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## Analysis of Fire Debris by Nuclear Magnetic Resonance Spectroscopy

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**ABSTRACT:** This paper describes a new technique for analyzing fire debris using nuclear magnetic resonance (NMR) spectroscopy. Petroleum distillates, which are commonly used as accelerants, were weathered, burned, and steam-distilled. These, as well as virgin samples of the accelerants, were analyzed by gas chromatography and NMR spectroscopy. The use of NMR is described as a valuable adjunct to the existing methods of analysis.

**KEYWORDS:** criminalistics, accelerants, chemical analysis, fire debris, petroleum distillate, nuclear magnetic resonance spectroscopy

In today's society, arson is one of the most significant criminal problems [1]. Only limited research and development have been expended on the arson problem, its investigative techniques, and related equipment [2]. Currently, the most popular method of analysis of debris from a suspected arson case is gas chromatographic (GC) analysis [3], even though this method has several drawbacks [4]. Other methods of analysis, such as infrared spectrometric analysis, energy-dispersive X-ray analysis, and mass spectrometric analysis, have been applied to the arson problem [5], but they have limited use. The purpose of this paper is to describe the use of nuclear magnetic resonance (NMR) spectroscopy in the analysis of debris from fires of suspicious origin. This method complements the present analytical techniques and could provide a powerful analytical tool for use in fire debris analysis.

### Materials and Methods

The accelerants for this study, chosen on the basis of their frequency of use by arsonists [6],<sup>3</sup> are these:

Texaco unleaded gasoline  
Texaco leaded gasoline  
Exxon unleaded gasoline

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<sup>3</sup>Unpublished survey of arson cases from 31 July 1979 to 31 July 1980 submitted to the Dallas County Institute of Forensic Sciences.

Exxon regular gasoline  
 Shell unleaded gasoline  
 Shell leaded gasoline  
 Varsol  
 Tru-test paint thinner  
 Painter's naphtha  
 Gulf charcoal lighter fluid  
 Kerosine  
 Conoco diesel fuel

The brand names were chosen because of their availability, and they were tested to see whether brands could be distinguished with this method [3, 7]. After the accelerants were obtained they were stored in 0.9-L (1-qt) metal paint cans in a refrigerator at 2°C to reduce their volatility and to preserve their original composition [7].

Samples were taken from the stock accelerants and placed in 2-mL sample vials. In addition, 40 mL of each accelerant were evaporated to 10 mL on a hotplate at 90°C and were stored in this "weathered" condition in 2-mL sample vials.

Each accelerant was also used in an ignition study. Yellow pine two-by-fours were cut into 152-mm (6-in.) blocks, and each block was split into two pieces and identified by a scribed tack. One piece of the wood was used as a control and the other for the sample. Both sample and control pieces of wood were placed in a quart Pyrex® dish. One hundred millilitres of an accelerant were poured over the wood, and the dish was covered. The wood was allowed to soak in the accelerant for 3 min. Both pieces of wood were then removed and placed on a 230- by 230-mm (9- by 9-in.) pane of glass and allowed to dry for 1 min. Next, the control was immersed in a new gallon paint can filled with 1.9 L (½ gal) of water and sealed with a lid. The sample piece of wood was ignited with a match on the glass pane under a fume hood and allowed to burn for 1 min. The flame was extinguished with an air jet, and the sample was immersed in a similar paint can as the control and sealed. Both pieces of wood were steam distilled for 1 h as per the procedure described by Stone et al [5]. The distillate was collected, dried with sodium chloride, and placed in 2-mL sample vials.

The four samples of each accelerant, virgin, weathered, steam-distilled, and burned-steam-distilled, were analyzed by GC and with a Hitachi Perkin-Elmer R124A NMR spectrometer. Deuterated chloroform was used as a solvent, and tetramethylsilane was used as an internal standard. A study was also conducted with several NMR solvents to see whether there was any effect on the resulting spectra. The solvents used were deuterated chloroform, carbon tetrachloride, deuterated acetone, carbon disulfide, and no solvent (neat sample). In addition, analysis of 5, 3, and 2% accelerant samples was done to determine the detectability limits and effect of concentration on the analysis.

