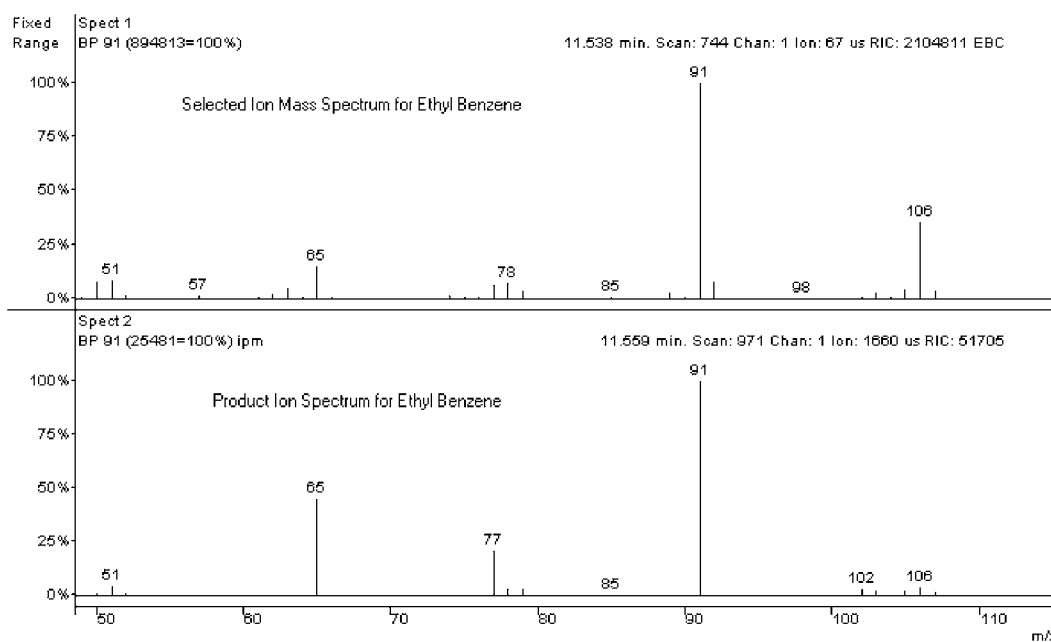


FIG. 11b—Background subtracted GC/MS mass spectrum for ethyl benzene above, with the product ion MS/MS spectrum for ethyl benzene below.

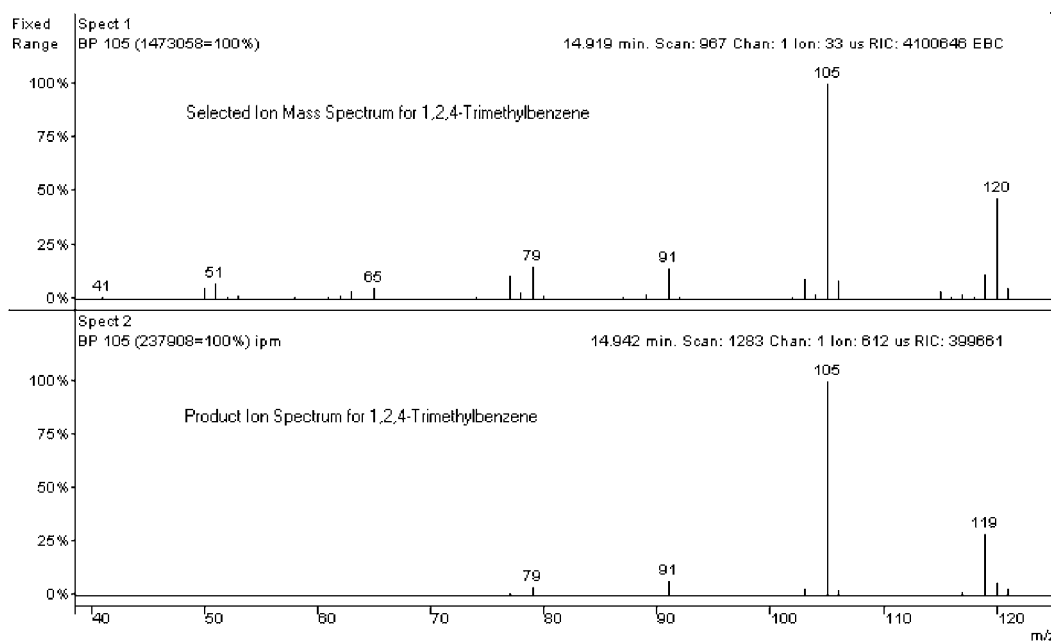


FIG. 11c—Background subtracted mass spectrum for 1,2,4-trimethylbenzene above, with the product ion spectrum for 1,2,4-trimethylbenzene below.

