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Forensic Analysis of Ignitable Liquids in Fire Debris by Comprehensive Two-Dimensional Gas Chromatography*

ABSTRACT: The application of comprehensive two-dimensional gas chromatography (GC × GC) for the forensic analysis of ignitable liquids in fire debris is reported. GC × GC is a high resolution, multidimensional gas chromatographic method in which each component of a complex mixture is subjected to two independent chromatographic separations. The high resolving power of GC × GC can separate hundreds of chemical components from a complex fire debris extract. The GC × GC chromatogram is a multicolor plot of two-dimensional retention time and detector signal intensity that is well suited for rapid identification and fingerprinting of ignitable liquids. GC × GC chromatograms were used to identify and classify ignitable liquids, detect minor differences between similar ignitable liquids, track the chemical changes associated with weathering, characterize the chemical composition of fire debris pyrolysates, and detect weathered ignitable liquids against a background of fire debris pyrolysates.

KEYWORDS: forensic science, arson, fire debris, accelerant, ignitable liquid, gasoline, pyrolysis, gas chromatography, comprehensive two-dimensional gas chromatography

Identifying traces of ignitable liquids in fire debris is a significant challenge for forensic scientists. The analysis requires extraction of volatiles from the fire debris followed by chemical analysis to determine if the volatiles indicate the presence of an ignitable liquid. There are a wide variety of ignitable liquids that may be used by an arsonist. They are grouped into five classes that include light petroleum distillates (Class 1), gasoline (Class 2), medium distillates (Class 3), kerosene (Class 4), and heavy distillates, such as diesel fuel and home heating oil (Class 5). In addition, there are other miscellaneous ignitable liquids like oxygenated, isoparaffinic, naphthenic, or aromatic solvents, which can be used as fire accelerants (Class 0) (1). Forensic scientists must examine the fire debris for the presence of all of these ignitable liquids.

The chemical analysis is complicated when the ignitable liquid has been weathered by the heat of the fire or by fire-fighting activities. Further complicating the analysis are volatiles originating from the pyrolysis of other materials in the fire debris. Pyrolysates from plastics, foam cushions, nylon or polyolefin carpets, and vinyl flooring are particularly troublesome in the chemical analysis because they may contain chemical components that are also present in ignitable liquids (2,3).

Advances in analytical chemistry technology have been important to the success of forensic scientists. With the invention of gas chromatography (GC) about forty years ago, forensic scientists made it the central instrument in fire debris analysis (1). Twenty years later, the widespread availability of gas chromatography-mass spectrometry (GC/MS) systems offered forensic scientists greatly improved capability to identify and fingerprint ignitable liquids (4,5).

In gas chromatography, chemical components are separated based on variations in their physical properties. Fire debris volatiles are most often analyzed with a chromatography column containing a nonpolar stationary phase. Nonpolar phases are called "boiling point phases" because they separate components by differences in their volatilities. The resulting gas chromatogram has a distribution and pattern of peaks that is useful for ignitable liquid fingerprinting. In instances when the ignitable liquid is weathered by fire, the change in chemical composition produces a significantly altered chromatogram. The most volatile components will be missing; the less volatile components will be relatively enhanced in concentration. These changes require that forensic scientists create a library of ignitable liquids at several states of weathering. In real fire debris samples, pyrolysates from building materials and furnishings are also present. These added chemicals further alter the pattern of the chromatogram and make recognition of the ignitable liquid more difficult (6).

For complex ignitable liquid and fire debris samples, the chromatographic separation is almost always incomplete. The overlap of multiple peaks produces an elevated baseline in the chromatograms. As a result, even the large, distinct peaks in the chromatogram often have several coeluting chemical components. When a mass spectrometer detector is used with the gas chromatograph, an additional dimension of chemical information is provided (5). The mass spectrometer is able to virtually separate chromatographic coeluents by mass because components of a specific chemical class have unique molecular fragmentation patterns (4,7). The different chemical classes are extracted as mass chromatograms from the total ion chromatogram data. The mass chromatogram profiles are used as fingerprints to detect ignitable liquids in the fire debris sample. The mass chromatogram helps to filter out the coeluters in the chromatogram and show only the distribution of specific chemical class components originating from the ignitable liquid. The GC/MS mass chromatogram is effective except when fire debris pyrolysates have ions with the same mass as the target

class. Pyrolysates from petroleum-based products such as carpet are particularly troublesome because they may contain chemical components identical to the ignitable liquid components (2–5,8). For example, mono-substituted benzenes like ethylbenzene, propylbenzene, and butylbenzene are produced by pyrolysis of petroleum-based products like carpet (5). These components are also present in petroleum-based ignitable liquids.

A different approach for analyzing GC/MS data called Target Compound Chromatogram (TCC) analysis has been developed (9–11). In this method, the total ion chromatogram data is searched for specific target compounds that will confirm the presence of an accelerant. Specific accelerant compounds are found by searching for specific parent/daughter fragmentation ions in a certain retention time window. The ion abundance of the located parent/daughter fragments is compared to the known mass spectrum abundances for the compound to confirm its presence. In the TCC method, the data typically contained in multiple mass chromatograms are reduced to one data product for a more rapid comparison of ignitable liquid patterns.

Regardless of whether the mass chromatogram or target compound chromatogram analysis methods are used, the mass spectrometer detector offers significant improvements over the use of gas chromatography alone. Data show that since the mid 1980s, the percentage of laboratories routinely using gas chromatography-mass spectrometry for fire debris analysis has climbed from below 10% to nearly 90% (12). More importantly, laboratories using GC/MS have a significantly higher probability of performing a successful fire debris analysis (13).

Because of the significant analytical challenge posed by the detection of ignitable liquids in fire debris, researchers continue to explore new analytical techniques. One example is the application of heartcut multidimensional gas chromatography by Jayatilaka and Poole (14). They argued that to make best use of the target compound approach for ignitable liquid identification, a better chromatographic separation was needed. They used a multidimensional gas chromatographic system that could sample a group of coeluents from the nonpolar-phase chromatography column and inject it into a second polar-phase chromatography column for separation. Since the second column had a different selectivity, the aromatic target compound was separated from its predominantly alkane or cycloalkane coeluents. The multidimensional system could perform several heartcuts during the analysis so multiple target compounds could be chromatographically resolved.

A second example of new technology applied to fire debris analysis is the gas chromatography, tandem mass spectrometry (GC/MS/MS) method demonstrated by Sutherland (15). Tandem mass spectrometry (MS/MS) uses two coupled mass spectrometers. The first mass spectrometer uses a low energy ionization source to create a molecular ion without inducing molecular fragmentation. The first spectrometer then isolates molecular ions with a particular mass. The molecular ions are then subjected to collision-induced fragmentation and a mass spectrum is collected with a second mass spectrometer (16). GC/MS/MS is fundamentally a three-dimensional separation because each target has been separated by chromatographic retention, molecular ion mass, and then fragmentation pattern. GC/MS/MS offers significant advantages for identifying target compounds by better filtering out the chemical interferences from matrix pyrolysates.

Recently, FT-ICR mass spectrometry was applied to fire debris analysis by Rodgers et al. (17). Without a chromatographic separation, their high resolution mass spectrometry analysis identified up to five hundred unique chemical formulas for complex ignitable liquids. This information was used to distinguish the ignitable liquids from several hundred additional matrix components produced by the fire debris.

In this work, we will demonstrate that the new technology of comprehensive two-dimensional gas chromatography (GC × GC) has great potential for improving the chemical analysis of ignitable liquids in complex fire debris samples. GC × GC is a two-dimensional separation and has many similarities with the heartcut chromatography and GC/MS/MS methods described above. In fact, comprehensive two-dimensional gas chromatography is a refinement of multidimensional heartcut chromatography. Instead of taking selected heartcuts to isolate specific target compounds, GC × GC separations are comprehensive because all of the components are separated with two chromatography columns. Comprehensive two-dimensional gas chromatography provides an order of magnitude improvement in the separation of complex mixtures such as fire debris and ignitable liquids. It has been used to separate over three hundred chemical components from gasoline (18,19) and up to one thousand components in more complex samples like diesel fuel (20).