## Results and Discussion

Figure 1 shows two NMR spectra whose chemical shifts are expressed in  $\delta$  units, relative to tetramethylsilane. For accelerants, a spectrum can be divided into four major regions: aliphatic portion (A) (0 to 2 ppm), aliphatic moieties of aromatic components (B) (2 to 3 ppm), a space where no large peaks are observed (C) (3 to 6.5 ppm), and an aromatic region (D) (6.5 to 7.5 ppm). No peaks were observed farther downfield than about 7.5 ppm. In the gasoline spectrum, the peaks contained in the B and D regions are due, at least in part, to the benzene, toluene, and xylene components. These components are easily identified and are present to some extent in many accelerants. From inspection of the spectra obtained, it can be seen that the relative size and shape of the peaks in Regions B and D, compared to the size and shape of the peaks in Region A, are strongly indicative of any particular accelerant. Therefore, the accelerant can be identified by the relative sizes of the peaks. Figure 2 shows that, regardless of the condition of the accelerant, the general relative abundance of the B

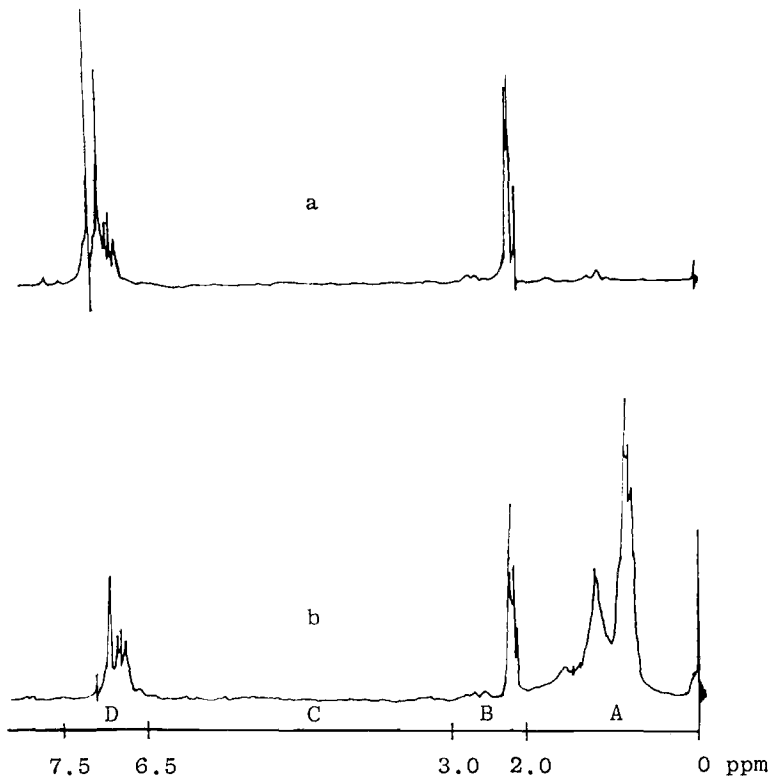


FIG. 1—Nuclear magnetic resonance spectra of (a) benzene, toluene, and xylene mixture and (b) virgin Texaco unleaded gasoline.

and D peaks remains fairly constant. Within the parameters of the study, an accelerant can be identified by NMR regardless of the condition of the accelerant. This identification is not always possible by GC analysis because burning or separating the accelerant can cause losses of components, complicating identification [4].