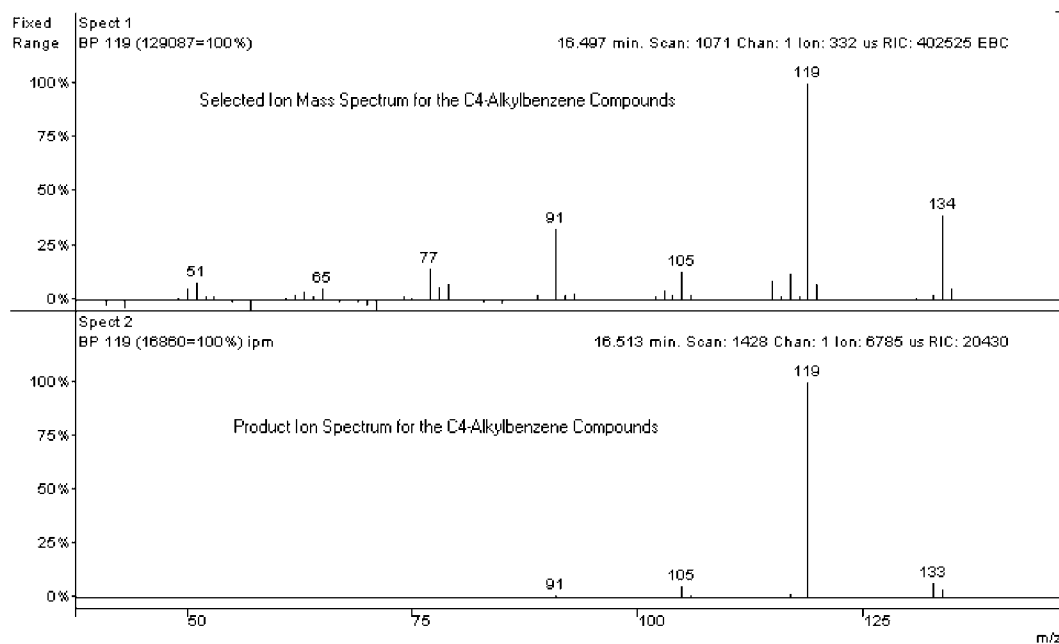


FIG. 11d—Background subtracted GC/MS mass spectrum for the C4-alkylbenzenes above, with the product ion MS/MS spectrum for the C4-alkylbenzenes below.

