Compositional Analysis for Identification of Arson Accelerants by Electron Ionization Fourier Transform Ion Cyclotron Resonance High-Resolution Mass Spectrometry*

REFERENCE: 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(2): 268–279.

ABSTRACT: Elemental compositions of each of 100 to 500 different constituents (i.e., every peak in a mass-to-charge ratio range, 50 < m/z < 300) of lighter fluid, kerosene, turpatine, gasoline, diesel fuel, and two brands of mineral spirits (and their weathered analogs) make possible direct identification of each accelerant in a experimental fire, based on electron ionization 6.0 Tesla Fourier transform ion cyclotron resonance (EI FT-ICR) ultrahigh resolution mass spectrometry. Septum injection of as little as 500 nL of accelerant into an all-glass heated inlet system yields definitive elemental compositions (molecular formulas) based on accurate (< ± 1 ppm average error) mass measurement alone. Extraction and EI FT-ICR mass analysis of fire debris from a controlled burn of a couch with simple (lighter fluid) and complex (turpatine) ignitable liquid yielded dozens of elemental compositions serving as a unique "fingerprint" for each petroleum product, despite the presence of up to 249 additional extracted matrix and pyrolysis components. Fortyfive of 56 lighter fluid constituents and 126 of 133 turpatine constituents (not counting 13C-containing species) were identified in the debris from a fire staged for each respective accelerant.

KEYWORDS: forensic science, arson, fire debris, arson accelerant, ignitable liquid, weathering, ion cyclotron resonance, Fourier transform ion cyclotron resonance, mass spectrometry, Fourier transform mass spectrometry, electron ionization, elemental composition

In 1997 the State of Florida Bureau of Fire and Arson Investigations conducted 5437 investigations (up 35% from 1994). Of those, total losses were valued at an estimated \$234,452,737 with losses from arson totaling nearly \$39 million. Furthermore, of the 148 fire-related deaths reported that year, 23% were a result of arson related fires. Incendiary related fires comprised 40% of all fire investigations and led to 751 arrests. In the same year, the State of

Received 26 Aug. 1999; and in revised form 4 Jan. and 25 April 2000; accepted 1 May 2000.

Florida Fire and Arson Laboratory analyzed 1392 fire debris cases containing over 3100 samples (1). Nationally, about one in five reported fires is of suspicious origin (2). As a result, the simple, rapid identification of ignitable liquids in suspected arson fires is crucial to the timely criminal investigation of suspected arson cases. Furthermore, new analytical techniques and sample preconcentration methods are needed to provide reliable information when traditional analysis techniques fail.

Analytical Difficulties

Gas Chromatography (GC) with Flame Ionization Detection (FID) has been used for the identification of ignitable liquids in fire debris for well over 30 years (3). It provides a simple, rapid chromatogram that may be compared to known standards to detect and identify the presence of an ignitable liquid (4). Advances in sample preconcentration methods (5), such as solid phase microextraction (6-10) and the use of activated carbon strips or coated fibers (11-15) have addressed the problems encountered with traditional solvent extraction (16) or steam distillation (17,18). However, in some cases, the presence of an ignitable liquid can neither be established nor discounted due to coeluting substances that interfere with chromatogram comparisons to standards (19). Both pyrolysis and matrix volatile organics can complicate the GC chromatogram and make detection and subsequent identification of suspected arson accelerants difficult to impossible (20-23). Another complication is microbial degradation of the ignitable liquid prior to analysis (24). Multidimensional GC (25), reverse phase liquid chromatography (26), or acid stripping (27,28) can remove or separate interfering components; however these methods cannot be used at microscale. Efforts to overcome these interferences can be difficult and time consuming, as well as unsuccessful, due to compositional overlaps between the ignitable liquid standards and pyrolysis species produced from common petroleum-based products used in building construction (26,28–30). The present method cannot distinguish an ignitable fluid component from matrix/pyrolysis components of the same elemental composition (i.e., the same molecule and/or its isomer(s)). However, that distinction does not significantly affect our ability to identify an ignitable fluid. The worst that can happen is that a few compounds from matrix/pyrolysis could add to the signal already present from the reference ignitable fluid. That won't affect our "matching" procedure, because (unlike "pattern recognition" methods) we do not rely on relative abundances of resolved peaks. Moreover, our method does resolve and eliminate

¹ National High Magnetic Field Laboratory, Florida State University, Tallahassee, FL.

² Department of Chemistry, Florida State University, Tallahassee, FL.

^{*} This work was supported by the NSF National High-Field FT-ICR Mass Spectrometry Facility (CHE-94-13008), American Chemical Society Division of Analytical Chemistry Graduate Fellowship (RPR) sponsored by the Society of Analytical Chemists of Pittsburgh, Florida State University, and the National High Magnetic Field Laboratory at Tallahassee, Florida.

all matrix/pyrolysis products whose elemental composition differs from those in the reference ignitable fluid.

