

TECHNICAL NOTE

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High-Speed Extraction of Accelerants from Arson Debris

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ABSTRACT: Since the early 1960s, gas chromatography has been used as a means of determining the presence of hydrocarbons in fire residues. Recently, the sensitivity of headspace analysis of the vapors over samples which are contained in metal paint cans and heated to 90°C in a conventional oven has been improved with the use of a charcoal-adsorption tube fitted to a vacuum system. However, the use of paint cans for the collection of samples in the field by the investigator has caused both numerous transportation and storage problems and the loss of valuable laboratory time, which varies from 1 to 3 h, in the analysis of these samples. This paper discusses the replacement of the conventional, convection oven with the microwave oven for sample heating and thereby also the replacement of metal paint cans with polyester bags for sample storage and collection in order to effect minimal laboratory analysis time and to increase the subsequent sensitivity of the accelerant vapor collection.

KEYWORDS: criminalistics, arson, accelerants, vapors

The crime of arson has been notably difficult to prove and even more difficult in which to obtain a conviction. Definite proof of an accelerant in the fire debris helps to establish the fact that arson has been committed. In the criminal investigation of arson, it is well recognized that the most commonly found accelerants are liquid hydrocarbons [1]. Since the early 1960s, gas chromatography has been used as a means of determining the presence of hydrocarbons in fire residues [2]. Laboratory analysis of fire debris samples relies on the assumption that traces of the original flammable liquid remain after the fire. In analyzing for this residue, the headspace over samples, taken and preserved at fire scenes, is most useful for the identification of the volatile hydrocarbon components.

Numerous methods are available for the recovery of trace quantities of flammable acceler-

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ants from arson debris. Of these, four basic methods are generally applied and have been found to be adequate in the majority of the cases encountered by the forensic chemist [1]. These include gas chromatographic examination of a sample of pure liquid, steam-distillation, solvent-wash techniques, and gas chromatographic examination of headspace above a heated specimen.

The sensitivity of the latter method has been increased by placing samples, contained in a metal paint can, into a preheated convection oven (90°C) while drawing a vacuum through an activated charcoal tube⁴ [3-5] which has been attached to the lid of the can. The time of heating is dependent upon the size and fullness of the container, and varies anywhere from 30 min to 2 h. Thus, a total analysis time exceeding 2½ h is conceivable.

In addition to the great deal of analysis time associated with the traditional charcoal tube adsorption technique is the difficulty and inconvenience that cans may impose on the investigator. The need for a variety of can capacities and the resulting bulk may limit the investigator's effectiveness, especially if he uses air travel as a means of transportation from case to case.

The purpose of this research was thus proposed to address both of these problems, namely, the collection and storage of samples before submission and the subsequent high-speed laboratory analysis with minimum sample handling. With this criteria in mind, polyester bags of varying capacities were chosen for the collection and storage of samples from arson scenes and the microwave oven was chosen for the purpose of heating the samples at a relatively high speed. The bulk of this research came about as a result of a study to determine if polyester bags⁵ might prove to be viable substitutes for the metal paint cans used for arson sample collection. To assess this, a number of tests were performed.

Experimental Procedure

The first study performed focused on the loss of packaged accelerants versus time. This test was accomplished by taking 150 mL of fresh gasoline and sealing it within one of the polyester bags (0.102 mm [4 mils] thick). The bag was then placed within a clean, 0.95-L (1-qt) metal paint can. The can was stored at ambient temperature and its inner atmosphere was tested with a Laboratory Instrumentation Services (L.I.S.) Combustible Gas Detector⁶ every week (the probe being introduced through 6.35-mm [¼-in.] hole that had been drilled in the cover and subsequently plugged). A time span of over four months passed before the L.I.S. Combustible Gas Detector (sensitivity 0.1 ppm) registered a reading of 50 ppm, thus indicating that the polyester bags could definitely serve as potential replacements for metal paint cans in reference to arson sample storage prior to laboratory analysis. Further testing is still being conducted in this area.