Phillips, the inventor of GC × GC, first applied GC × GC separations to the separation of complex petroleum products (21). Later work by Blomberg et al. (22) and Beens et al. (23,24) with an early commercial GC × GC instrument identified and quantified individual chemical components in complex petroleum samples. Frysinger and Gaines developed analytical methods to separate and quantify oxygenates (18) and aromatic components in gasoline (19). Gaines also applied GC × GC to trace detection of gasoline pollutants in groundwater (25). GC × GC has already been applied to forensic analysis by Gaines et al. to determine the source of a water-borne oil spill (20). The GC × GC chromatograms were used for visual and quantitative comparisons between pure and weathered diesel fuels to determine the source. This oil spill application generated interest in applying GC × GC to the challenges of fire debris analysis.

In this work, we will demonstrate how GC × GC chromatograms can be used to rapidly classify and identify ignitable liquids, track the chemical changes associated with weathering, and detect weathered ignitable liquids in the presence of a significant amount of fire debris pyrolysates.

Experimental Methods

GC × GC Instrumentation

The comprehensive two-dimensional gas chromatography system is based on an HP 6890 gas chromatograph containing two chromatography columns connected serially by a modulator. The modulator is used to periodically transfer analyte between the two chromatographic dimensions in GC × GC (26). Modulator systems are commercially available from Zoex Corp. (Lincoln, NE). The key components of the modulator are a rotating slotted heater and a small section of thick-film capillary column called the modulator tube, which connects the two GC columns. The heater periodically rotates over the modulator tube to desorb trapped analyte and inject it into the second column.

The concept of modulation and comprehensive two-dimensional gas chromatography is described pictorially in Fig. 1a–e. Figure 1a represents a typical chromatogram peak as it elutes from a nonpolar chromatography column in the first dimension of a GC × GC separation. The broad, 25-s peak may contain multiple coeluters that have nearly the same boiling point. Figure 1b shows how the rotating heater modulates the first-dimension peak into a series of
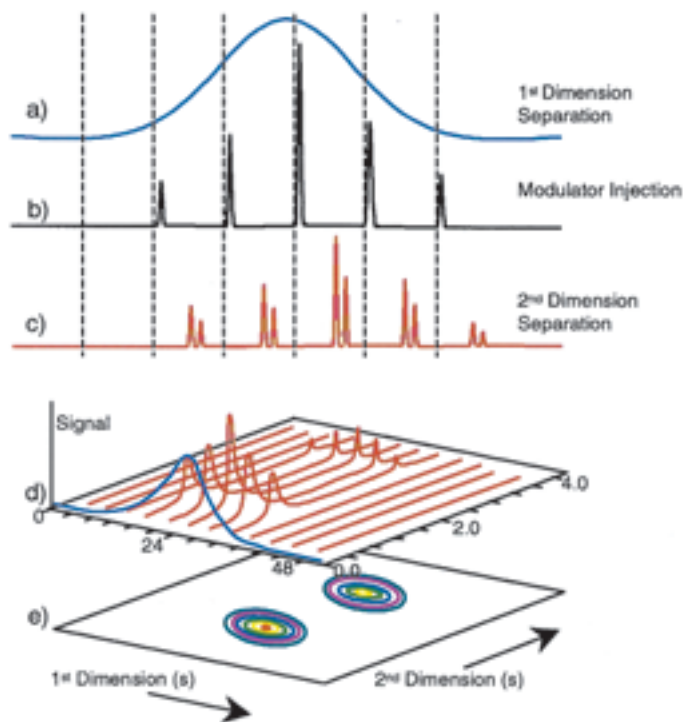
FIG. 1—*Conceptual image of GC × GC operation.*

narrow second-dimension injections. The peak compression resulting from the modulation produces an order of magnitude improvement in signal to noise. The signal-to-noise increase is especially important for detecting minor components in a complex mixture. The vertical dashed lines in the figure indicate the start of the modulation cycle. Figure 1c shows how a short, narrow-bore polar chromatography column can separate the coeluting compounds. Note that each second-dimension separation is complete before the next injection. Figure 1d demonstrates how the detector data stream is sliced into chromatogram segments and packed into a two-dimensional array. Since the mass of an individual component is split between several second-dimension chromatograms, quantification requires integration and summation of several peaks. Lastly, Fig. 1e shows a color contour plot created from the two-dimensional array.

The first-dimension chromatography column was 4.75 m × 0.10 mm I.D. with a 3.5 μm nonpolar polydimethylsiloxane phase (Phase 007-1, Quadrex, New Haven, CT). The modulator tube was 0.08 m × 0.10 mm I.D. with a 3.5 μm polydimethylsiloxane phase. The first column and modulator tube were temperature programmed from −20°C (10 min hold) to 240°C at 2°C per min. Low starting temperatures are needed to effectively retain and modulate volatile components with a rotating modulator. The second-dimension column was 2.00 m × 0.10 mm I.D. with a 0.10 μm 14% cyanopropylphenyl-polydimethylsiloxane phase (Phase 007–1701, Quadrex, New Haven, CT). The second column was temperature programmed from 20°C (20 min hold) to 260°C at 2°C per min. Segments of deactivated fused silica column and glass pressfit connectors (Alltech, Deerfield, IL) were used to connect the chromatography columns between the two different heated zones. Hydrogen was used as the carrier gas in constant flow mode (0.4 mL min^{-1}) to produce a linear velocity of 65 cm s^{-1} at −20°C. The thermal modulator heater was maintained 100°C above the temperature of the modulation tube. The heater rotated at 0.25 rev s^{-1}

over the modulator tube to desorb trapped analyte and inject it into the second-dimension column. Second-dimension injections occurred every 2.5 s, and injected peaks were typically less than 90 ms wide at half-height. The flame ionization detector sample rate was 100 Hz.

Ignitable Liquids

Ignitable liquids were obtained from local sources: Coleman™ camp fuel, Klean Strip™ paint thinner, Parks™ lacquer thinner, and Sunnyside™ turpentine. Regular and Super reformulated gasoline samples were collected from a local Texaco service station. Weathered gasoline samples were reduced to a specific weight percent by evaporative weathering at 40°C. Gas chromatograph injections were 0.1 μL of each neat ignitable liquid with a 300:1 split.

Simulated Fire Debris

Matrix samples were produced by laboratory combustion of carpet samples. In separate experiments, three 2 in. × 2 in. squares of nylon carpet (100% continuous heatset nylon, StainMaster Xtra Life™, Dupont) and polyolefin carpet (100% olefin, Interloom™, Coronet Industries, Inc.) were placed in a 4-in.-diameter crucible and heated from below with a Meker burner for 120 s. Each sample ignited after about 60–90 s. The flames were extinguished by smothering with a metal lid. After 10 min cooling time, the crucible with the charred carpet was placed in a one-half gallon, unlined paint can. Pyrolysis volatiles were sampled with an activated carbon strip (DFLEX, Albrayco Laboratories, Inc., Cromwell, CT) for 18 h at 80°C (27,28). The carbon strips were eluted with 0.5 mL carbon disulfide. Gas chromatograph injections were 1 μL carbon disulfide solution with a 10:1 split. Simulated fire debris was produced by adding 5 μL of 75% weathered gasoline to the charred carpet immediately before placement in the paint can.

