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Accelerant Detection in Fire Residues

In 1975 personnel at the Institute of Forensic Sciences realized that a full range of analytical technics was not being used in the examination of evidence from suspicious fires. Simple steam distillation was followed by infrared spectroscopic examination, but in a distressing number of cases no apparent accelerant was detected. Midkiff and Washington [1] described the use of gas-liquid chromatography (GLC) with headspace sampling, and Cain [2] followed with capillary column GLC. Later Yip and Clair [3] developed a system for identifying trace amounts of petroleum produced from fire debris. As they pointed out, the most common accelerants encountered are naphtha (C_5 to C_8 hydrocarbons), gasoline (C_5 to C_{12} hydrocarbons), and fuel oils (C_8 to C_{22} hydrocarbons). From work described in these papers, modifications suitable to available instrumentation evolved.

Sampling

Workshops were held with Dallas City and County Fire Department personnel and a sampling procedure was devised. For each sample taken at the suspected point of origin of fire, a corresponding control sample was taken nearby. All specimens were placed in 4-litre (1-gal) unused metal paint cans with lids. Analysis was conducted soon after receipt of the cans in the laboratory.

Experimental Procedure

Rather than describe the specific experimental conditions of each examination or analysis, only general technics will be discussed. Each laboratory must determine the proper, reproducible conditions suitable to available instrumentation.

A headspace sample of 50 μl is obtained after punching a hole in the lid. It is useful to heat the cans to about 70°C before sampling. The headspace gas is injected into a Finnigan Model 3100D gas chromatograph/mass spectrometer (GC/MS) with computer data system. Water is then added to the can and steam distillation performed using a modified collar and attachment which interfaces the metal can with the condenser-distillation receiver apparatus (Fig. 1); this modification was developed and described by Armstrong

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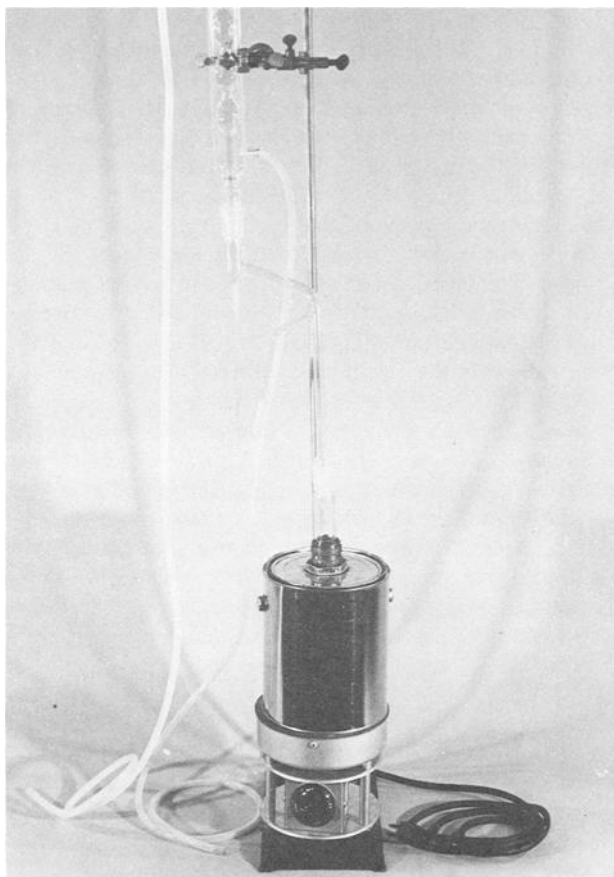
FIG. 1—*The condenser-distillation receiver apparatus interfaced with metal can used for specimen collection.*

and Wittkower [4]. Distillation time is relatively short, usually about 20 min after the first drop of distillate and no longer than 1 h. The water-immiscible layer, if present, is withdrawn by pipet and placed in a stoppered 10-ml test tube with about 50 mg of sodium chloride to remove traces of water. In some cases, analysis of the headspace gas above the distillate is then carried out with the GC/MS. A portion of the distillate is placed on salt plates or in a liquid cell for infrared spectroscopic (IR) examination.