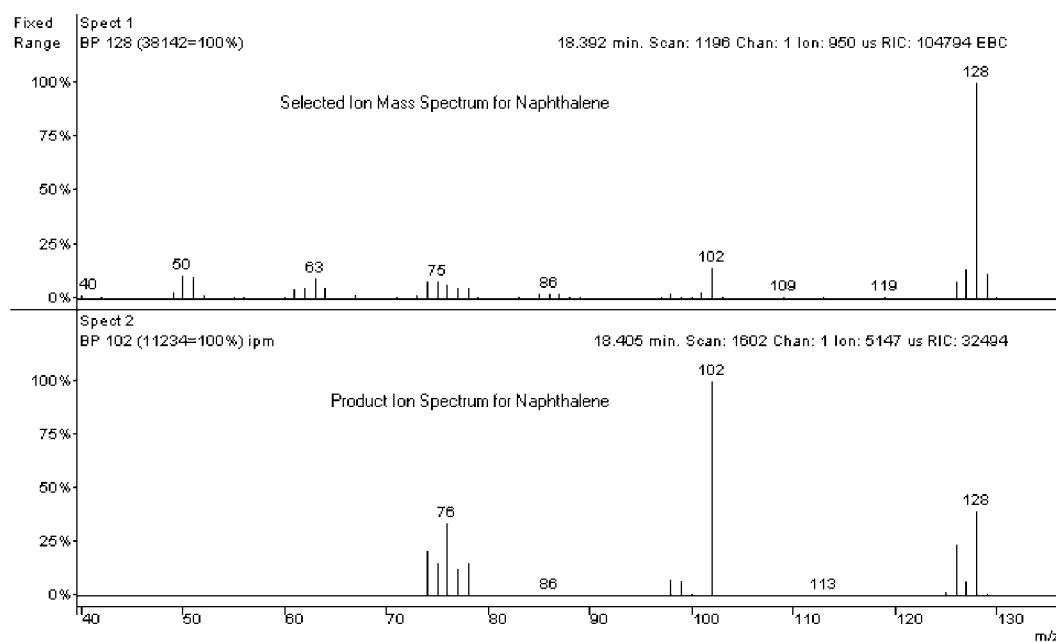


FIG. 11e—Background subtracted GC/MS mass spectrum for naphthalene above, with the product ion MS/MS spectrum for naphthalene below.

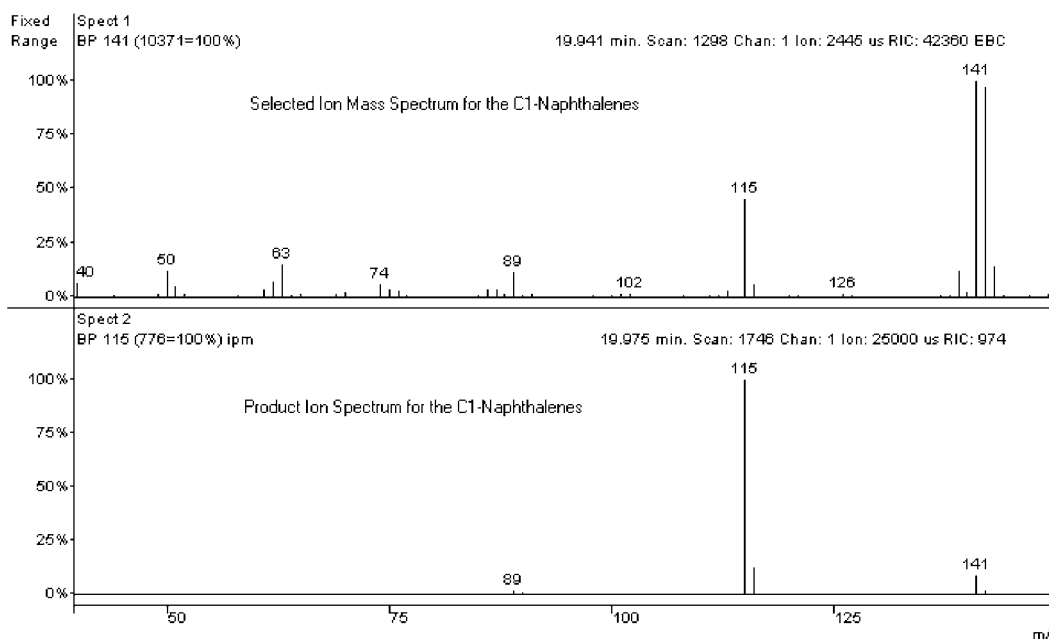


FIG. 11f—Background subtracted GC/MS mass spectrum for the C1-naphthalenes above, with the product ion MS/MS spectrum for the C1-naphthalenes below.

sponses seen in the GC/MS analysis due to pyrolysis interferences or if the sample is very weak and is not definitive evidence for presentation in court by GC/MS alone.

GC/MS/MS provides ultra specificity by greatly eliminating pyrolysis interferences still prevalent in the GC/MS profile. The method allows longer scanning of selected ion fragments specific to the aromatic hydrocarbons found in petroleum-based ignitable liquids. GC/MS/MS can be very definitive and has an associated level of confidence in the result, especially since the ion trap is “tuned” for detection of ignitable liquids.

As the ion trap mass spectrometer becomes more widely used and software becomes more powerful, so the use of MS/MS in arson analyses can become routine laboratory practice.

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