Results and Discussion

GC × GC Chromatograms and the Ordering of Chemical Components

A high resolution one-dimensional gas chromatogram of gasoline is shown in Fig. 2a. The gas chromatogram pattern of this common ignitable liquid is well known. The large peak at 20 min is MTBE. The peak at about 43 min is toluene. The group of three peaks at about 55 min are C_2-alkylbenzenes. The cluster of peaks at about 63 min are the C_3-alkybenzenes. Although the peaks in the chromatogram appear resolved, GC × GC analysis proves that there are multiple coelutions throughout. Slice A is a single second-dimension GC × GC chromatogram occurring at 31 min. The fast second-dimension separation on the polar column resolved two peaks that coeluted on the first dimension. The large peak at 1.50 s is benzene, and the small peak at 0.50 s is an unknown alkane coeluter. It is important to note that in the polarity-based separation in the second column, the nonpolar alkane components elute before the more polar aromatic components. Slice B shows three peaks. The large peak at 1.25 s is 1,3,5-trimethylbenzene, a C_3-alkylbenzene; the other two peaks at about 0.25 and 0.50 s are alkane and cycloalkane coeluters, respectively. Slice C shows three peaks. The peak at 1.75 s is a C_4-alkylbenzene isomer, and the peak at 1.25 s is a C_5-alkylbenzene isomer. The chromatographic resolution of the C_4- and C_5-alkylbenzene groups in GC × GC is important because these groups have common ions and poor resolution in GC/MS analysis (12). If second-dimension separations are per-

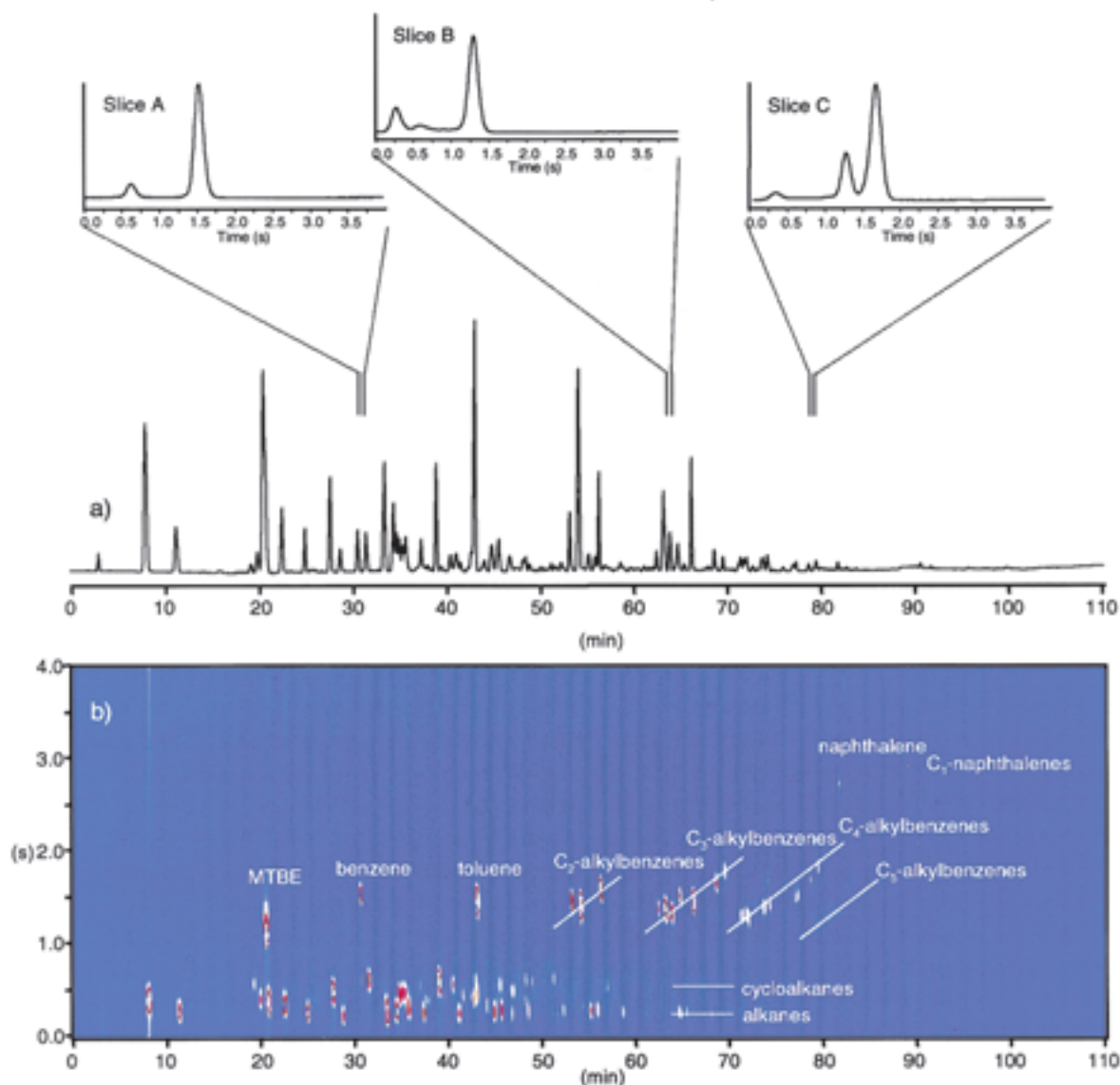FIG. 2—*a) Gas chromatogram of regular gasoline. Slices A–C are selected second-dimension chromatograms. b) GC × GC chromatogram of regular gasoline. The x-axis is retention on the nonpolar first-dimension column. The y-axis is relative retention on the polar second-dimension column. The background is blue. Small peaks are white, and larger peaks are red to dark blue.*

formed at every position in the gasoline chromatogram and displayed as a color contour plot, a GC × GC chromatogram results (Fig. 2b).

The ordering of peaks in the gasoline GC × GC chromatogram is immediately visible. The band of peaks across the bottom of the image at less than 0.50 s retention is the alkanes. The next layer of peaks between 0.5 and 1.0 s is the cycloalkanes. The MTBE peak at about 20 min on the first dimension and 1.25 s on the second dimension is labeled. All of the other peaks above 1.0 s are aromatics. The benzene, toluene, C_2-, C_3-, C_4-, and C_5-alkylbenzene isomers are grouped together in inclined bands.

One advantage of isomer grouping is that it enables rapid quantification. For example, all of the isomers in the C_3-alkylbenzene band can be integrated at once. First, an integration box containing the peaks is selected, second, the background noise is subtracted, then the remaining signal is summed (19). Integration of multiple GC × GC bands in this manner allows comparison of the relative abundance of alkybenzene classes.

In GC × GC chromatograms, the definition of alkylbenzene isomers must be expanded. For example, there are eight C_3-alkylbenzenes isomers resulting from combinations of propyl, ethyl and methyl, and trimethyl substitutions, but GC × GC also groups the compound indan with the other isomers because it has similar volatility and polarity properties. Likewise, the C_4-alkylbenzene band also contains four methylindan components and tetrahydronaphthalene. The ordering and grouping of peaks in a GC × GC chromatogram is analogous to the isolation of peaks in a GC/MS mass chromatogram. Both the mass-selectivity in GC/MS and the polarity-selectivity in GC × GC isolate specific chemical classes from the complex mixture.

GC × GC Chromatograms of Selected Ignitable Liquids

The standard approach to accelerant fingerprinting in GC or GC/MS analysis is to compare the chromatogram, total ion chromatogram, mass chromatogram, or target compound chro-

matogram of the extracted fire debris volatiles with reference data from an ignitable liquid library (5,29). We believe that this should be the fundamental approach with GC × GC data analysis as well, so GC × GC chromatograms of selected ignitable liquids from our library are presented. Gasoline, the most frequently used arson accelerant was already presented in Fig. 2b. Figure 3a is the GC × GC chromatogram of Coleman™ camp fuel. In this image, it can be readily seen that the alkane distribution for Coleman™ fuel and gasoline are similar. On the other hand, Coleman™ fuel appears to have greater cycloalkane content than gasoline. The major difference between the two is that Coleman™ fuel contains limited aromatics; only toluene and trace C_2-alkylbenzenes (xylenes) are visible. Figure 3b is the GC × GC chromatogram of Klean Strip™

paint thinner. The paint thinner is a medium petroleum distillate containing alkane, cycloalkane, and aromatic chemical classes. Figure 3c is the GC × GC chromatogram of Parks™ lacquer thinner. Lacquer thinner contains a significant toluene peak as well as several alcohols and ketones. Figure 3d is the GC × GC chromatogram of Sunnyside™ turpentine. This GC × GC image has almost no peaks in common with the other accelerants. The major peak at about 62 min is α-pinene.