Mass Spectrometry

Problems with typical GC-FID analyses stimulated the replacement of the FID with a mass spectrometer. GC-quadrupole, GC-ion trap, GC-time-of-flight, and GC-magnetic-sector instruments are currently available. GC-quadrupole mass filters are most commonly used and provide a wealth of information for ignitable liquid identification (23,31-33). However, despite its ability to greatly reduce the number and impact of both pyrolysis and matrix species, the limited mass resolving power of GC-MS typically necessitates specific data interpretation schemes optimized for specific fuel classes or specific petroleum products (21). Both target compound chromatograms (19,20,34,35) and mass chromatograms (36) have been employed for the interpretation of GC-MS data, each with its own difficulties. A target compound chromatogram, as its name implies, requires the selection of target species characteristic of the ignitable liquid under standard GC conditions; moreover the selected species must persist detectably after prolonged weathering, dilution, and/or contamination from coeluting compounds (19,35). Alternatively, as reported in the early 1990s, the requisite number of different mass chromatograms can be problematic (19,35).

Fourier transform ion cyclotron resonance mass spectrometry offers ultrahigh mass resolving power ($m/\Delta m_{50\%} > 1,000,000$ @ mass-to-charge ratio < 500 or so, where $\Delta m_{50\%}$ is the mass spectral peak full width at half-maximum peak height), high mass accuracy (to <1 ppm) and rapid analysis (<10 min) (37–43), making it an attractive alternative for the analysis of complex volatile mixtures (44). The high mass resolving power afforded by FT-ICR mass spectrometry allows for the baseline resolution of multiple species of different elemental composition at the same nominal mass (e.g., ${}^{12}C_{12}H_{23}$ vs. ${}^{12}C_{11}{}^{13}C_{1}H_{22}$, differing by just 0.0045 Da at a nominal mass of 167 Da) without prior chromatographic separation. The resolution of isobaric species combined with the subppm determination of accurate mass not only resolves multiple species at a given nominal mass, but also provides unique assignment of molecular formulas (elemental compositions) for all peaks in the mass spectrum (45,46). The elemental composition assignments constitute a molecular formula "fingerprint" of the ignitable liquids and their weathered analogs. Inter-standard presence/absence comparisons of such elemental "fingerprints" yield a set of components unique to a given ignitable liquid and its weathered analogs. In fact, as long as one can resolve and identify all of the components of a complex mixture, it is the very complexity of that mixture (i.e., the principal problem for traditional methods) that makes its "fingerprint" so specific. Here we report the first forensic application of FT-ICR mass analysis for discrimination between unweathered/weathered arson accelerants and for identification of those accelerants ignitable liquids in associated fire debris by use of a homebuilt 6.0 T FT-ICR mass spectrometer coupled to an All-Glass Heated Inlet System (AGHIS) (47).

Experimental Methods

All experiments were carried out with a homebuilt FT-ICR mass spectrometer equipped with a 15 cm horizontal bore 6 Tesla magnet (Oxford Corp.) and a MIDAS data station (48) described in more detail elsewhere (44). Briefly, the mass spectrometer features dual closed perforated cylindrical Penning ion traps (49) and is evacuated by a pair of 1500 L/s (N_2) cryopumps (CryoTorr 8, CTI Cryogenics, Mansfield, MA). The system is coupled to an All-Glass Heated Inlet System (AGHIS) (R.J. Brunfeldt Company) via a resistively heated glass transfer line (0.5 mm i.d.) containing a drawn glass conductance limit (~80 µm i.d.). The conductance limit enables moderate inlet pressures (1-500 mTorr) in the AGHIS while maintaining ultrahigh vacuum (5 \times 10⁻⁹ Torr) in the source vacuum chamber. The sample is volatilized in either a septum or ampoule inlet and passes to the source cell through a heated glass capillary terminating within a couple of inches of the dual Penning ion traps. A second conductance limit (2.5 mm) between the two Penning ion traps allows for an additional pressure drop (factor of 10–50) to 5×10^{-10} Torr for high resolution mass measurements. The current sample introduction arrangement restricts the sample vapor to an all-glass path from the septum inlet to the ICR cell and enables hydrocarbon samples to be analyzed with a minimum of fragment ions that could otherwise be produced by catalytic cracking at a hot metal surface. The AGHIS oven temperature (~250°C) and transfer lines (~200°C) are maintained at elevated temperature to ensure that the sample remains vaporized throughout the course of the analysis. The source vacuum cross was kept at ~150°C to prevent the sample vapor from condensing on the chamber walls.