A second test involved heating the polyester bags in a metal paint can to 90°C for 4 h and subjecting the headspace to chromatographic analysis to determine if the bags themselves would contribute extraneous, unwanted peaks in the resultant chromatogram. Headspace analyses were performed in the exact manner that a normal arson sample would be examined. Results (Fig. 1) indicate that the bags did not release extraneous products associated with pyrolysis or chemical breakdown at normal attenuations, that is, 32 × 100, under our operating parameters, which include the use of a photoionization detector. It is important to state here that one of the most significant characteristics of the HNU photoionization detector⁷ is its sensitivity. The lower limits of detection for organics are 10 to 100 times better than those of a flame ionization detector [6].

⁴Commercially available through SKC Inc., R.D. 1, 395 Valley View Rd., Eighty-four, PA 15330, Catalog No. 226-09.

⁵Supplied from Kapak Corp., 9809 Logan Ave., S. Bloomington, MN 55431.

⁶Laboratory Instrumentation Services, 46 Clayton St., Boston, MA 02122.

⁷HNU Systems, Inc., 30 Ossipee Rd., Newton, MA 02164.



FIG. 1—Kapak/Scotchpak polyester pouch heated 4 h in metal can (convection oven, attenuation 32×100).

As an approach to decreasing analysis time as well as eliminating the need to transfer samples from polyester bags to paint cans, the use of a microwave oven was proposed. A series of tests were conducted to compare the amount of time required to bring identical samples to 90°C using microwave and convection heating techniques. For the convection study, this involved filling a 0.95-L (1-qt) metal container with firmly packed sand, which had been saturated with water, and placing it in a convection oven that had been preheated to 90°C . The temperature of the sand was monitored over a period of time (Fig. 2) with a standard laboratory thermometer which had been placed into the can through a hole drilled in the cover and secured so that the tip of the thermometer was located in the center of the sand. Substituting a plastic quart container for the metal one and using the same quantity of sand saturated with water, the procedure was repeated with the microwave oven. The temperature in this case was monitored with the food sensor probe used in microwave cooking (Fig. 3). Results indicate a 50-fold decrease in the amount of time required to bring the sand to 90°C in the microwave as compared to the convection oven.

The last test to be performed was designed to compare the extraction efficiencies of the two heating techniques. Equal pieces of unburned carpeting material were spiked with $10 \mu\text{L}$ of dodecane. Dodecane was chosen as the hydrocarbon used in this portion of the testing both because it does not readily volatilize at room temperature and also because of its retention time under the gas chromatographic operating conditions used in this study. Dodecane's retention time of 20.8 min (Fig. 4) represents an approximate center of most of the common gas chromatographic patterns associated with residues of petroleum distillates found in arson samples. One piece of carpeting material was sealed in a Kapak polyester bag along with 50 mL of distilled water, the other was placed in a quart, metal paint can along with 50 mL of distilled water. The polyester bag was placed in a Litton Model 540 microwave oven and a 3.175-mm ($1/8$ -in.) diameter Teflon[®] tube (which is discarded after each extraction to avoid the possibility of contamination) was inserted into the bag through a small hole. At the point of insertion, a simple sponge clamp (Fig. 5) was used to seal the small hole. The Teflon tubing was passed through the side of the microwave oven through a hole drilled in its side (Fig. 6) and connected to a charcoal sample tube through which a vacuum was drawn (Fig. 7). To avoid any of the dangers associated with the leakage of microwaves through this hole which had been drilled in the side of the oven, the following measures were taken: (1) the location was selected in an area where there is an insignificant level of microwave energy; (2) there are two metal walls (inside and outside) that inhibit any angular radiation from penetrating the walls; (3) an aluminum foil shield was wrapped around the Teflon tubing; and, (4) a monitor was placed at the port and no external radiation was detected. The bag was heated for a total of 10 min (1 min on high power, 9 min on 20% power) while changing the charcoal sample