Another portion, or the wiping from the salt plate, is used for the detection of lead and bromine. The sample is placed on a 1-cm square piece of cotton cloth. The cloth is then placed in a Nuclear Semiconductor energy-dispersive X-ray apparatus (EDX) and analyzed utilizing molybdenum-filtered radiation and a 100-s counting time in normal atmosphere. A separate piece of cotton cloth serves as the blank.

A Hitachi Perkin-Elmer Model R-24A high resolution nuclear magnetic resonance spectrometer (NMR) has been used in a number of cases. One tenth of a millilitre of distillate is mixed with deuterated chloroform and a spectrum obtained.

Results and Discussion

The analysis of the headspace gas of samples taken and preserved at fire scenes is most useful for the identification of volatile components. The limitations on these identifications

are those of mass spectrometry. For example, paraffinic hydrocarbons are difficult to identify by mass spectrometry as their mass spectra consist mostly of mass 43 and 57 peaks, resulting from propyl and butyl groups, respectively. In the absence of significant higher mass peaks, especially those of even-numbered mass units indicative molecular ions, identification of accelerants by mass spectrometry is not possible. However, samples yielding only these 43 and 57 mass peaks in any abundance generally give large steam distillates, allowing identification by other analytical methods.

Samples showing large mass 93 peaks indicate the presence of terpenes, which are normal wood components, especially in pine wood. In many cases the terpenes are a by-product of wood steam distillation. An analysis by GC/MS of the distillate can reveal the presence of diterpenes (mass 136), sesquiterpenes (mass 204), and triterpenes (mass 272), which are normally present in certain woods. However, if diterpenes occur with practically no sesquiterpene or triterpene, the possibility of the use of turpentine as an accelerant is suspected.

The accelerant most commonly found is gasoline and, in this instance, mass spectral analysis is extremely useful. The components most indicative of gasoline are the aromatic hydrocarbons that give strong molecular ions characteristic of the individual compound. These compounds can be individually identified as there are no interferences with the molecular ions from one aromatic hydrocarbon to another. For example, toluene (molecular weight = 92) gives a peak at mass 92. Xylene, the next higher homolog (molecular weight = 106), does not fragment to yield a mass 92 peak, but gives a strong mass 91 instead. Similarly, C_3 benzenes do not yield a mass 106 peak that could interfere with xylenes but do produce mass 105 peaks.

Analysis by GC/MS is also useful when lacquer thinner and other such mixtures are used as accelerants as the esters and ketones present give readily identifiable mass spectra.

The application of NMR to arson investigations has not been reported previously. The scope of the application of the NMR technic will be elementary in this report in comparison with the general advanced technics that have been reported in the literature during recent years.

For this study, however, the simplistic approach concerning only the coupling between equivalent or nearly equivalent protons was employed. The assumption of "nearly equivalent" protons identifies the simplicity of this theory. Therefore, by examining only the chemical shifts and first-order spin-spin splittings, attempts were made to compare known with unknown mixtures of hydrocarbons, such as those found in gasoline. With the nuclear environment of similar hydrocarbons being relatively the same, it was assumed that an NMR spectrum of one mixture would have a spectrum similar to another with similar components. The initial results observed were encouraging. The observed proton environments were reproducible from spectrum to spectrum of various similar mixtures of hydrocarbons. In one case an unknown was matched with a known mixture. Confirmation was made using GLC and IR data. Before any absolute and definitive statements are made on the use of NMR in cases such as this, more data must be obtained and the reliability of the technic established. Among the experiments that should be performed in this area are spin-spin decoupling of single hydrocarbons as well as mixtures of various hydrocarbons and a combination of these experiments with known hydrocarbon mixtures of various ratios. Once these data are established, it may be possible to apply more advanced NMR technics.

Recently a preliminary evaluation was reported on the use of low-resolution NMR spectrometry for the determination of the hydrogen content of aviation turbine fuels [5]. In this report, the NMR method was more precise than the American Society for Testing and Materials combustion and a microcombustion method (ASTM Specifications for Aviation Turbine Fuels, D 1655-75). No interferences of NMR were found resulting from magnetic properties of conductivity-promoting additives or iron oxide contamination. Dissolved oxygen content was also shown to have no effect.