The identities of major peaks in each of the GC × GC chromatograms are known by comparison with GC/MS data. Additional peaks are known by comparing the retention times on two dimensions with chemical standards. Future research by the authors will use a mass spectrometer in a GC × GC/MS system to allow
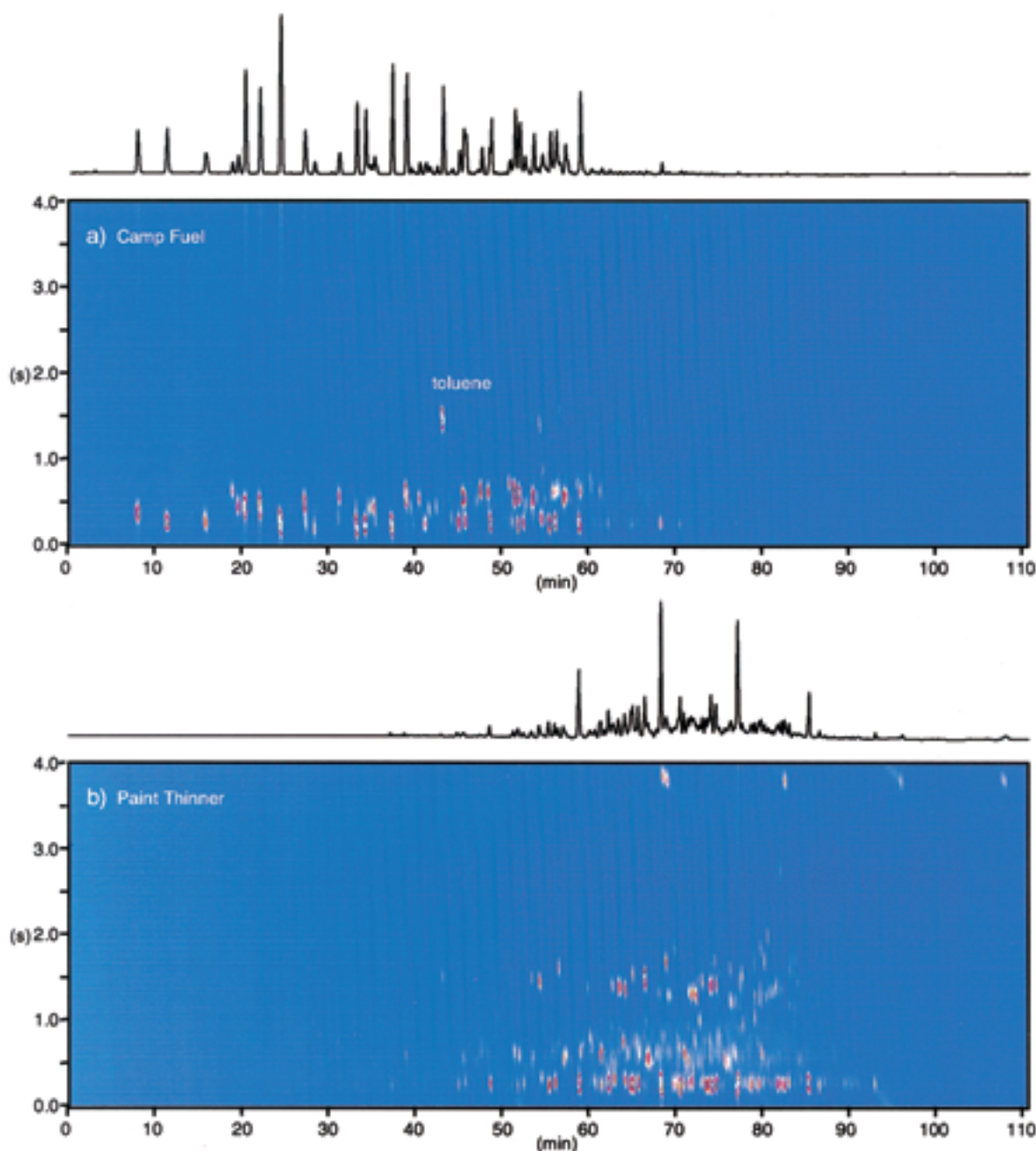

FIG. 3—*GC × GC chromatograms of a) Coleman™ camp fuel, b) Klean Strip™ paint thinner, c) Parks™ lacquer thinner, d) Sunnyside™ turpentine.*
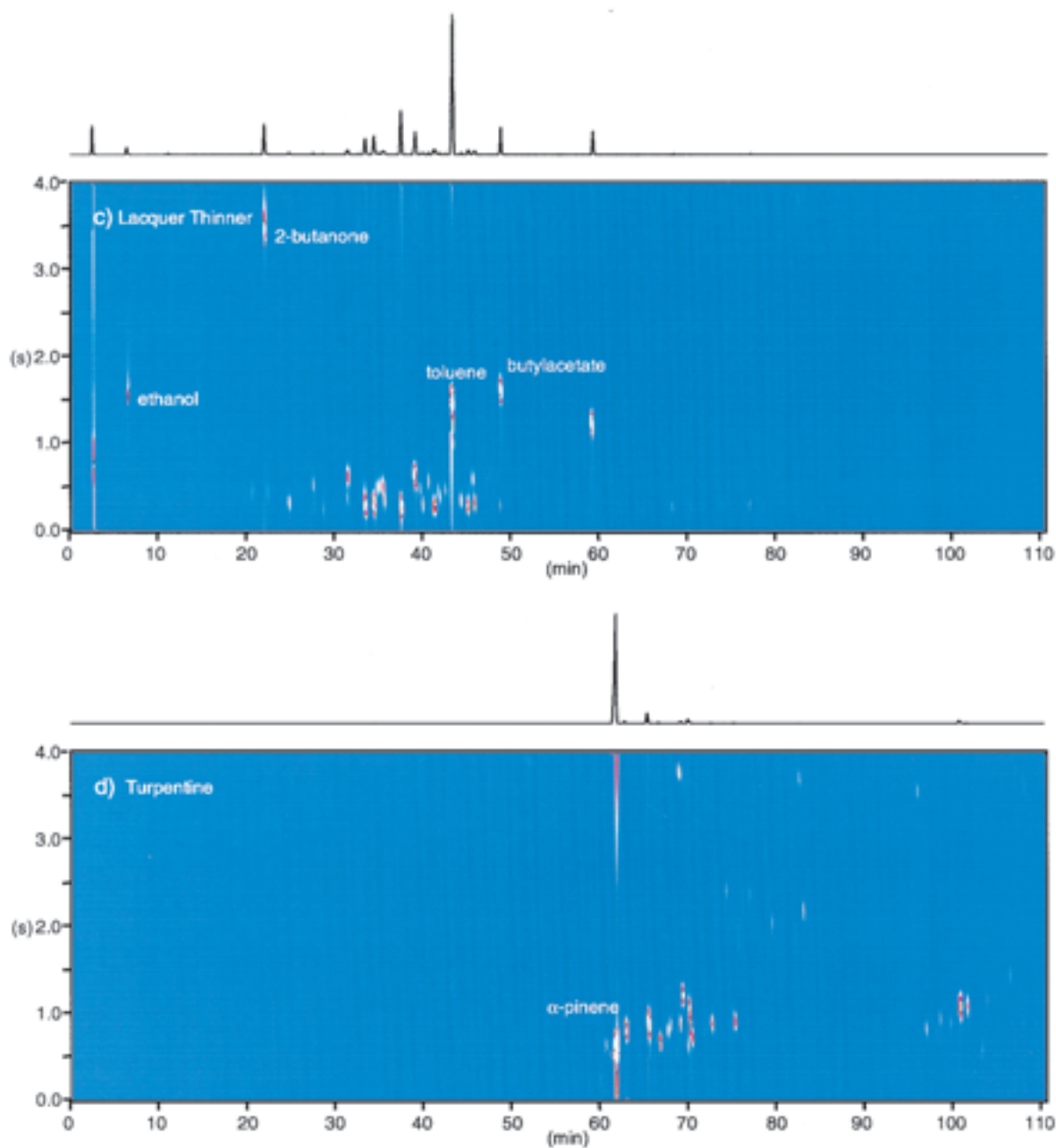
FIG. 3   *(continued)*

the identity or chemical class of every peak in the image to be known (30). GC × GC/MS technology is complicated because a fast mass spectrometer like a time-of-flight must acquire spectra at a high frequency (100 Hz) so that narrow second-dimension peaks are adequately sampled. However, once the mass spectrum of every peak is measured, it will be possible to create other GC × GC chromatogram images containing peaks possessing specific mass fragments. Selected ion GC × GC chromatograms for petroleum products have been recently published by van Deursen et al. (31).