Figure 3 shows representative spectra of other accelerants tested. Note that each accelerant has its own unique pattern. The peak shapes and intensities of B and D vary relative to A. This unique pattern for each accelerant varies only slightly due to sample condition and brand of product, so that one is unable to distinguish between brands of a product. With the NMR technique, it is easy to distinguish between gasoline, medium-range petroleum distillates (Varsol, paint thinner, naphtha, charcoal lighter fluid), and heavy petroleum distillates (kerosine, diesel), whereas distinctions between accelerants within a class can be accomplished with a well-tuned instrument.

Figure 4 shows spectra of gasoline from two cases submitted to the laboratory. Note that (b) matches the standard gasoline spectrum nicely. The (c) spectrum sample was distilled from severely burned and dehydrated debris. Upon GC analysis, it was concluded that gasoline could be present, but there were too many interfering peaks to make a positive identification. The NMR spectrum, however, reveals the presence of gasoline in the sample. Because the NMR is not as sensitive to minute quantities of a compound as GC is, interfering substrate does not offer the problem with the NMR technique as it does with GC. In Fig. 5, the charcoal lighter fluid and kerosine spectra are from cases submitted to the laboratory. Similarities with the standards already presented are readily apparent. Spectrum c is an example of a typical nonaccelerant-type distillate obtained from a case sample. An interesting



FIG. 2.—Nuclear magnetic resonance spectra of gasoline: (a) virgin; (b) weathered; (c) steam-distilled; (d) burned-steam-distilled.

aspect of the NMR method seen here is that the peaks between 5.0 and 7.1 can be attributed to styrene, a common interfering substance.

The solvent study revealed that the solvent used has no appreciable effect on the spectrum obtained. Carbon tetrachloride can be used to obtain the same quality spectrum as the noxious-smelling carbon disulfide and the more expensive deuterated chloroform. The sample can even be analyzed without the use of a solvent (neat) in those situations where very little

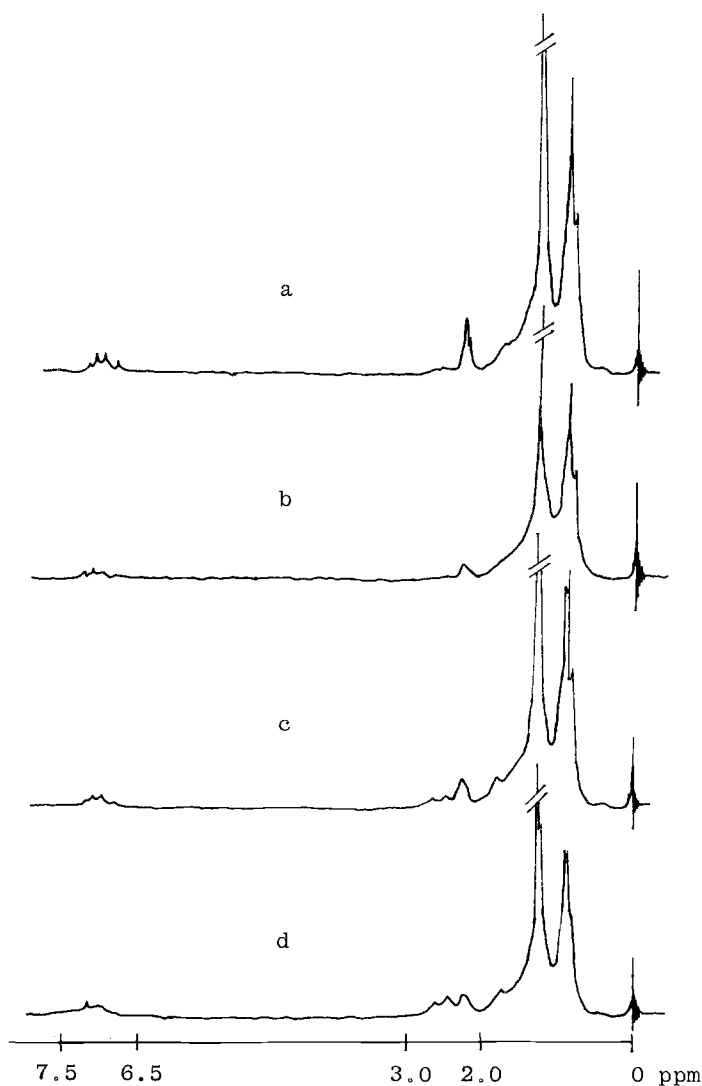


FIG. 3—Nuclear magnetic resonance spectra of (a) paint thinner, (b) charcoal lighter fluid, (c) kerosine, and (d) diesel.