Unweathered, 25, 50, and 75% weathered #2 diesel fuel, kerosene, gasoline, and mineral spirit standards were obtained from Restek Corp. (Bellefonte, PA) as neat liquids. Bulk lighter fluid, turpatine (an ASTM class 0.4 ignitable liquid and a petroleum based replacement for turpentine), mineral spirits, and paint thinner were obtained from Walmart (Tallahassee, FL) and used as unweathered standards. Weathered standards were prepared from the unweathered bulk petroleum products as follows. Aliquots of each unweathered petroleum product were transferred to glass vials and placed under a gentle stream of dry nitrogen. Percent weathering (25, 50, 75, 85, and 95%) for each petroleum product was determined by weight loss: i.e., 50%-weathered petroleum product has lost 1/2 of its initial weight by evaporative loss. Two mineral spirit samples, Restek Corp. (Bellefonte, PA) and Gillespie made by W.M. Barr and Company Inc. (Memphis, TN) were included to find out if the technique could distinguish between two different batches sold as the same commercial petroleum product.

Fire debris samples were collected from a controlled burn of a couch conducted on-site, accelerated by the addition of ~1 L of ignitable liquid. Samples were collected from the combustion of individual couch cushions and then the entire couch. A portion of the fire debris sample (~5 g) was placed in a pure cellulose extraction thimble and Soxhlet extracted in chloroform (~200 mL) for 24 h. The remaining extract was distilled over a hot plate until only ~10 mL remained. The liquid was then placed in a SpeedVac for ~1 h to remove the excess solvent and then stored at -20°C until analysis. Prior to analysis, the sample was transferred to a small glass dish where the remaining (~200 μ L) of the extraction solvent was evaporated with a dry nitrogen purge that yielded (e.g.,) a green, brownish-black solid (turpatine sample) or a brownish-yellow film (lighter fluid sample) in the sample dish. The glass dish containing the sample was placed in the ampoule inlet of the AGHIS and cooled with liquid N₂ prior to evacuation by a mechanical pump and then a diffusion pump. The liquid N₂ was then removed from the sample and the temperature of the AGHIS ampoule compartment was ramped to 250°C in ~7 min to volatilize the sample.

The FT-ICR MS experimental event sequence is described elsewhere (42). Briefly, ionization and detection were performed in separate compartments of a dual ion trap. In this way, electron ionization may be conducted efficiently at relatively high pressure in the "source" compartment, with subsequent transfer of ions to the "analyzer" compartment for high-resolution detection at much lower pressure. Specifically, the volatilized sample (1 µL injection volume for unweathered/weathered standards or the solvent extract from the fire debris) was ionized by a low-energy electron beam (18 eV and 500 ms beam duration) at a source pressure of ~5 \times 10^{-9} Torr (measured ~1 m above the source cell) before isolation in the analyzer trap (5 \times 10⁻¹⁰ Torr, measured ~1 m above the analyzer vacuum cross) for dipolar cyclotron excitation and detection. The trapping potential applied to each end cap of the analyzer cell was successively lowered from 2 V (initially, to prevent loss of translationally "hot" ions) to 0.4 V (once the ions had cooled) prior to broadband excitation (100 kHz - 1.56 MHz, sweep rate of 1 imes 10^9 Hz/s, at an amplitude of 21.3 V_{p-p}) followed by direct-mode image current detection of 2 Mword time-domain data. The timedomain data were Hanning-apodized, then padded with another 2 Mword of zeroes, and subjected to fast Fourier transform, magnitude calculation, peak location by quadratic fit to the three highestmagnitude frequency-domain data points and centroid computation for each above-threshold peak, and frequency-to-mass conversion (50) to generate a final accurate-mass m/z peak list. All observed species were singly charged (as evidenced by the absence of mass spectral peaks separated by less than 1 nominal mass unit).

The high-resolution mass spectra were further processed to yield a molecular formula for each resolved above-threshold peak in each m/z spectrum. Depending on the ignitable liquid, the analysis resulted in the resolution and assignment of 100–500 peaks in each mass spectrum (50 < m/z < 300). Molecular formulas were automatically assigned to all peaks in the peak list by use of the Molecular Formula Calculator in the MIDAS FTMS analysis software. Molecular formulas were limited to isotopic contributions from ¹²C, ¹³C, ¹H, ¹⁴N, ¹⁶O, ³²S, ³⁴S, and ³¹P.