GC × GC Chromatograms of Weathered Ignitable Liquids

GC × GC can also be used to monitor the changes in ignitable liquid composition as a result of weathering. Weathering often results from evaporation, which preferentially removes the most

volatile components. This can be seen in the GC × GC image of 75% weathered gasoline in Fig. 4a. By comparing the image with the gasoline GC × GC chromatogram in Fig. 2b, it can be seen that gasoline components more volatile than toluene are missing. The GC × GC image of 90% weathered gasoline is presented in Fig. 4b. In this case, components more volatile than the C_2-alkylbenzenes are missing. These are examples of evaporative weathering. Weathering resulting from other mechanisms like water washing may show a different chemical distribution.

GC × GC Chromatograms for Ignitable Liquid
Source Determination

Since nearly every component of an ignitable liquid is separated and displayed in the GC × GC image, it is quite easy to visually

identify similarities and differences between two samples. In Fig. 5, the GC × GC chromatograms of regular and super Texaco™ gasolines are shown. A quick inspection of the two images shows one major difference. The super gasoline GC × GC chromatogram contains a peak at about 33 min on the first dimension and 1.0 s on the second dimension that is not present for the regular gasoline. That peak is TAME (*tert*-amylmethylether), an oxygenate that is sometimes used in gasoline. This difference is significant and may be used to determine if two gasoline samples are from a common source. However, it may not be useful for fire debris analysis because after significant weathering of the gasoline, the TAME may have evaporated. It would be advantageous to find differences among the less volatile components.

To find minor differences between GC × GC images, we have employed a "blink" method where two GC × GC chromatogram images are alternately displayed on a computer screen. The chemical components that are the same in each image do not change between the images, but the components that differ blink on and off between the two images. This "blink" technique is well known in the astronomy field for finding asteroids and comets hidden in the star-filled sky (32,33).

Some minor differences between the regular and super gasoline were discovered with "blink" analysis. Figure 6 shows an extracted and enlarged section of the GC × GC image for both gasoline samples. In these images, it is clear that there are components present

in the super gasoline that are absent in the regular gasoline. We believe that these components are part of an additive package, but at present, their identities are unknown. Future work with GC × GC/MS methods will identify these peaks and may make them useful markers for differentiating gasoline types.

GC × GC Chromatograms for the Analysis of Fire Debris Pyrolysates

There is an unlimited number of materials or combination of materials that can be pyrolyzed during a fire. However, there are some materials like carpet, carpet padding, wood, vinyl flooring, plastics, and paper that are most often found in fire debris (12). Our goal was to examine the most common materials to determine what major types of pyrolysis products interfere with the identification of an ignitable liquid. For example, Fig. 7 shows GC × GC chromatograms for nylon and polyolefin carpet samples. The chemical complexity of these carpet pyrolysates and the number of peaks appearing in the GC × GC chromatograms are unequaled by any other complex sample that we have studied. There are multiple coelutions at every position in the one-dimensional gas chromatogram. Previously in the GC × GC chromatogram for gasoline (Fig. 2*b*), we resolved at most four coeluters in the second-dimension separation. For the carpet pyrolysates, up to ten coeluters are resolved in some second-dimension chromatograms. We estimate
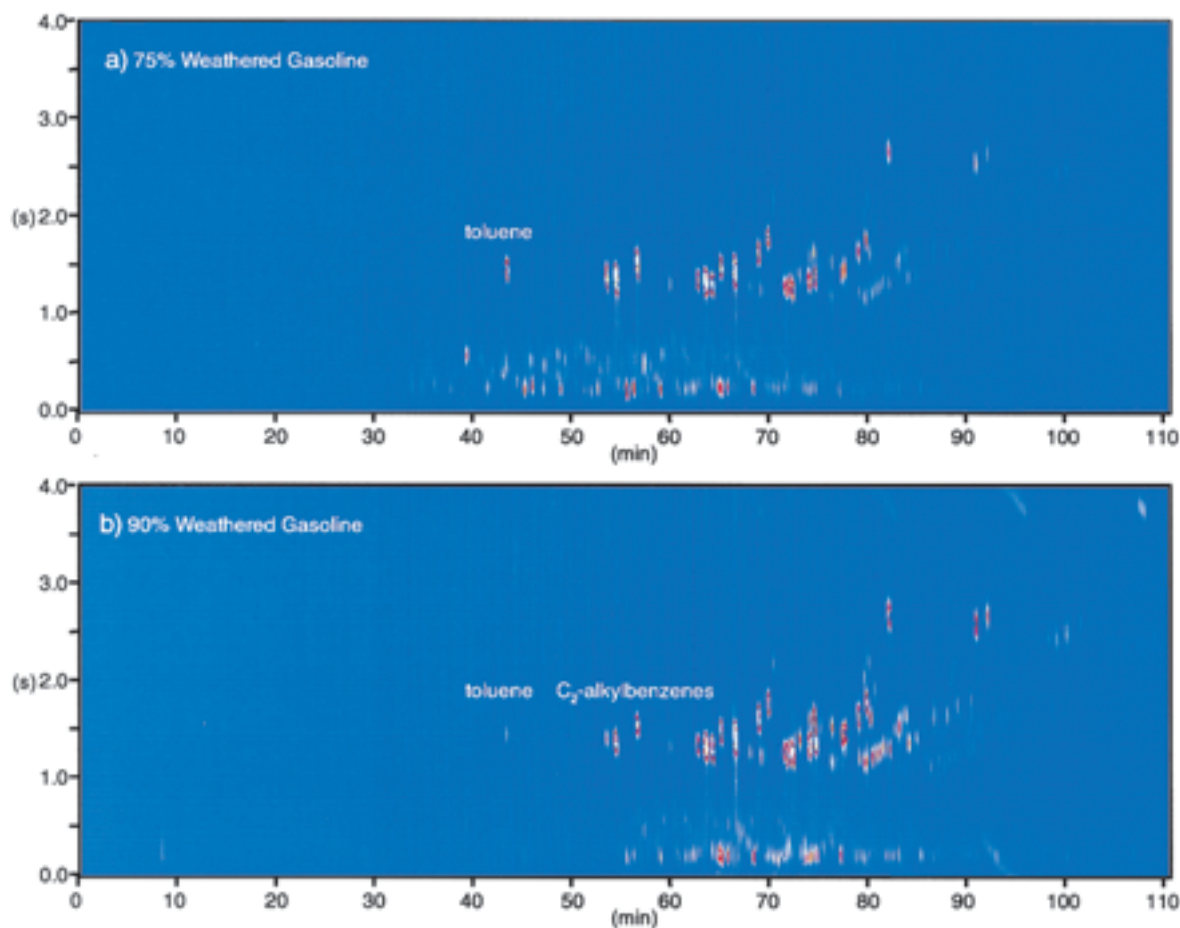

