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The Incidence of Ignitable Liquid Residues in Fire Debris as Determined by a Sensitive and Comprehensive Analytical Scheme

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ABSTRACT: An overall scheme is presented for the comprehensive analysis of flammable and combustible liquid residues in fire debris, mainly utilizing passive adsorption onto Tenax TA followed by thermal desorption. Records of all suspected arson cases submitted to the author's laboratory for analysis during a 12 month period have been reviewed and results tabulated. Information included location of fire incident, type and frequency of sample exhibit items, results of analysis, and the interrelationships between each of these factors. A total of 1040 items were examined from 437 cases. Fires within residential premises and motor vehicles accounted for the largest group of exhibits submitted. Flammable or combustible liquid residues were detected in 47.4% of items, with petrol the most common ignitable liquid. As a group, fabric items, carpets, and plastics exhibited the highest incidence of flammable or combustible liquid residues, and ashen debris and soil the lowest.

KEYWORDS: forensic science, arson, flammable liquids, combustible liquids, chromatographic analysis, thermal desorption

Numerous studies have been undertaken on the methods used in the analysis of accelerant residues in fire debris samples (1–6). Comparison of these methods has also been addressed in an effort to obtain the most efficient and effective procedure (7–9). Sampling techniques include direct headspace analysis, solvent extraction, steam distillation, and adsorption/desorption methods. Each technique has its advantages and disadvantages and many laboratories use more than one method. Adsorption onto charcoal with subsequent solvent desorption is a widely used technique.

A number of studies profile the results of laboratory investigations into arson. Saferstein and Park (10) have compared the number of positive, negative, and inconclusive determinations using headspace and concentration analysis of 275 arson specimens. Bertsch et al. (11) have reported on the frequency of accelerants detected in arson and fire cases, while other work by Bertsch and Zhang (12) has detailed the composition of matrices submitted for accelerant analysis.

One of the functions of this laboratory is to examine fire debris samples and other exhibit items, submitted by police, to determine whether flammable or combustible liquids may have been used as accelerants. Offenses investigated range from suspected arson of buildings and motor vehicles to assault and murder. The methods and techniques described below have been developed over a number of years to enable a reliable, efficient and effective means of analysis to be performed on a relatively large number of items submitted for fire investigation.

The aims of this study were to present an overall scheme for the comprehensive analysis of flammable and combustible liquid residues in fire debris and to profile the results of suspected arson cases analyzed over a 12 month period. Various relationships between analytical findings, type of sample matrix, and location of fire incident are shown. The relatively large number of items examined could well reflect the overall pattern of arson cases seen in most laboratories involved in the chemical analysis of fire debris samples for flammable and combustible liquid residues.

Examination Procedure

The following analytical scheme describes the techniques used in casework for examining fire debris samples.

Headspace Analysis—A sample of the headspace vapor from the exhibit container is obtained at room temperature and injected directly into a gas chromatograph set isothermally at 50°C using a nonpolar dimethyl polysiloxane capillary column.

Passive Adsorption/Thermal Desorption

Stainless steel tubes (9 cm long by 6 mm OD) containing 100 mg Tenax TA are placed inside the sample exhibit container and placed in an oven at 60°C overnight. The tubes are allowed to cool to room temperature and transferred to an Automated Thermal Desorber (Perkin-Elmer ATD-400) connected to a gas chromatograph (Perkin-Elmer AutoSystem) equipped with a nonpolar dimethyl polysiloxane capillary column and programmed from 60°C to 315°C. This constitutes an initial screening test.

The results of the headspace analysis and the initial screening test are assessed on the basis of visual comparison of the sample chromatograms with a library of reference chromatograms for flammable and combustible liquids. Appropriate confirmatory tests are performed depending on the nature of the suspected flammable or combustible liquid.

For samples suspected of containing petroleum-based hydrocarbon products, a second passive adsorption procedure is carried out in the same manner as in the initial screening, except that samples suspected of containing higher boiling products such as kerosene and diesel fuel are heated at 90°C overnight, compared to 60°C used for petrol and mineral spirits.

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Steam Distillation—Steam distillation is carried out on those samples suspected of containing water-miscible components such as low molecular weight alcohols and some "thinners" type mixtures containing ketones, esters, and glycols. The technique is also applied to exhibits thought to contain hydrocarbon fractions of an indeterminate nature. The aqueous and nonaqueous fractions are subsequently analyzed by gas chromatography using polar (polyethylene glycol) and nonpolar (dimethyl polysiloxane) columns, respectively, under temperature program conditions.