Results and Discussion

Before analyzing specific ignitable liquids, we pause here to note two important aspects of the present approach. First, the act of assigning elemental compositions to all mass spectral peaks effectively reduces an 8 Mbyte FTMS data file to a 10 Kbyte peak list containing elemental composition and relative peak height with no loss of information. Thus, computer storage is reduced for simple, rapid, easily interpreted searches against elemental composition lists from a suspected arson debris sample. Second, the present method of comparison for ignitable liquid identification is based simply on presence or absence of reference compounds in an unknown analyte mixture. The present method does *not* rely on relative abundances of those components, and thus may be more robust than "pattern-recognition" methods, which depend on matching the relative magnitudes of (resolved but unidentified) chromatographic or spectroscopic signals.

Unweathered/Weathered Ignitable Liquid Standards

Aliquots (1 μ L) of each of the standard ignitable liquids and its weathered analog were separately injected into the septum inlet of the AGHIS, each resulting in a source base pressure of ~5 × 10⁻⁹ Torr that was stable for more than an hour. From the ultrahigh-resolution FT-ICR mass spectrum ($m/\Delta m_{50\%} \approx 100,000$), elemental compositions could be assigned for *all* of the above-threshold mass spectral peaks, with an average mass error of ±0.5 ppm. Compositional changes as a function of degree weathering are easily observed from changes in the broadband mass spectrum. Due to the compositional diversity in both the ignitable liquids proper and between different ignitable liquids, the weathering characteristics of the ignitable liquids differed slightly, but seemed to fall into one of two weathering patterns.

Ignitable liquids such as gasoline, kerosene, lighter fluid, paint thinner, and mineral spirits display similar or less compositional diversity as the degree of weathering increased. Figure 1 shows the compositional changes in gasoline as the degree of weathering increases from unweathered (top) to 75% weathered (bottom). Note that the number of mass spectral peaks decreases with increased weathering. Figure 2 shows broadband mass spectra of both unweathered and 75% weathered kerosene along with corresponding mass scale-expanded segments. The compositional diversity of kerosene is much greater than that of gasoline. From the broadband mass spectra, it is obvious that the most abundant species have shifted from $m/z \approx 130$ (unweathered kerosene) to higher mass $(m/z \approx 155)$ in the 75% weathered kerosene. Although the average m/z value increases on weathering, the compositional diversity remains about the same. Mineral spirits (Fig. 3), lighter fluid (Fig. 4, top), and paint thinner (Fig. 4, bottom) exhibit similar behavior, even after extensive weathering (95% for both lighter fluid and paint thinner). We can offer two explanations as to why the low-m/zcomponents persist even after weathering. First, for a simple mixture such as gasoline or lighter fluid, the difference in vapor pressure is not huge between the various components present. Even if there were zero difference in vapor pressure between different components, the heavier low-abundance species will soon evaporate below our detection limit, leaving more abundant (albeit lighter) components to dominate the mass spectrum. In support of that mechanism, weathering does not produce a shift on weathering to lower-m/z components for more complex fuels, for which there are many more species of comparable abundance. Second, at 18 eV incident electron energy, most of the saturated hydrocarbons will undergo some fragmentation during ionization. In a simple mixture (e.g., gasoline, lighter fluid, or jet fuel (51), composed almost entirely of saturated hydrocarbons, one would thus expect to see fewer peaks after evaporation, with little or no change in the m/zdistribution range, due to fragmentation that continues to generate lower-mass peaks.

A different weathering pattern is observed for turpatine and diesel fuel, for which the mass spectral complexity actually increases as the degree of weathering increases to 50% or more (see Figs. 5 and 6). Of course, weathering as defined here (namely, evaporative losses) cannot increase the number of species. Rather, it is that the capacity of the ion trap is finite, and the unweathered substances fill the trap primarily with lower-m/z species; as those species are preferentially lost by evaporation, the same trap can be filled primarily with higher-m/z species (some of which were below threshold in abundance initially).

Such mass spectral changes on increased weathering are potentially useful for identifying an ignitable liquid in arson debris, because the state of the ignitable liquid after prolonged burning should be similar to that from extended weathering, in the absence of matrix effects. Developing a library of weathering patterns should therefore increase the number of characteristic elemental compositions for a given ignitable liquid profile, increasing the chance of correctly identifying the ignitable liquid, even after partial combustion/evaporation.

Distinguishing Between Two Brands of the Same Ignitable Liquid

The composition of a typical ignitable liquid depends on its petroleum source as well as commercial processing. We therefore



FIG. 1—Full-range FT-ICR mass spectra of gasoline. Proceeding from top to bottom: unweathered, 25, 50, or 75%-weathered. Note the decrease in number of above-threshold peaks on increased weathering.



FIG. 2—Full-range FT-ICR mass spectra of kerosene. Top: unweathered. Bottom: 75% weathered. The insert in each case is a mass scale-expanded segment. Although the average mass shifts from \sim 135 to \sim 155 Da on weathering, the spectral complexity (i.e., compositional diversity) is relatively unchanged (see text).