As a result of this report, coupled with our preliminary investigation, the use of NMR in arson investigations appears to be an extremely promising approach.

Infrared spectroscopy provides valuable correlation and helps in distinguishing the aromatic hydrocarbons that absorb strongly in the 700 to 800 wave number region. Figure 2
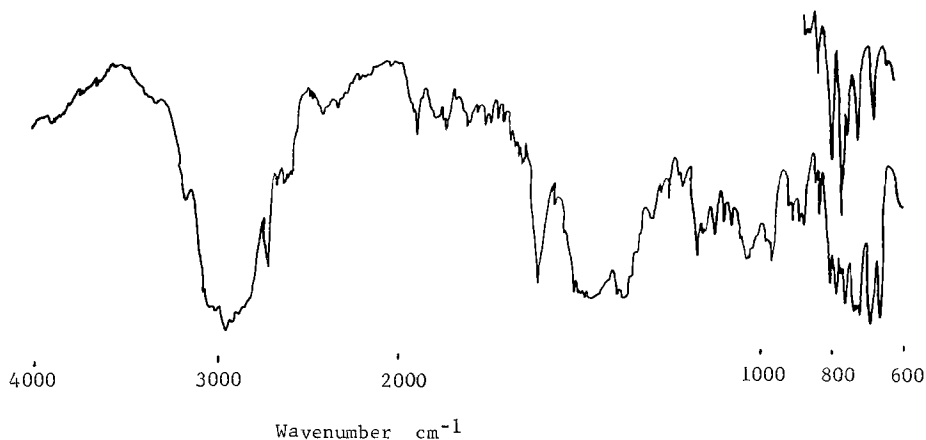

4000   3000   2000   1000   800   600

Wavenumber   cm⁻¹

FIG. 2—*Infrared spectrum of gasoline.*

is an IR spectrum of gasoline illustrating this; shown also is a partial scan in the aromatic region for an actual distillate identified as a leaded gasoline.

In addition to the aromatic hydrocarbons being an invaluable indicator of gasoline-type accelerants, the presence of lead or bromine, or both, is highly useful. Bromine has been detected in many unleaded fuels, as have lead and bromine in leaded gasolines. This is strongly supportive evidence when GC/MS and IR data indicate a gasoline. In several cases the presence of lead and bromine has aided in differentiating gasoline from the white gasolines and lantern fuels.

The GLC analysis is performed with a Perkin-Elmer Model 3920B GLC with an OV-101 capillary column. Primarily this technic is most useful in our experience for analysis of liquid samples and distillates. Headspace gas analysis is performed by GC/MS as described above. Both fresh and weathered hydrocarbons have been detected by GLC, but actual identification requires corroborating information from all of the analytical technics used. A shortcoming of GLC, in our view, is that it relies on pattern recognition and matching for identification. An extensive collection of reference samples, both aged and fresh, is necessary.