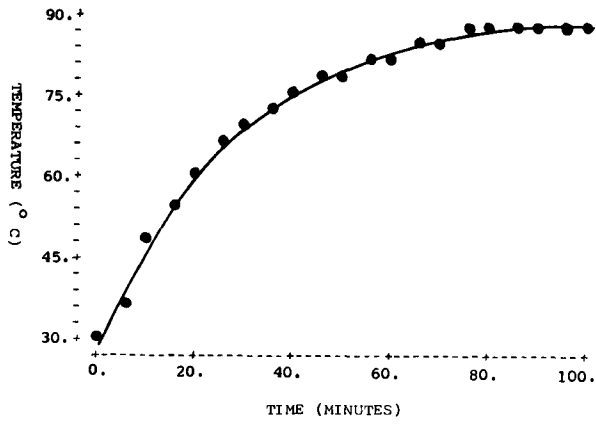


FIG. 2—A container, 0.95 L (1 qt), of moistened sand heated in convection oven.

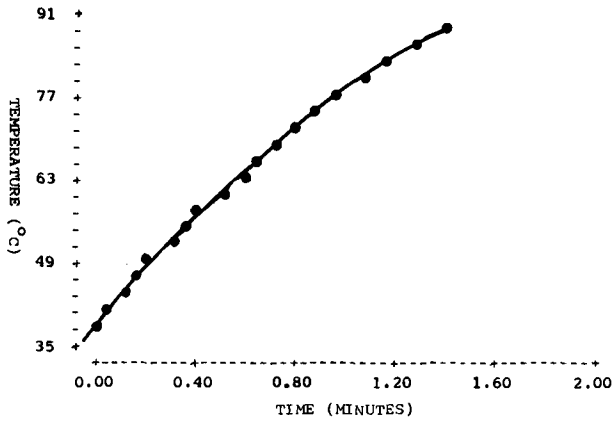


FIG. 3—A container, 0.95 L (1 qt) of moistened sand heated in microwave oven.

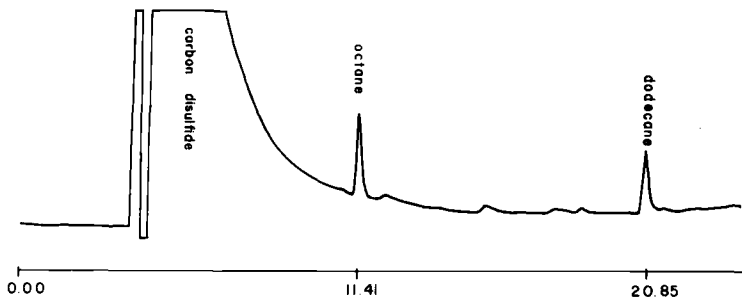


FIG. 4—Fifth-minute fraction of microwave oven extraction technique, 32 × 100 attenuation.

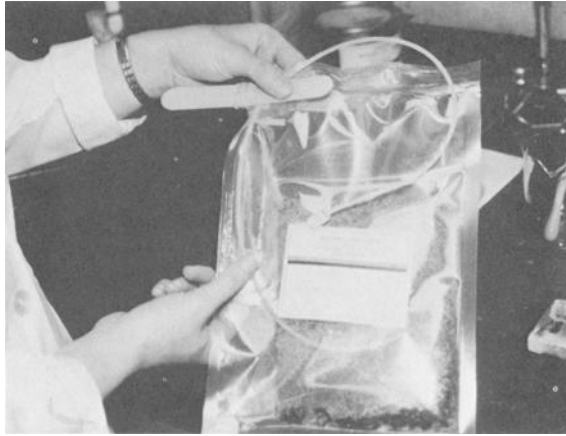


FIG. 5—Sponge clamp and Teflon tubing assembly; polyester bag contains sample of spiked carpeting material.