Passive Adsorption/Solvent Elution—Unusual "thinners" type mixtures and other "unidentified" samples are further analyzed by passive adsorption onto Tenax TA which is placed in a glass dish inside the sample container which is heated in an oven at 60°C overnight for most samples. Any adsorbed vapors are then recovered by solvent elution with pentane or decane and analyzed by gas chromatography and/or gas chromatography—mass spectrometry.

Solvent Extraction—After the initial screening tests for volatile components, samples suspected of containing hydrocarbon or vegetable oils are extracted with cyclohexane and the filtered extract is evaporated on a steam bath to an oily residue which is usually identified by infrared spectroscopy. This is a useful technique for examining very small samples such as glass fragments and swabs and when examining the interior of burnt or "empty" containers. It is also applicable to the analysis of hydrocarbon oils present in "2-stroke" motor fuels.

Results and Discussion

Analytical Scheme

The analytical scheme presented here permits a comprehensive range of flammable and combustible liquid residues to be analyzed from water-soluble fractions to fresh and weathered samples of typical hydrocarbon liquid accelerants.

Passive adsorption with thermal desorption is used on most of the sample exhibit items. This method provides the most sensitive technique for detection of hydrocarbon liquids among the methods used by our laboratory. Minimum detection limits for this technique were not determined, but 1 μL of petrol or mineral spirits and 2 μL of the higher boiling fractions from kerosene to diesel fuel are readily detected when applied to filter paper contained in a 3.8 L metal can. The Perkin Elmer ATD 400 has a capacity for 50 tubes to be loaded on a carousel for automated desorption and injection onto the gas chromatograph.

Quality Control Aspects in the Adsorption/Thermal Desorption Technique

Prior to initial use and after an adsorption cycle, each of the Tenax TA tubes undergoes a cleaning procedure. A key step during this cleaning procedure involves heating for a period of 7 min at 310°C while purging with an inert gas. This removes lower molecular weight impurities and adsorbed volatiles from the tube. A high desorption efficiency is also achieved during the analysis cycle with a desorption time of 20 min also at 310°C.

Several blanks and laboratory standards are processed during each carousel run and are subjected to the same adsorption and desorption conditions as the samples. At least two standards are included in each run. One consists of a fresh sample of petrol and the other contains a mixture of 20% diesel fuel in mineral spirits. A known amount of each standard on filter paper is placed inside a clean metal can and processed as described.

The raw data generated is stored using Turbochrom 3 software developed by PE Nelson. In this way data can be evaluated and reprocessed on an individual basis or under batch processing conditions. Chromatograms are normally printed out after each sample and used for comparing peak patterns with reference chromatograms. Each carousel run is then batch reprocessed with a scaling factor adjusted to 5, (normally scaled by 1), in order to detect any mixtures of liquid accelerants with a low ratio of one of the components. This is particularly important when there is a low ratio of diesel fuel or heating oil to petrol.

Charts for each of the standards, blanks, and controls during each run are retained and checked against previous results to ensure satisfactory performance of the technique.

The laboratory maintains and updates a comprehensive library of chromatograms including flammable and combustible liquids, typical matrix materials (carpets, plastics, roofing, and floor materials), and their pyrolysis products together with simulated arson samples. The latter consist of samples obtained from the controlled burning of various materials with different liquid accelerants. This library together with the identification and classification system as described in ASTM Test Method E 1387-90 (13) is used as a guide in determining the presence of flammable or combustible liquid residues in the sample exhibit items.

Case Profiles

There were 437 cases, comprising 1040 individual items, submitted to the laboratory during the 12 month period under review. Approximately 44% of these cases contained only a single item for examination, whereas the bulk of all cases (82.1%) contained 3 or fewer items. Most of the submitted items (86%) were packaged in either unlined, metal paint cans (3.8 L) or specially laminated polyvinylidene chloride plastic bags. Glass containers were occasionally used, primarily for liquid samples.

Location

Items from residential premises (houses, flats, and units) made up the largest group (44.6%) submitted for analysis. The next highest category was motor vehicles with 17.6%. Industrial and commercial premises contributed 8.1% and 7.5% respectively, and in total, these four categories made up 77.8% of all items submitted for examination (Table 1).