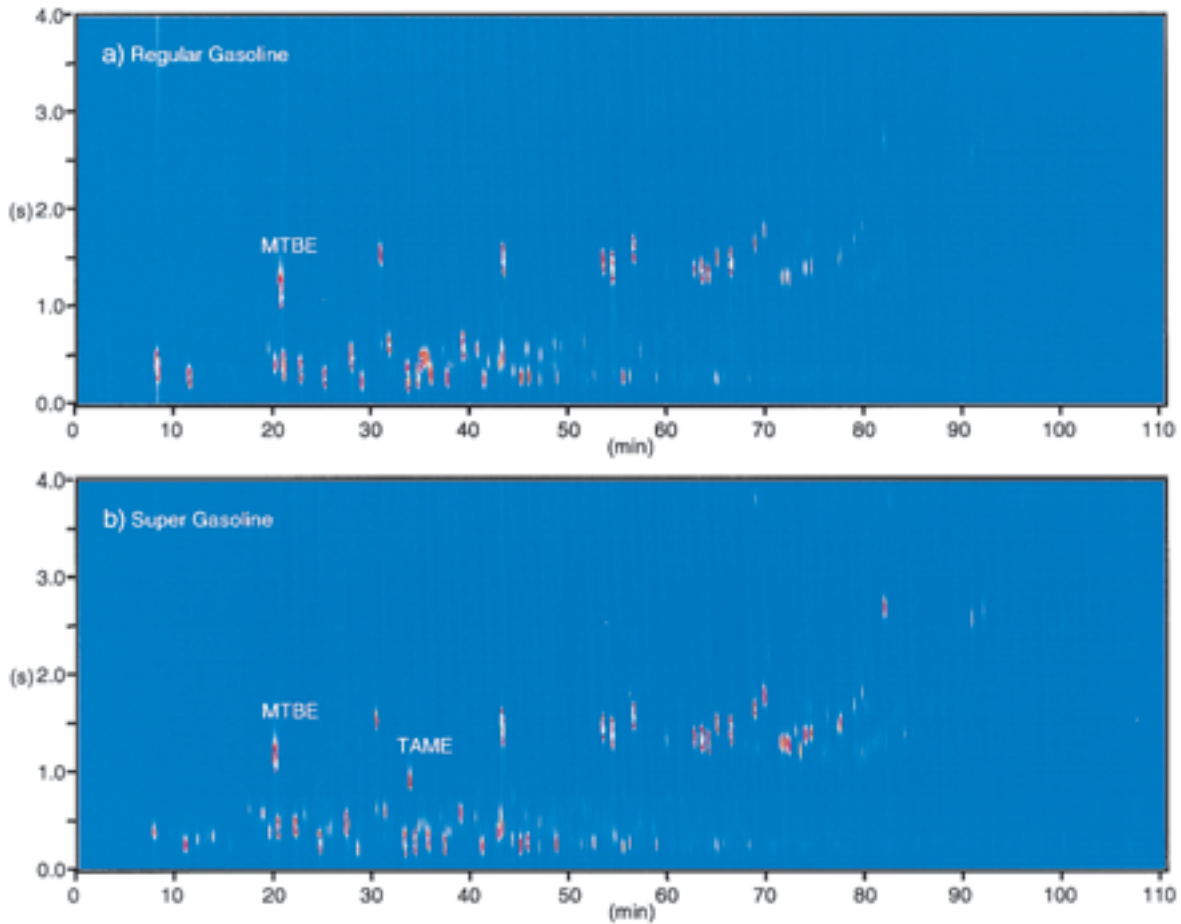FIG. 4—*GC × GC chromatograms of a) 75% weathered gasoline, b) 90% weathered gasoline.*

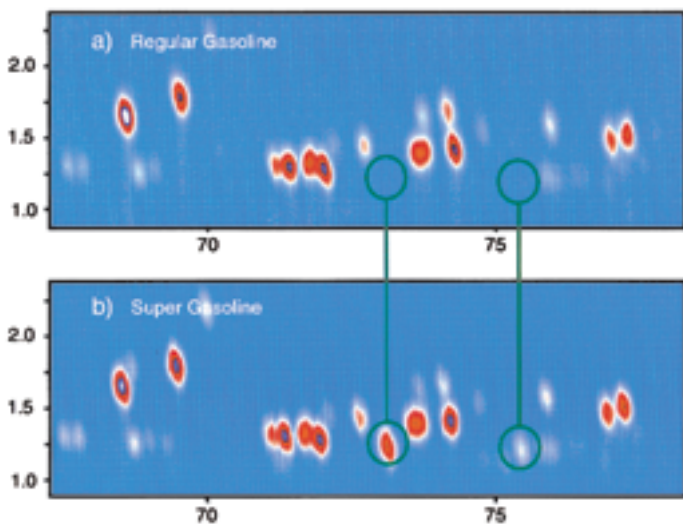FIG. 5—*GC × GC chromatogram of a) regular gasoline, b) super gasoline.*

FIG. 6—*Partial GC × GC chromatogram of a) regular gasoline, b) super gasoline. Circles indicate component differences.*

that there are over one thousand peaks in the GC × GC chromatograms for both the nylon and polyolefin pyrolysate samples.

The class distribution of chemical components is significantly different for the two different carpet samples. Of the thousands of nylon carpet pyrolysates, the most abundant peak in the GC × GC chromatogram is styrene, which appears at about 53 min on the first dimension and 1.5 s on the second dimension. The nylon carpet produced several important aromatics, including toluene, ethylbenzene, propyl, and isopropylbenzene. Alkanes and cycloalkanes, the band of peaks across the bottom of the GC × GC chromatogram at about 0.25 s retention, are few. The polyolefin carpet also had styrene as its most abundant pyrolysate. Another major peak at 50 min and 0.5 s was identified as 2,4-dimethyl-1-heptene by comparison with GC/MS data. The polyolefin also produced significant amounts of alkane and branched alkane hydrocarbons that are distributed across the bottom of the GC × GC chromatogram at about 0.25 s retention. Among the aromatics, the polyolefin carpet pyrolysis produced toluene, ethylbenzene, small amounts of each xylene, and selected C_2- and C_3-alkybenzenes.

Relatively few of the peaks in the GC × GC chromatograms of the carpet pyrolysates are known. Since many of the unknown peaks exhibit significant retention on the polar second-dimension of the GC × GC chromatogram, we expect to find many oxygen-containing components like alcohols, ketones, aldehydes, and furans, as well as nitrogen-containing components like pyridines. A mass spectrometer, or oxygen and nitrogen-selective detectors, will
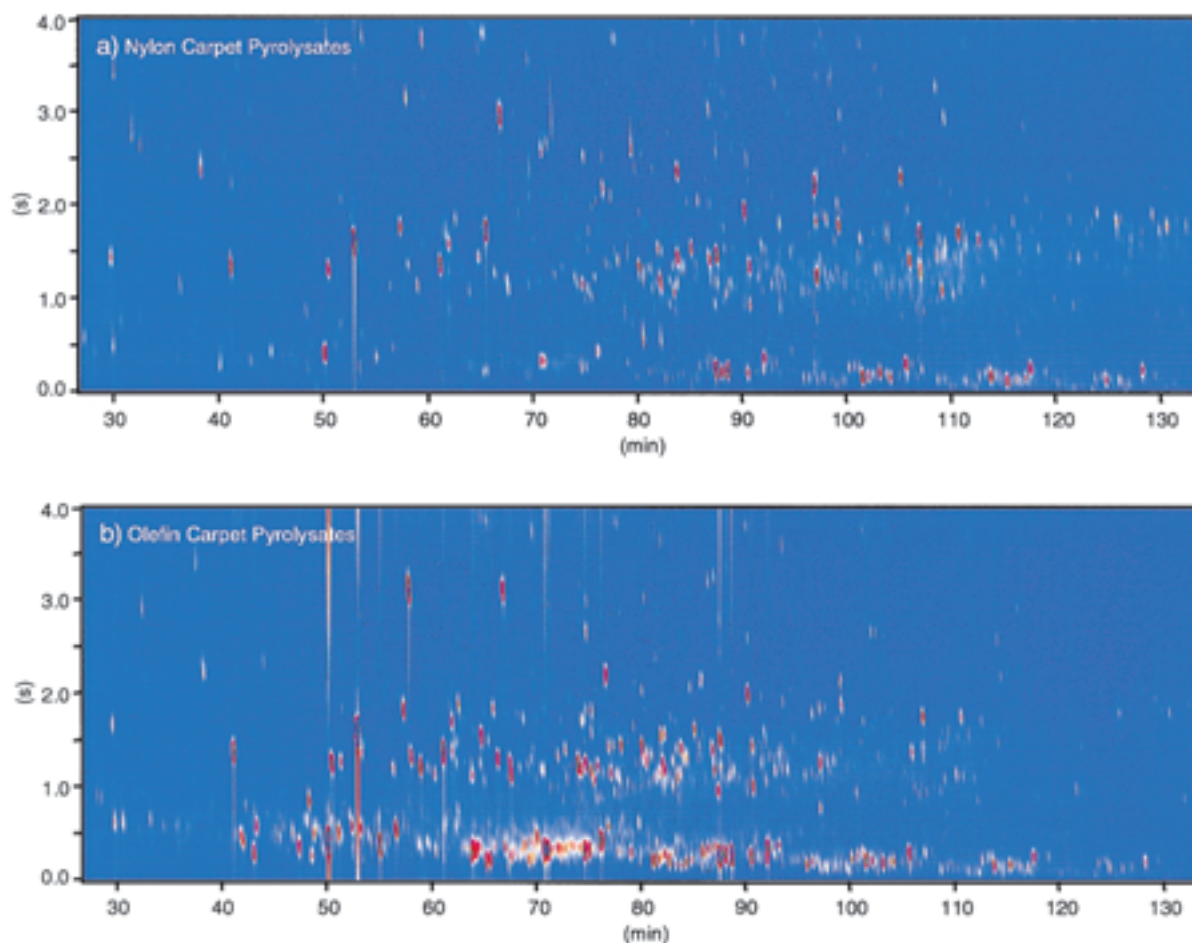
FIG. 7—*GC × GC chromatogram of a) nylon carpet pyrolysates, b) polyolefin carpet pyrolysates.*

allow a more comprehensive understanding of the pyrolysates produced.