FIG. 3—Full-range FT-ICR mass spectrum of Restek Corp. mineral spirits. Top: unweathered. Bottom: 75% weathered. In this case, weathering results in only minor changes in the relative abundances of mid- to high-mass species.



FIG. 4—Full-range FT-ICR mass spectrum of lighter fluid (top: unweathered and 95% weathered), and paint thinner (bottom: unweathered and 95% weathered). Here, weathering affects relative abundances but does not significantly alter the number or identity of chemical constituents.

analyzed two brands of mineral spirits to determine whether or not the present technique could distinguish between different brands of the commercial products with the same generic name. FT-ICR mass spectra of two brands (Restek and Gillespie) of mineral spirits (Fig. 7) reveal a pronounced shift to lower m/z in the m/z distribution for Gillespie mineral spirits (top) relative to that for the Restek mineral spirits sample (bottom). Based on these results for mineral spirits, we predict that it may be possible to identify an ignitable liquid (even after severe weathering) within a commercial petroleum class.

Arson Debris Analysis

Vaporization of the arson debris extracts resulted in a significantly higher base pressure (5 \times 10⁻⁸ to 1 \times 10⁻⁷ Torr) in the source vacuum cross and therefore lower (but still very high) mass resolving power (30,000 < $m/\Delta m_{50\%}$ < 50,000). One complex (turpatine) and one simple (lighter fluid) ignitable liquid were used for the arson debris test. An elemental composition could be assigned for every ignitable liquid peak in the mass spectrum at a mass accuracy of ± 1 ppm. However, it was not possible to assign an elemental composition to every matrix peak in the turpatine debris extract mass spectrum, due to large number of matrix peaks with molecular formulas that could contain elements other than those searched (C, N, O, S, P, H). In any case, those unassigned peaks do not affect identification of an ignitable liquid, because unassigned peaks are assumed to originate from the matrix or pyrolysis rather than the ignitable liquid. For example, for the turpatine debris extract ~85% of all peaks in the broadband mass spectrum could be assigned at a mass accuracy similar to that obtained for the lighter fluid debris extract, namely, ± 1 ppm.



FIG. 5—Full-range FT-ICR mass spectrum of #2 diesel fuel. Top: unweathered. Bottom: 75% weathered. The mass scale-expanded segments (200 < m/z < 300) shown above each broadband mass spectrum reveal a significant increase in the number and relative abundance of high-mass species after weathering.



FIG. 6—Full-range FT-ICR mass spectrum of turpatine. Proceeding from top to bottom: unweathered, 50, 85, or 95%-weathered. Note the significant increase in the number and relative abundance of species throughout the broadband mass spectrum after weathering.



FIG. 7—Full-range FT-ICR mass spectrum of both Gillespie (top) and Restek (bottom) mineral spirits. Note the difference in the molecular weight range for components of the two commercial brands of the same ignitable liquid. Such compositional differences, maintained even after severe weathering, promise to allow identification of the origin of an ignitable liquid.

Figure 8 shows the broadband mass spectra resulting from the vaporization (250°C) of the arson debris from the accelerated (lighter fluid) combustion of a couch. The debris extract was relatively transparent and brownish-yellow in color. Vaporization of the extraction solvent in the glass sample dish led to a light brown film on the dish along with a small amount of precipitate. As a result, few matrix peaks appear in the broadband mass spectrum. A molecular formula "fingerprint" is generated by assigning molecular formulas to all mass spectral peaks. This "fingerprint" may then be projected onto the unweathered/weathered library of standards discussed earlier. Figure 8 (bottom) shows the debris extract mass spectrum (displayed as negative peaks) lined up against the best match library spectrum, namely 85% weathered lighter fluid (displayed as positive peaks). By visual inspection alone, the two mass spectra are clearly very similar. Clinching evidence is provided by the mass scale-expanded segments (Fig. 8, top), 94 < m/z < 101. Specifically, of the 56 mass spectral peaks (elemental compositions) assigned for the 85% weathered lighter fluid standard, 45 (excluding low-abundance ¹³C-containing species) could be positively identified from the arson debris extract.