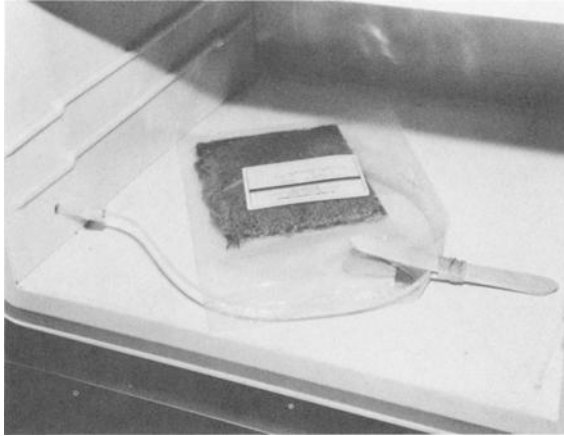


FIG. 6—Internal view of microwave oven and polyester bag setup.

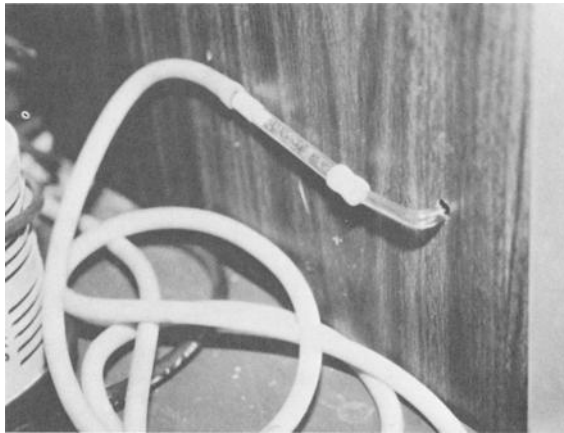


FIG. 7—External view of microwave oven and charcoal tube attachment.

tube every minute in order to make a determination as to when the maximum amount of extraction would occur. Each charcoal sample tube was washed with 2 mL of carbon disulfide, 1 μ L of which was subjected to gas chromatographic analysis under the following experimental conditions:

- FM Model 700 gas chromatograph modified with an HNU photoionization detector, 10.2 eV;
- 3.65-m by 3.18-mm (12-ft by $\frac{1}{8}$ -in.) stainless steel column packed with 15% Apiezon L and 2% potassium hydroxide on Chromosorb WAW 80-100 mesh;
- 30.0-cm³/min N₂ flow rate;
- temperature programming: initial temperature = 40°C, 4-min hold, ramp rate = 10°C per minute, and final temperature = 260°C;
- 32 \times 100 attenuation; and
- 1-cm/min chart speed.

The sample in the paint can was heated in a preheated convection oven for 30 min and charcoal sample tubes were changed every 3 min. Again, each charcoal sample tube was washed with 2 mL of carbon disulfide, 1 μ L of which was subjected to gas chromatographic analysis under the above-listed experimental conditions.

As depicted in Fig. 8, the maximum amount of the spiked hydrocarbon is extracted at 2 min with microwave heating and at 20 min with convection heating and paint can.

Results and Discussion

The results of this study indicate that the microwave oven offers a number of distinct advantages over convection heating. These include the rapid heating of samples with a concomitant decrease in total analysis time, the low dead volume in the bag which collapses about the sample as the vacuum is being pulled through it, the decrease in the gas chromatographic effect within the charcoal tube which occurs on prolonged heating, and the efficiency of the microwave extraction method as shown in Table 1. In addition to the advantage of the low

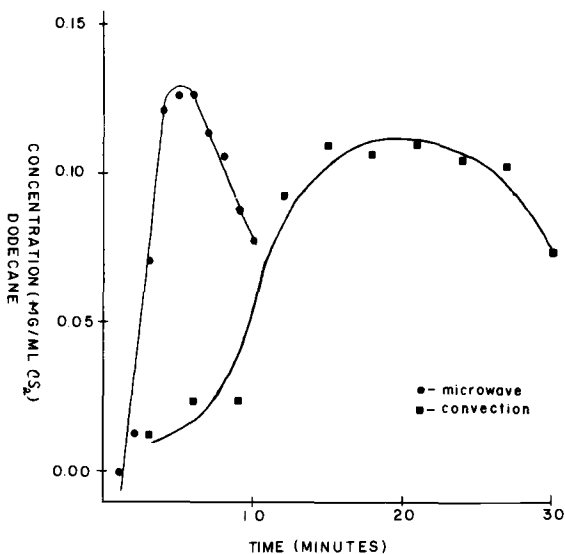


FIG. 8—Comparison of microwave and convection methods of heating arson debris.