TABLE 1—*Location and number of items.*

Location	Total Items	% Items
Assembly (church, civic center, etc.)	31	3.0
Commercial	78	7.5
Entertainment (club, cafe, restaurant)	50	4.8
Garage/Shed	31	3.0
Industrial	84	8.1
Motor vehicle	183	17.6
Offices	41	3.9
Personal (assault, murder, suicide)	36	3.5
Residential	464	44.6
Educational	36	3.5
Other	6	0.6
Total	1040	

TABLE 2—*Sample exhibit items.*

Sample	Total Items	% Items
Ashen debris	219	21.1
Carpet materials	158	15.2
Fabric	185	17.8
Liquid	126	12.1
Paper	58	5.6
Other	38	3.7
Plastic	35	3.4
Residues	55	5.3
Soil	110	10.6
Wood	56	5.4
Total	1040	

TABLE 4—*Number of items at selected locations containing flammable or combustible liquid residues.*

Ignitable Liquid	Residential	Motor Vehicle	Industrial	Commerical
Alcohols	7	4	5	0
Diesel fuel	1	3	4	0
Heating oil	1	1	4	0
Kerosene	15	1	4	2
Lighter fluid	1	1	0	0
Mineral spirits	16	1	0	3
Nil	272	95	45	34
Oil-hydrocarbon	1	0	2	0
Petrol	132	69	14	34
Thinners	8	0	2	1
White spirits	0	1	1	0
Mixture	10	7	3	4
Total	464	183	84	78

Sample Exhibit Type

Exhibits were classified as ashen debris where visual examination could not identify any particular matrix material, with the sample essential composed of burnt debris and ash. The term "residues" is used to describe various containers with no visible traces of liquids, glass fragments (possibly from molotov cocktails), and occasionally "gaseous" samples from the crime scene, where police suspect volatile accelerant components are present.

The major types of exhibit received were ashen debris, carpet materials, soil, liquids, and fabric materials. As a group, these represented more than 76% of all sample items examined (Table 2).

Analytical Findings

Flammable or combustible liquid residues were detected in 47.4% of the items submitted (Table 3). Petrol was the major ignitable liquid residue found, making up 68.8% of items that tested positive for the presence of flammable or combustible liquid residues. Kerosene, mineral spirits, and mixtures of two or more ignitable liquids each made up 6.3% of all positive findings. In reviewing the analytical results of 668 exhibits tested for accelerants over a seven year period, Tranthim-Fryer (7) reports 50.4% contained petrol and 28.0% kerosene.

Findings at Selected Locations

Details of the flammable or combustible liquid residues detected in residential, motor vehicles, industrial, and commercial locations are presented in Table 4. Ignitable liquid residues were found in 41.4% of items from residential premises, 46.4% of industrial sites, 48.1% of motor vehicle sample items, and 56.4% of commercial locations. Petrol was the most frequently detected ignitable liquid in each of these locations, ranging from 35.9% of positive results in industrial sites to 78.4% from motor vehicles. The nature, location, type of exhibit sample items from motor vehicle fires, together with the relative amount of petrol detected suggests that it is more likely that the high incidence of petrol arises from added accelerant rather than from the rupture of petrol tanks and associated pipes during the course of the fire with contamination of subsequent sample exhibits.

Sample Exhibits and Analytical Findings

Table 5 presents details of flammable or combustible liquid residues detected in ashen debris, carpet, liquid, soil and fabric sample items. No ignitable liquid residues were detected in 88.1% of ashen debris samples and 72.7% of soil exhibit items. The presence of large amounts of ashen debris indicates that the fire has progressed almost to completion. Any flammable or combustible liquid residues initially present would most likely have been used up, so that it is not surprising that no ignitable liquid residues were detected in most of the ashen debris samples. Petrol was found in 43.0% of carpet materials and 41.2% of liquid samples submitted and 35.1% in fabric exhibit samples. These results suggest that there is a much lower chance of

TABLE 3—*Analytical findings.*

Ignitable Liquid	Total Items	% Items
Alcohols	22	2.1
Diesel fuel	9	0.9
Heating oil	7	0.7
Kerosene	31	3.0
Lighter fluid	2	0.2
Mineral spirits	31	3.0
Nil	547	52.6
Oil-hydrocarbon	5	0.5
Petrol	339	32.6
Thinners	14	1.3
White spirits	2	0.2
Mixture	31	3.0
Total	1040	