Figure 9 displays a similar match for turpatine accelerated fire debris. Figure 9 (bottom) shows the broadband mass spectrum for both the debris extract (shown as negative peaks) and the best match library spectrum, namely, 85% weathered turpatine (shown as positive peaks). In this case, the extract consisted of a browngreen black solid that most certainly is the source of the large number of matrix peaks in the broadband mass spectrum. Again, strong visual similarities between the debris extract and 85% weathered turpatine are evident from both the broadband mass spectrum (bottom) and a mass scale-expanded segment (middle). Figure 9 (top) displays the advantage and power of the high-resolution mass spectrometric technique. A mass scale-expanded segment is shown for species of $m/z \approx 139$. The ultrahigh mass resolving power and ultrahigh mass accuracy afforded by FT-ICR MS yield baseline resolution of multiple peaks at a given nominal mass, so that library comparisons may be based on actual elemental compositions. The best-match library mass spectrum (85% weathered turpatine) is shown on top (as positive peaks) along with the debris extract (negative peaks) on the bottom. Note the increase in the number and relative abundance of oxygenated species as well as a new species (m/z = 139.0541) presumably a matrix or pyrolysis product. The peak arising from two ¹³C atoms at m/z = 139.1392 drops below threshold in the debris extract mass spectrum due to a decrease in the relative abundance of its congener all-12C isotopic species as a result of either evaporative loss or combustion.

In spite of multiple peaks at a nominal mass, a correlation between the debris and library standard is possible. Of the 133 resolved peaks (elemental compositions) assigned in the 85% weathered turpatine standard, 126 (excluding ¹³C peaks) were identified and assigned in the arson debris extract mass spectrum. Moreover, the success of the match was unaffected by the presence of more than 249 *additional* matrix and pyrolysis peaks in the debris extract mass spectrum, resulting in as many as five peaks at the same nominal mass. Table 1 shows cross-comparisons for elemental compositions of each of five ignitable fluids vs. the extract from the turpatine-accelerated couch debris. It is encouraging to note that the largest fraction (95%) of elemental compositions found in both



mass scale-expanded segment

FIG. 8—Full-range FT-ICR mass spectrum (bottom) of Soxhlet extracted arson debris collected from a lighter fluid-accelerated control burn (shown as negative peaks) along with the best match from the arson standard library, namely 85% weathered lighter fluid (shown as positive peaks). Both the broadband mass spectrum (bottom) and (much more definitively) a mass scale-expanded segment (top, allowing for elemental composition identification) demonstrate an excellent match between the arson extract and a library standard.

pure ignitable liquid and couch extract is observed for the correct ignitable liquid (turpatine). However, two relatively simple ignitable fluids (lighter fluid and mineral spirits) show surprisingly high fractions of common compositions as well. That's because any matrix contributions or matrix fragmentation products from ionization will increase the number of low m/z species and therefore increase the possibility of matching to a simple standard. Thus, in actual arson situations, it will be advisable first to obtain a reference library of matrix elemental compositions, and subtract those from the list of compositions in the extract of burned material to eliminate "background" species, before trying to match the remaining compositions to a pure ignitable liquid. No matter what matching criterion is used, it is clear that the reliability of the match will increase with increasing compositional complexity of the actual accelerant.

Future Projections

The initial ignitable liquid library in the present demonstration is obviously very limited. However, because of the very large number of chemically distinct components that can be identified in fire debris, we feel safe in predicting that this method could become the most definitive means for identifying ignitable liquids with high reliability. We next plan to conduct double-blind studies of accelerated test fires conducted on-site. We shall also analyze actual case samples provided by the State of Florida Arson Investigation Lab (Tallahassee, FL). In addition, our existing inlet will be modified to improve the robustness and user friendliness of the current system. We shall also adapt the inlet to allow activated carbon strip sample preconcentration prior to introduction to the mass spectrometer.

Acknowledgments

The authors thank Daniel McIntosh for machining all of the custom parts required for the 6 T instrument construction and Randall Pelt for glasswork on the AGHIS. The authors also thank Christopher L. Hendrickson, John P. Quinn (National High Magnetic Field Lab), and Carl Chasteen and Carl Lugville (State of Florida Fire and Arson Laboratory) for many helpful discussions.



FIG. 9—Full-range FT-ICR mass spectrum (bottom) of Soxhlet extracted arson debris collected from a turpatine-accelerated control burn (shown as negative peaks) along with the best match from the arson standard library, namely, 85% weathered turpatine (shown as positive peaks). Both the broadband mass spectra (bottom) and mass scale-expanded segments (middle) illustrate good agreement between the arson extract and library standard. Clinching evidence is provided by mass scale-expended segments such as that near m/z 139 (top). The high resolution and high mass accuracy provided by FT-ICR mass spectrometry allows for peak matching against the arson library even when multiple peaks are present at a nominal mass (e.g., matrix or pyrolysis products).