TABLE 1—Comparison of overall extraction efficiency of microwave and convection heating techniques.

	Extraction Efficiency			
	Amount Spiked, mg	Amount Recovered, mg	Percent Recovery	Time Heated, min
Microwave	7.49	2.76 ± 0.18	36.8 ± 2.4	10
Convection	7.49	2.36 ± 0.65	31.5 ± 8.7	30

dead volume in the bag as a result of its collapse, is the advantage of the kind of purging effect of the volatile hydrocarbons which occurs as the result of the constant inflation and deflation of the bag about the sample during the heating and caused by the cycling of the microwaves. In other words, as the hydrocarbons and the water in the bag volatilize, the bag expands accordingly and then as a result of the vacuum, contracts, forcing the vapors out through the Teflon tube and into the charcoal sample tube. This process, the continued expansion and contraction of the bag, forces volatile hydrocarbons out of areas in the sample where they may otherwise be trapped and therefore increases the amount of sample collected on the charcoal.

The tests that have been discussed above, as well as many subsequent analyses, have shown the polyester bag to be an excellent alternative for the collection and analysis of both liquid and solid arson samples. The arson investigator will certainly find it much easier to store 100 3.7-L (1-gal) size polyester bags than to store 100 3.7-L (1-gal) size paint cans. The polyester bags can be sealed with a portable sealer in the field or merely taped closed at the scene and sealed later. The bags are of heavy duty construction and are puncture resistant. Where puncturing may be of concern because of the type of samples contained in the bag, that is, fragments of glass, it has been found that, in most cases, double-bagging will prevent it. Finally, the bags come in all shapes and sizes and therefore can accommodate most samples.

One important note must be made in connection with the extraction procedure when using the microwave oven. If arson samples are in a very dry condition upon receipt, 25 to 50 mL of water should be added to the bag before proceeding with the extraction. It is the water that heats the sample and maintains a temperature of 90°C within the bag during microwave heating.

References

- [1] Yates, C., "Recovery and Identification of Residues of Flammable Liquids from Suspected Arson Debris," *FBI Bulletin*.
- [2] Stone, I. C., Lomonte, J. N., Fletcher, L. A. and Lowry, W. T., "Accelerant Detection in Fire Residues," *Journal of Forensic Sciences*, Vol. 23, No. 1, Jan. 1978, pp. 78-83.
- [3] Higgins M. K., "Improvements in Sensitivity in Arson Sample Analysis Due to Pre-Concentration Techniques," presented at the Joint Meeting of Northeastern Association of Forensic Scientists (NEAFS), Southern Association of Forensic Scientists (SAFS), and Mid-Atlantic Association of Forensic Scientists (MAAFS), Louisville, KY, May 1980, sponsored by the three aforementioned associations.
- [4] Wineman, P. L., Strobel, R. A., Tontarski, R. E., and Stewart, L. F., "Detection of Volatile Accelerants in Fire Debris. I. A Comparative Evaluation," abstract presented at the 32nd Annual Meeting of the American Academy of Forensic Sciences, Feb. 1980, sponsored by the American Academy of Forensic Sciences, Colorado Springs, CO.
- [5] Tontarski, R. E. and Strobel, R. A., "Automated Sampling and Computer-Assisted Identification of Hydrocarbon Accelerants," *Journal of Forensic Sciences*, Vol. 27, No. 3, July 1982, pp. 710-714.
- [6] Driscoll, J. N., Marshall, J. K., Jaramillo, L. F., Hewitt, G., and Alongi, V., "Applications of a Gas Chromatographic Employing an Integrated Photoionization Detector," *American Laboratory*, Jan. 1980, pp. 84-93.

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