TABLE 5—*Number of items among sample exhibits containing flammable or combustible liquid residues.*

Ignitable Liquid	Ashen Debris	Carpet	Liquid	Soil	Fabric
Alcohols	3	3	9	2	3
Diesel fuel	0	0	7	0	2
Heating oil	0	0	0	1	3
Kerosene	1	4	12	0	10
Lighter fluid	0	0	2	0	0
Mineral spirits	0	13	5	1	6
Nil	193	64	17	80	86
Oil-hydrocarbon	0	0	5	0	0
Petrol	17	68	52	22	65
Thinners	1	2	3	0	5
White spirits	0	0	1	0	1
Mixture	4	4	13	4	4
Total	219	158	126	110	185

TABLE 6—*Number of items among sample exhibits at selected locations containing flammable or combustible liquids.*

Sample Exhibit	Residential	Motor Vehicle	Commercial	Industrial
Ashen debris	6	9	3	6
Carpet	56	2	4	8
Fabric	40	22	5	4
Liquid	33	15	10	15
Paper	9	5	9	4
Other	4	6	3	0
Plastic	7	8	5	1
Residues	17	11	2	0
Soil	12	9	0	1
Wood	8	1	3	0
Total	192	88	44	39

obtaining worthwhile results from ashen debris and soil samples than from other samples.

Distribution of Flammable or Combustible Liquid Residues in Samples at Selected Locations

Table 6 shows that for residential premises, carpet materials exhibited most of the positive results (29.2%), followed by fabric materials (20.8%) and liquid samples (17.2%). For motor vehicles, flammable or combustible liquids were most frequently found in fabric material (25.0%), liquids (17.0%), and residues (12.5%). In commercial premises, liquid and paper samples gave 22.7% and 20.5% of positive results, respectively. For industrial sites 38.5% of the positive results were from liquid samples, whereas carpet materials (20.5%) and ashen debris (15.4%) made up the next highest categories.

Percentage of Sample Exhibits Containing Ignitable Liquid Residues at Selected Locations

The percentage of positive findings for flammable or combustible liquid residues in samples from residential, motor vehicles, commercial, and industrial locations is presented in Table 7.

Residential: 89.2% of liquid samples tested positive followed by residues (70.8%), paper (64.3%), and plastic materials (63.6%). Ashen debris recorded the lowest with only 7.0% of positive sample items.

TABLE 7—*Percentage of sample exhibit items containing flammable or combustible liquid residues at selected locations.*

Sample Exhibit	Residential	Motor Vehicle	Commercial	Industrial
Ashen debris	7.0	17.3	20.0	21.4
Carpet	56.0	28.6	80.0	66.7
Fabric	53.3	53.7	71.4	50.0
Liquid	89.2	75.0	76.9	93.8
Paper	64.3	50.0	90.0	80.0
Other	20.0	85.7	75.0	0.0
Plastic	63.6	88.9	100.0	50.0
Residues	70.8	73.3	66.7	0.0
Soil	21.1	47.4	0.0	20.0
Wood	20.0	33.3	50.0	0.0

Motor vehicles: plastic materials exhibited a positive result in 88.9% of items submitted, whereas liquid samples and residues recorded, 75.0% and 73.3% positive results, respectively. Ashen debris, again, had a low positive result of only 17.3%.

Commercial premises: none of the soil samples tested positive and only 20% of ashen debris items gave positive findings. Most of the other sample items had a high incidence of positive results ranging from 71.4% for fabric material to 100% for plastic materials.

Industrial sites: liquid (93.8%) and paper samples (80.0%) presented the highest number of positive results. Only 21.4% of ashen debris items tested positive for ignitable liquid residues.

Conclusions

The overall analytical scheme presented allows a comprehensive range of flammable or combustible liquid residues to be examined, including water-soluble components such as alcohols, ketones, and esters to medium and high boiling hydrocarbon fractions such as kerosene, diesel fuel, and oils.

A summary of analytical findings from 437 cases containing 1040 items is presented. Approximately 47.4% of these items tested positive with petrol being the most commonly found ignitable liquid residue. Highly absorptive materials such as carpet, fabric, and plastic items exhibited most of the positive findings for flammable or combustible liquid residues. Ashen debris and soil samples recorded only a low number of positive results reflecting limited usefulness in establishing the presence of flammable or combustible liquid residues in fire debris samples.

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