TABLE 1—Number of distinct elemental compositions for various pure ignitable liquids (middle column), number of those compositions found in an extract of couch material onto which turpatine had been deposited prior to burning (left column), and fraction (in percent) of pure liquid components identified in the couch extract (right column). Elemental compositions containing ¹³C are not included in the elemental composition counts. Note that the best match is for the correct accelerant (turpatine), and that simple mixtures (lighter fluid, mineral spirits) tend to give higher percent matches than more complex mixtures (turpatine, diesel, kerosene)—see text.

| | Elemental Compositions | | |
|-------------------------|------------------------|--------|-----------------|
| Ignitable liquid | Extract | Liquid | Percent Matches |
| Turpatine | 126 | 133 | 94.7% |
| Diesel | 196 | 382 | 51.3% |
| Kerosene | 148 | 195 | 75.9% |
| Lighter fluid | 49 | 56 | 87.5% |
| Walmart mineral spirits | 60 | 75 | 80.0% |

References

- 1. Florida Department of Insurance- Treasury- and Fire Marshall Florida Fires, Division of State Fire Marshall, 1997.
- National Fire Protection Association National Fire Experience Survey, 1988.
- Lucas DM. The identification of petroleum products in forensic science by gas chromatography. J Forensic Sci 1960;5:236–47.
- Koussiafes P, Bertsch W. Profile matching for the analysis of accelerants in suspected arson cases. J Chromatogr Sci 1993;31:137–44.
- Dietz WR. Improved charcoal packaging for accelerant recovery by passive diffusion. J Forensic Sci 1991;36:11–121.
- Zhang Z, Pawliszyn J. Headspace solid-phase microextraction. Anal Chem 1993;65:1843–52.
- Newman RT, Dietz WR, Lothridge K. The use of activated charcoal strips for fire debris extractions by passive diffusion. Part 1: the effects of time, temperature, strip size, and sample concentration. J Forensic Sci 1996;41:361–70.
- Dietz WR. In combined meeting of forensic science societies; Lexington, KY, 1985.

- 9. Furton KG, Bruna J, Almirall JR. A simple, inexpensive, rapid, sensitive, and solventless technique for the analysis of accelerants in fire debris based on SPME. J High Resolution Chromatogr 1995;18:625–9.
- Steffen A, Pawliszyn J. Determination of liquid accelerants in arson suspected fire debris using headspace solid-phase microextraction. Anal Commun 1996;33:129–31.
- Twibell JD, Home JM, Smalldon KW. A splitless curie-point pyrolysis capillary inlet system for use with the adsorption wire technique of vapor analysis. Chromatographia 1981;14:366–70.
- Saferstein R, Park SA. Application of dynamic headspace analysis to laboratory and field arson investigations. J Forensic Sci 1982; 27:484–94.
- Bertsch W, Zhang QW. Sample preparation for the chemical-analysis of debris in suspect arson cases. Anal Chim Acta 1990;236:183–95.
- Bertsch W, Sellers CS. Limits in arson debris analysis by capillary column gas-chromatography mass spectrometry. J High Resolution Chromatogr 1986;9:657–61.
- Reeve V, Jeffrey J, Weihs D, Jennings W. Developments in arson analysis—a comparison of charcoal adsorption and direct headspace injection techniques using fused-silica capillary gas-chromatography. J Forensic Sci 1986;31:479–88.
- Bracket JW. Separation of flammable material of petroleum origin from evidence submitted in cases involving fire and suspected arson. J Crim Law Crim 1955;46:554.
- Clodfelter RW, Hueske EE. A comparison of decomposition products from selected burned materials with common arson accelerants. J Forensic Sci 1977;22:116.
- Hrynchuk R, Cameron R, Rogers PG. Vacuum distillation for the recovery of fire accelerants from charred debris. Can Soc Forensic Sci J 1977;10:41.
- Keto RO, Wineman PL. Detection of petroleum-based accelerants in fire debris by target compound gas chromatography/mass spectrometry. Anal Chem 1991;63:1964–71.
- Lennard CJ, Rochaix VT, Margot P, Huber KA. GC-MS database of target compound chromatograms for the identification of arson accelerants. Science and Justice 1995;35:19–30.
- 21. Smith RM. Mass chromatographic analysis of arson accelerants. J Forensic Sci 1983;28:318–29.
- Bertsch W. Volatiles from carpet: a source of frequent misinterpretation in arson analysis. J Chromatogr A 1994;674:329–33.
- Kelly RL, Martz RM. Accelerant identification in fire debris by gaschromatography-mass spectrometry techniques. J Forensic Sci 1984;29:714–22.
- Kirkbride KP, Yap SM, Andrews S, Pigou PE, Klass G, Dinan AC, Peddie FL. Microbial degradation of petroleum hydrocarbons: implications for arson residue analysis. J Forensic Sci 1992;37:1585–99.
- Jayatilaka A, Poole CF. Identification of petroleum distillates from fire debris using multidimensional gas chromatography. Chromatographia 1994;39:200–9.
- 26. Aldridge TA, Oates M. Forensic Sci Soc 1986;31:666.
- 27. Levadie B, MacAskill S. Anal Chem 1978;48:76.
- Juhala JA. Determination of fire debris vapors using an acid stripping procedure with subsequent gas chromatography and gas chromatography/mass spectrometry. Arson Analysis Newsletter 1979;3:1–19.
- Bertsch W, Sellers CS, Babin K, Holzer G. Automation in the chemical-analysis of suspect arson samples by GC MS—A systematic approach. J High Resolution Chromatogr & Chromatogr Commun 1988;11:815–9.
- Holzer G, Bertsch W. Recent advances toward the detection of accelerants in arson cases. Amer Laboratory 1988;20:15–9.
- Nowicki J. Analysis of fire debris samples by gas chromatography/mass spectrometry (GC-MS): case studies. J Forensic Sci 1991;36:1536–50.
- Nowicki IJ. An accelerant classification scheme based on analysis by gas-chromatography mass-spectrometry (GC-MS). J Forensic Sci 1990;35:1064–86.