distillate is obtained and further analysis is desired. The sample size required for analysis is less than 0.25 mL. The detectability study was encouraging because it showed that, in the case of gasoline, identification can be made at a 2% level of concentration (approximately 0.005 mL).

The merits of the NMR technique are significant enough to be considered by the analyst for use in cases of suspected arson. It has purposely been kept simple so that it can be easily adapted to the specific needs of the analyst. The procedure has been used by the Dallas County Forensic Laboratory in cases involving fuel contamination and gasoline seepage, as well as arson. As already seen, it aids in the identification of interfering species and is not sensitive to small amounts of interfering species, which is a major problem with present methods of analysis [4,8,9]. Another advantage of the NMR method is that spectra of stan-

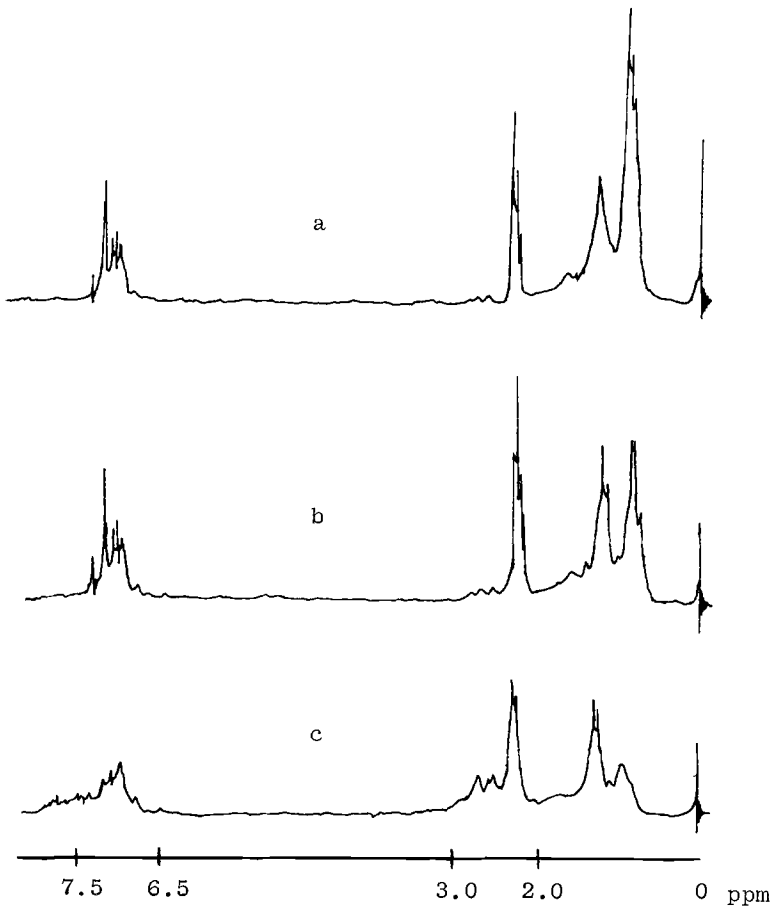


FIG. 4—Nuclear magnetic resonance spectra of (a) virgin gasoline, (b) spectrum of case sample, and (c) spectrum of case sample.

dards and samples from different laboratories are easily compared, which is not necessarily true for GC because of the diversity of columns and instrumental parameters in use today [10].