Examples

Approximately 0.2 ml of distillate was collected from a specimen taken from the scene of a fire. However, no distillate was obtained from the control sample. Figure 3 depicts the gas chromatogram of the headspace gas sample from a distillate and the molecular ion spectra for components obtained by performing a limited mass search via the dedicated minicomputer. The mass spectra show the presence of mass 120 (C_3 benzene) and 134 (C_4 benzene) as well as mass 128 (naphthalene) and 142 (methyl naphthalenes). By the use of the computer, the mass spectrum of different components within the gas chromatogram may be obtained. With this technic, positive identifications are made. The IR spectrum revealed the presence of aromatics, as illustrated in Fig. 2. The EDX analysis identified both lead and bromine, and the conclusion was that evidence of leaded gasoline was detected in the sample from the suspected point of origin.
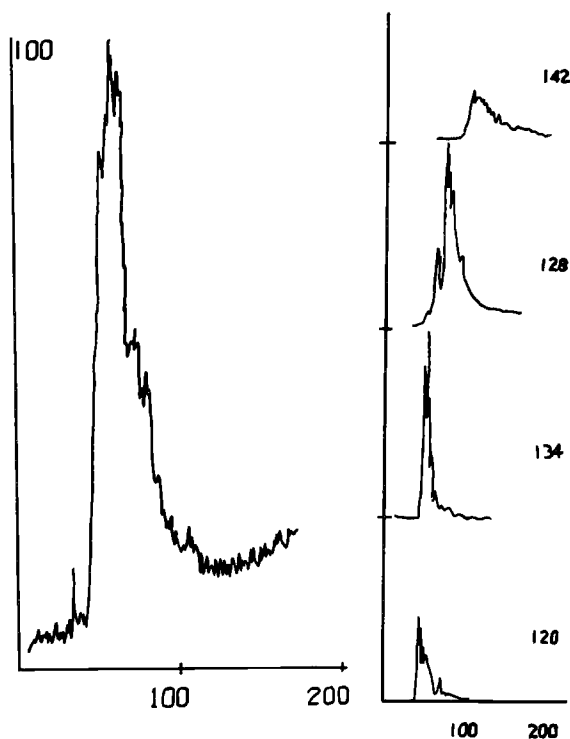
FIG. 3—*Gas chromatogram for headspace gas sample and characteristic molecular ion chromatagrams.*

In a separate case, a restaurant was destroyed and arson was suspected. Samples submitted by the fire investigators failed to reveal conclusive evidence of an accelerant, yet the investigators were adamant in their belief that arson was involved because of burn patterns. Two of the authors accompanied the investigators to the scene; this trip was made fully two weeks after the fire. Suspicious burn patterns were observed in two locations, one under a metal counter and the other at the baseboard-floor interface in another room. Analysis of the concrete floor under the counter revealed traces of lead but no water-immiscible distillate was obtained by steam distillation. Pieces of the stainless steel counter were removed, including a control; EDX showed strong lead and bromine on the underside of the shelf, but not on the top surface. The control contained no evidence of these elements. Even more striking was the analysis of the wood baseboard at the other suspected point of origin. The entire 2½ m (8 ft) of baseboard was taken, with one end being the control. Analysis by EDX revealed strong lead and bromine at the suspected point of origin, but no lead or bromine was detected in the other end of the same piece of wood. A third sample was taken from the storeroom where rice and beans were stored. Alcohol was detected by GLC, but was eventually attributed to fermentation of the wet mash.

In the third example, the odor of gasoline was suddenly encountered in the storm drains of a large downtown Dallas building. Fire inspectors sampled the drain, as well as four possible sources within one block of the building. Sufficient petroleum product was present such that about 10 ml was skimmed from the drain liquid. This material had the strong odor of gasoline but was dyed black because of organic constituents from the sewer and asphalt caulking. The GC/MS headspace gas, IR, and EDX analyses showed the presence of gasoline with no lead but significant bromine. Two of the four suspected

sources were leaded gasolines and were eliminated. Each of the other two sources were un-leaded gasoline pumps. By using the chromatography procedure described by Pearce [6] the dyes were stripped from the gasoline on an alumina column, eluted with acetone, and separated by TLC. Only one of the two sources showed the same band formation as the unknown. This information was passed on to the fire inspector. With this data in hand, the inspector determined that 760 litres (200 gal) were unaccounted for and ordered the tank unearthed for repairs.

Summary

Analysis of residues from suspicious fires can be useful only if properly located and packaged samples are obtained. We have found the following technics and instrumentation provide complementary and corroborating information:

(1) gas chromatograph/mass spectrometer analysis of headspace gas for type and distribution of hydrocarbons;

(2) infrared spectroscopic analysis of extracts and distillates for identification of hydrocarbons, especially aromatics;

(3) energy-dispersive X-ray analysis for detection of lead and bromine;

(4) gas-liquid chromatography with capillary column for hydrocarbon identification;

(5) nuclear magnetic resonance spectroscopy for aromatic/aliphatic hydrocarbon content and branching indexes; and

(6) thin layer chromatographic separation of gasoline dye components.

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