- Holzer G, Bertsch W, Zhang QW. Design criteria of a gas chromatography-mass spectrometry based expert system for arson analysis. Anal Chim Acta 1992;259:225–35.
- Keto RO. GC/MS data interpretation for petroleum distillate identification in contaminated arson debris. J Forensic Sci 1995;40: 412–23.
- 35. Wineman PL, Keto RO. Target-compound method for the analysis of accelerant residues in fire debris. Anal Chim Acta 1994;288:97–110.
- Hites RA. Computer evaluation of continuously scanned mass spectra of gas chromatographic effluents. Anal Chem 1970;42:855–60.
- Laude DA, Stevenson E, Robinson JM. In: electrospray ionization mass spectrometry. Cole RB, editor. New York: John Wiley & Sons, Inc., 1997; 291–319.
- Amster IJ. A tutorial on Fourier transform mass spectrometry. J Mass Spectrom 1996;31:1325–37.
- Int. J. Mass Spectrom. Ion Processes 137/138: Special Issue: Fourier transform ion cyclotron resonance mass spectrometry; Marshall AG, editor. 1996, 410 pp.
- McLafferty FW. High-resolution tandem FT mass spectrometry above 10 kDa. Acc Chem Res 1994;27:379–86.
- Dienes T, Pastor S, Schürch S, Scott JR, Yao J, Cui S, Wilkins CL. Fourier transform mass spectrometry—advancing years (1992-Mid 1996). Mass Spectrom Rev 1996;15:163–211.
- Marshall AG, Hendrickson CL, Jackson GS. Fourier transform ion cyclotron resonance mass spectrometry: a primer. Mass Spectrom Rev 1998;17:1–35.
- Freiser BS. Gas phase metal ion chemistry. J Mass Spectrom 1996; 31:703–15.
- 44. Rodgers RP, White FM, McIntosh DG, Marshall AG. 5.6 Tesla Fourier transform ion cyclotron resonance mass spectrometer for analysis of volatile complex mixtures. Rev Sci Instrum 1998;69:2278–84.
- 45. Rodgers RP, White FM, Hendrickson CL, Marshall AG, Andersen KV. Resolution, elemental composition, and simultaneous monitoring by Fourier transform ion cyclotron resonance mass spectrometry of organosulfur species before and after diesel fuel processing. Anal Chem 1998;70:4743–50.
- 46. Guan S, Marshall AG, Scheppele SE. Resolution and chemical formula identification of aromatic hydrocarbons containing sulfur, nitrogen, and/or oxygen in crude oil distillates. Anal Chem 1996;68: 46–71.
- Stafford C, Morgan TD, Brunfeldt RJ. Crude oil MS (all-glass heated inlet). Int J Mass Spectrom Ion Processes 1968;1:87–92.
- Senko MW, Canterbury JD, Guan S, Marshall AG. A high-performance modular data system for FT-ICR mass spectrometry. Rapid Commun Mass Spectrom 1996;10:1839–44.
- Littlejohn DP, Ghaderi S. U.S.A. Patent No. 4,581,533, issued 8 April, 1986.
- Ledford EB Jr., Rempel DL, Gross ML. Space charge effects in Fourier transform mass spectrometry. Mass Calibration. Anal Chem 1984;56: 2744–8.
- Rodgers RP, Blumer EN, Freitas MA, Marshall AG. Jet fuel chemical composition, weathering, and identification as a contaminant at a remediation site, determined by Fourier transform ion cyclotron resonance mass spectrometry. Anal Chem 1999;71:5171–6.

Additional information and reprint requests: Alan G. Marshall Director, Ion Cyclotron Resonance Program National High Magnetic Field Laboratory Florida State University 1800 East Paul Dirac Drive Tallahassee, FL 32310 Tel: 850-644-0529 Fax: 850-644-1366 E-mail: marshall@magnet.fsu.edu