GC × GC Chromatograms of Simulated Fire Debris Samples

The ultimate goal of GC × GC methods is to improve the detection of ignitable liquids in fire debris. For this work, we prepared simulated fire debris samples in the laboratory by combining charred carpet samples with weathered gasoline. Figure 8 shows the GC × GC chromatogram for weathered gasoline and simulated fire debris. The pattern of alkybenzenes in the weathered gasoline (Fig. 8a) can be seen on top of the complex pattern of the nylon carpet pyrolysates (Fig. 8b). If one is able to rapidly "blink" between the images on a computer screen, the peak pattern of the weathered gasoline is clearly seen in the simulated fire debris sample.

Selected regions of the GC × GC data can be enlarged and analyzed in detail to show how the weathered gasoline pattern is visible among the nylon carpet pyrolysates. Figure 9a shows the C_3-alkybenzene isomers in gasoline; the m/z 120 mass chromatogram is overlaid for comparison. The last peak in the GC × GC band is indan, which does not appear in the m/z 120 mass chromatogram. Figure 9b shows the pyrolysates from the nylon carpet. There are numerous pyrolysate peaks in the GC × GC window. The only C_3-alkybenzenes produced by nylon carpet pyrolysis were isopropyl and propylbenzene. Two peaks corresponding to isopropyl and propylbenzene appear in the m/z 120

mass chromatogram. A third peak, marked with a star, appearing in the m/z 120 mass chromatogram, is not a C_3-alkybenzene. From GC/MS analysis, we believe that this peak is 2,4,6-trimethylpyridine, which has a small m/z 120 fragment in its mass spectrum. Figure 9c shows the simulated fire debris. By comparing the three images, it is clear that the detection of every C_3-alkybenzene isomer in the fire debris is consistent with the presence of a petroleum-based ignitable liquid.

Conclusion

The application of comprehensive two-dimensional gas chromatography for the analysis of ignitable liquids in fire debris is an example of how novel methods in analytical chemistry can provide new information for challenging problems in forensic science. GC × GC offers an order of magnitude improvement in the separation of chemical components from complex fire debris samples containing both ignitable liquids and a complex background of fire debris pyrolysates. The chemical components are displayed in a multi-color two-dimensional GC × GC chromatogram image that is well suited to accelerant fingerprinting. GC × GC chromatograms were used to rapidly classify and identify ignitable liquids, detect minor differences between similar ignitable liquids, track the chemical changes associated with weathering, and detect weathered ignitable liquids in the presence of significant fire debris pyrolysate interference.
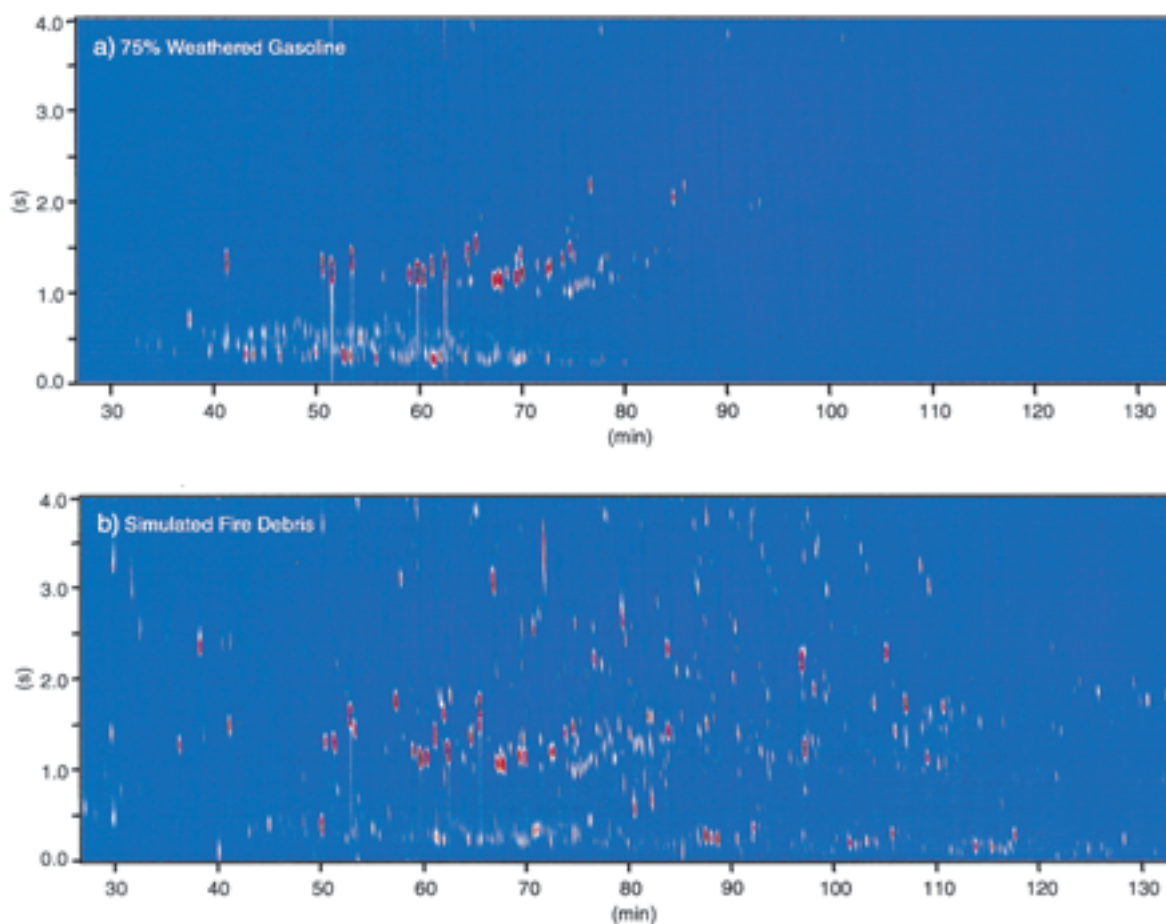
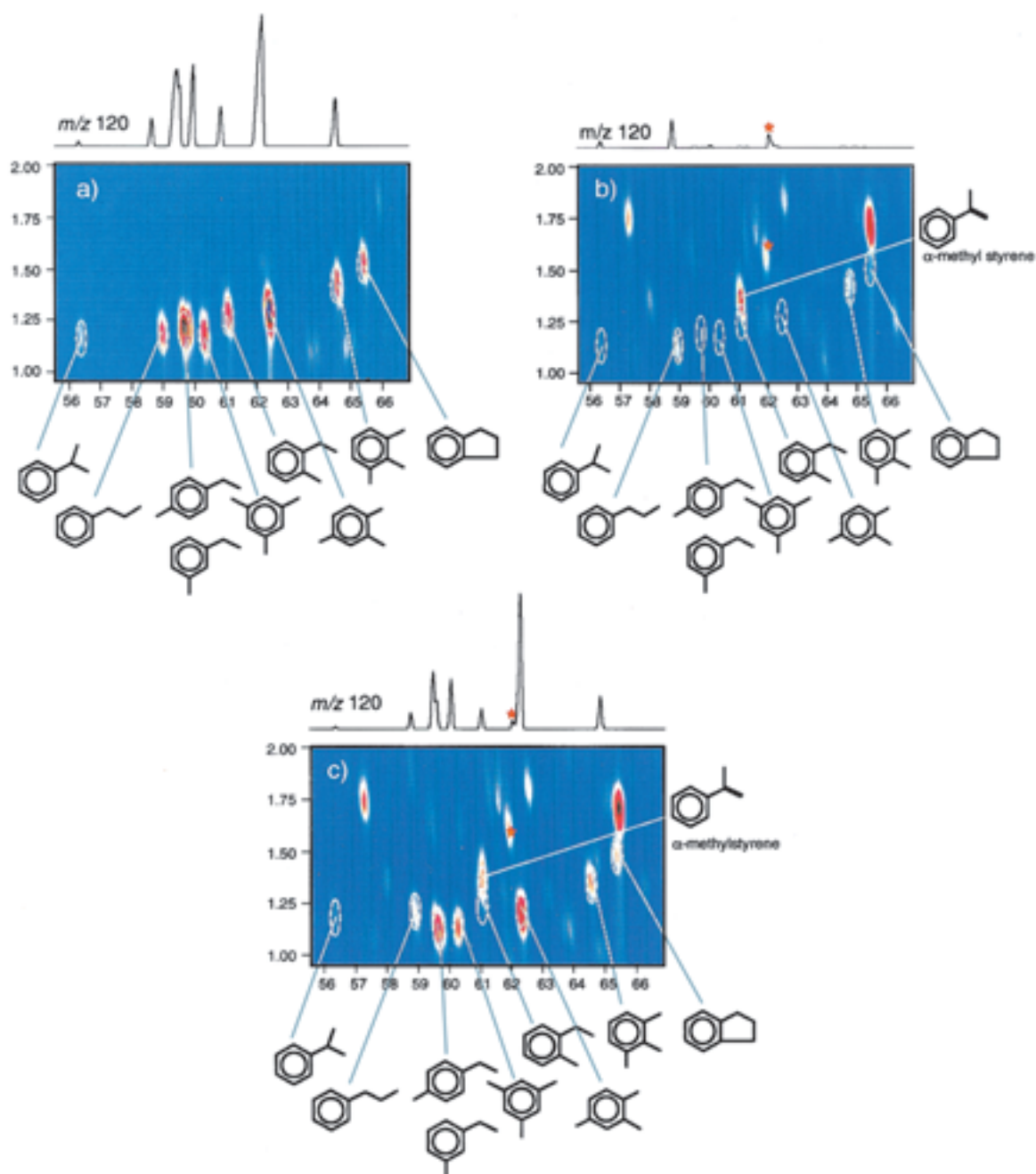FIG. 8—*GC × GC chromatograms of a) 75% weathered gasoline, b) simulated fire debris.*