The method suggested in this paper represents an unconventional use of NMR spectroscopy. This can be partially attributed to the composition of accelerants, which are sometimes mixtures of hundreds of components [11]. This makes peak-splitting studies ineffective. Integration is also ineffective because of the change of peaks that occur as a result of evaporation, weathering, and distillation. More elaborate NMR techniques could have been studied, but looking for peaks in specific regions of the spectrum and comparing their relative intensities to other peaks should yield an easy, quick, and specific analysis with the advantage of simplicity.

Two drawbacks were discovered with the procedure. As previously reported, NMR is less sensitive than GC, which could present a problem if only a minute concentration of accelerant is present in the sample. Also, separation of the accelerant from the burned debris is a necessary prerequisite to analysis.

In conclusion, the use of NMR spectroscopy will provide the arson analyst with a powerful analytical tool that can be used to complement existing methods of analysis.

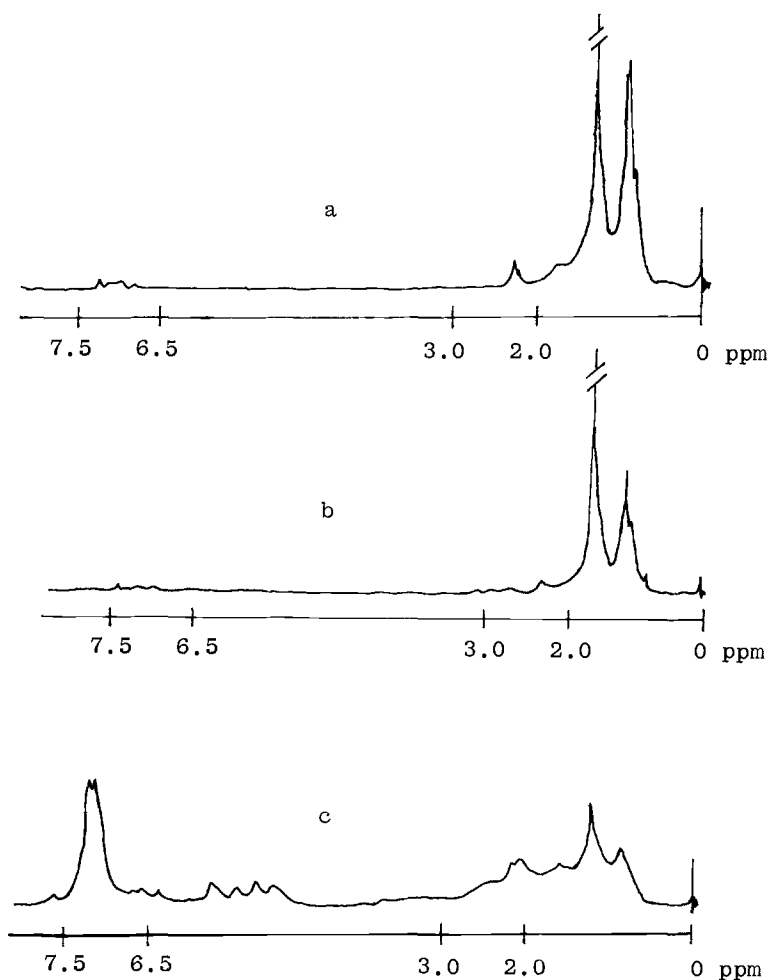


FIG. 5—Case spectra identified as (a) charcoal lighter fluid, (b) kerosine, and (c) nonaccelerant material containing styrene.

### Summary

A coordinated technique for the analysis of debris from fires of suspicious origin is reported using NMR spectroscopy. Virgin, weathered, steam-distilled, and burned-steam-distilled samples of common accelerants are analyzed by NMR spectroscopy, and the resulting spectra are identified by the presence of certain peaks and their relative intensities. The results are significant enough to warrant the use of this method by analysts in cases of suspected arson.

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