FIG. 9—*Partial GC × GC chromatogram of the C$_3$-alkylbenzene region. a) 75% weathered gasoline, b) nylon carpet pyrolysates, c) simulated fire debris. Peak labeled with a star is 2,4,6-trimethylpyridine. GC/MS mass chromatograms are overlaid for comparison.*

References

1. ASTM E 1387-95: Standard test method for ignitable liquid residues in extracts from fire debris samples by gas chromatography. Annual book of ASTM standards. West Conshohocken, PA: ASTM International, 1995.
2. Bertsch W. Volatiles from carpet: a source of frequent misinterpretation in arson analysis. J Chromatogr A 1994;674:329–33.
3. Bertsch W. Chemical analysis of fire debris, was it arson? Anal Chem 1996;68:541A–5A.
4. ASTM E 1618-97: Standard guide for identification of ignitable liquid residues in extracts from fire debris samples by gas chromatography-mass spectrometry. West Conshohocken, PA: ASTM International, 1997.
5. Bertsch W, Holzer G, Sellers CS. Chemical analysis for the arson investigator and attorney. Heidelberg, Germany: Huthig, Buch Verlag, 1993.
6. Bertsch W. Analysis of accelerants in fire debris—data interpretation. Forensic Sci Rev 1997;9:1–22.
7. Smith RM. Arson analysis by mass chromatography. Anal Chem 1982; 54:1399A–1409A.
8. Koussiafes P, Bertsch W. Profile matching for the analysis of accelerants in suspected arson cases. J Chrom Sci 1993;31:137–44.
9. Keto RO, Wineman PL. Detection of petroleum-based accelerants in fire debris by target compound gas chromatography/mass spectrometry. Anal Chem 1991;63:1965–77.
10. Keto RO. GC/MS data interpretation for petroleum distillate identification in contaminated arson debris. J Forensic Sci 1995;40:412–23.
11. Lennard CJ, Tristan Rochaix V, Mergot P. A GC-MS database of target compound chromatograms for the identification of arson accelerants. Sci Justice 1995;35:19–30.
12. Bertsch W, Ren Q. The chemical analysis of fire debris for potential accelerants. In: Bogusz MJ, editor. Handbook of analytical separations, volume 2, forensic science. New York: Elsevier, 2000.
13. Lentini JL. Analytical methods for ignitable liquid residues. J Forensic Sci 2000;45:1358.
14. Jayatilaka A, Poole CF. Identification of petroleum distillates from fire debris using multidimensional gas chromatography. Chromatographia 1994;39:200–9.
15. Sutherland DA. The analysis of fire debris by GC/MS/MS. Can Soc of Forensic Sci J 1997;30:185–99.
16. Skoog DA, Holler FJ, Nieman TA. Principles of instrumental analysis. 5th ed. Orlando: Harcourt Brace & Company, 1998.
17. Rodgers RP, Blumer EN, Freitas MA, Marshall AG. Compositional analysis for identification of arson accelerants by electron ionization fourier transform ion cyclotron resonance high-resolution mass spectrometry. J Forensic Sci 2001;46:268–79.
18. Frysinger GS, Gaines RB. Determination of oxygenates in gasoline by GC × GC. J High Resol Chromatogr 2000;23:197–201.
19. Frysinger GS, Gaines RB, Ledford EB Jr. Quantitative determination of BTEX and total aromatic compounds in gasoline by comprehensive two-dimensional gas chromatography. J High Resol Chromatogr 1999;22:195–200.
20. Gaines RB, Frysinger GS, Hendrick-Smith MS, Stuart JD. Oil spill source identification by comprehensive two-dimensional gas chromatography. Environ Sci Technol 1999;33:2106–12.
21. Venkatramani CJ, Phillips JB. Comprehensive two-dimensional gas chromatography applied to the analysis of complex mixtures. J Microcol Sep 1993;5:511–6.
22. Blomberg J, Schoenmakers PJ, Beens J, Tijssen R. Comprehensive two-dimensional gas chromatography (GC × GC) and its applicability to the characterization of complex (petrochemical) mixtures. J High Resol Chromatogr 1997;20:539–44.
23. Beens J, Boelens H, Tijssen R, Blomberg J. Quantitative aspects of comprehensive two-dimensional gas chromatography (GC × GC). J High Resol Chromatogr 1998;21:47–54.
24. Beens J, Blomberg J, Schoenmakers PJ. Proper tuning of comprehensive two-dimensional gas chromatography (GC × GC) to optimize the separation of complex oil fractions. J High Resol Chromatogr 2000;23:182–8.
25. Gaines RB, Ledford EB, Stuart JD. Analysis of water samples for trace levels of oxygenate and aromatic compounds using headspace solid-phase microextraction and comprehensive two-dimensional gas chromatography. J Microcol Sep 1998;10:597–604.
26. Phillips JB, Gaines RB, Blomberg J, van der Wielen FWM, Dimandja J-M, Green V, et al. A robust thermal modulator for comprehensive two-dimensional gas chromatography. J High Resol Chromatogr 1999;22:3–10.
27. ASTM E 1412–00: Standard practice for separation of ignitable liquid residues from fire debris samples by passive headspace concentration with activated charcoal. Annual book of ASTM standards. West Conshohocken, PA: ASTM International, 2000.
28. Ren Q, Bertsch W. A comprehensive sample preparation scheme for accelerants in suspect arson cases. J Forensic Sci 1995;44:504–15.
29. Newman R, Gilbert MW, Lothridge K. GC-MS guide to ignitable liquids. New York: CRC Press, 1998.
30. Frysinger GS, Gaines RB. Comprehensive two-dimensional gas chromatography with mass spectrometric detection (GC × GC/MS) applied to the analysis of petroleum. J High Resol Chromatogr 1999;22:251–5.
31. van Deursen M, Beens J, Reijenga J, Lipman P, Cramers C. Group-type identification of oil samples using comprehensive two-dimensional gas chromatography coupled to a time-of-flight mass spectrometer (GC × GC-TOF). J High Resol Chromatogr 2000;23:507–10.
32. Murdin P, editor. Blink comparator. Encyclopedia of astronomy and astrophysics. Bristol: Institute of Physics Publishing, London: Nature Publishing Group, 2001.
33. http://www.skypub.com/sights/asteroids/hunting.html

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