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Application of Dynamic Headspace Analysis to Laboratory and Field Arson Investigations

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ABSTRACT: A dynamic headspace procedure has been adopted to meet the special needs of the forensic scientist engaged in detecting and identifying trace accelerants present in physical evidence recovered from fire scenes. For common accelerants, sorbent trap concentration followed by thermal desorption directly onto a gas chromatographic column enhanced sensitivity by two orders in a magnitude over a static headspace technique. The procedure reduced negative findings 38% and inconclusive determinations 60% relative to static headspace analysis. Air at fire scenes can be drawn through a trap with a portable pump to allow monitoring for trace amounts of organic substances. The trap is then forwarded to the laboratory for analysis. Special precautions in sampling methods, transportation, and storage will be discussed as they relate to assuring the integrity of the collection and analysis of a fire scene atmosphere.

KEYWORDS: criminalistics, arson, accelerants, chromatographic analysis

Daily news accounts continually carry reports confirming that arson has reached near-epidemic proportions in our society. For instance, during 1980 the State of New Jersey classified 9772 fires as arson and reported arresting 548 people in connection with arson-related incidents. Forensic science laboratories throughout the United States, like those in New Jersey, are experiencing significant increases in case submissions related to arson investigations. The vast majority of this work relates to the detection and identification of accelerants that may be present in debris and other objects recovered from fire sites. A 1978 survey of 96 U.S. forensic science laboratories revealed that the most widely employed technique for analyzing arson evidence was sample collection by a heated headspace followed by gas chromatographic analysis [1]. Seventy-one laboratories reported using this approach. Other recovery methods proved far less popular; these included steam distillation (42 labs), solvent extraction (18 labs), and vacuum distillation (3 labs). Since that survey was published, a number of reports have appeared describing the applicability of solid adsorption methods to the collection of trace organic compounds present in arson evidence [2-6]. This report will deal with an evaluation of one such technique and the implications it has for the detection of accelerants that may be present both in physical evidence and in the atmosphere of the fire scene.

The use of chemical adsorbents for trapping trace quantities of organic vapors is neither new nor novel. In fact, the standard procedure recommended by the National Institute of

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Occupational Safety and Health (NIOSH) for the determination of organic vapors in industrial atmospheres involves vapor collection with the aid of a charcoal adsorbent [7]. The application of a modified version of the NIOSH procedure to arson evidence has been reported by Chrostowski and Holmes [2]. Here, a container partially filled with debris from a fire scene is purged with heated nitrogen. The nitrogen is then passed through a charcoal adsorbent that traps any accelerant present in the container's headspace. The collected sample is eluted from the charcoal with carbon disulfide. A similar approach was reported by Baldwin [3], who recommended using Florisil as a solid adsorbent.

Another technique for concentrating accelerant vapors has been suggested by researchers at the Central Research Establishment in Aldermaston, England [4,5]. Their method required coating a ferromagnetic coil with a thin film of carbon. The coated wire is then placed in a container with fire debris for approximately 2 h. The trapped organic vapors are thermally desorbed by placing the coil in a Curie point pyrolyzer interfaced with a gas chromatograph (GC). Significantly, this approach was reported to be 50 to 100 times more sensitive than a conventional headspace method. Another approach involves the thermal desorption of vapors collected on a Tenax-GC[®] trap as reported by White [6]. After comparing the normal headspace analysis with the concentration in the trap for a number of case specimens, White concluded that concentrating the accelerant vapors before the GC analysis gave significantly enhanced sensitivity over headspace analysis.

A comparison of solvent desorption versus thermal desorption reveals the latter to be significantly more sensitive [8] because it transfers virtually all of the sample onto a GC column. With solvent desorption, only a small portion of the solvent used to elute materials off the adsorbent is ultimately injected into the GC. For example, Chrostowski and Holmes [2] recommend injecting 5 μL of a 0.5-mL eluate into the GC. Thus, only a hundredth of the sample is actually used for analysis. Hence, a dynamic headspace approach designed to sweep volatile substances onto a solid chemical adsorbent followed by thermal desorption seems to offer the optimal conditions for high speed and sensitivity necessary for routine analysis of arson evidence. The design and implementation of this concept into an analytical scheme for arson evidence are the subjects of this paper.

Experimental Procedure

The system used to collect and concentrate accelerant vapors was a Chemical Data System Arson Accessory (Model 320-020). The system is designed to flush an inert gas, in this case nitrogen, through the airspace of a heated container and to trap the volatiles onto a solid adsorbent. The adsorbent is packed into a 76- by 6-mm (3- by $\frac{1}{4}$ -in.) stainless steel cartridge. The unit can accommodate up to three cartridges connected in parallel at the point the inert gas leaves the system. For routine analysis, two cartridges were used, each packed with 150 mg of Tenax GC, 60-80 mesh, a porous polymer of 2,6-diphenyl-*p*-phenylene oxide (Alltech Assoc., Arlington Heights, IL). The container was heated to 100°C for 15 min, and nitrogen was then passed through the container (normally a 3.8-L [1-gal] paint can) at a rate of 30 cm^3/min . One cartridge was removed after 5 min of flushing, the second after 10 min.

When the flushing cycle was completed, the Tenax GC-filled cartridge was placed in a Chemical Data System Model 310 desorber module directly interfaced to a Varian 3700 GC. The cartridge was thermally desorbed as it was pulse-heated to 250°C. A continuous flow of carrier gas transported the desorbed material onto a 610- by 3-mm (24- by $\frac{1}{8}$ -in.) U-tube trap also filled with Tenax GC. To insure complete desorption the temperature was held constant in the desorption chamber for 4 min. The U-tube trap was then pulse-heated to 250°C to transfer the material onto a GC column. This temperature was held constant for 4 min. In this manner, the sample was deposited onto the column as a narrow plug, reducing peak broadening and ensuring chromatographic reproducibility.

A heated headspace analysis was conducted on a specimen by first heating it in an oven at

100°C for 15 min and then removing 2 to 3 cm³ of airspace with a syringe for injection into the GC.

One of two GC columns was interfaced to the desorber unit:

1. Column 1 was 2.4 m long by 3 mm outside diameter (8 ft by 1/8 in.) stainless steel, packed with 7% Bentone 34 + 10% didecylphthalate and having a carrier gas flow rate of 30 cm³/min. The column temperature was set at 100°C, and the injector and flame ionization detector temperatures were kept at 250°C.
2. Column 2 was 6 m long by 3 mm outside diameter (20 ft by 1/8 in.) stainless steel, packed with 3% SP-2100 and having a carrier gas flow rate of 30 cm³/min. The column temperature was programmed at 12°C/min with an initial oven temperature of 50°C (held for 6 min) and a final temperature of 280°C (held for 5 min). The injector temperature was 250°C and the flame ionization detector temperature was 300°C.

Upon completion of the desorption process, the cartridges were regenerated for reuse by purging them with nitrogen at 250°C for 12 to 18 h. A hole was drilled through a door of a muffle furnace to permit nitrogen gas to pass through an adapter used to hold six cartridges within the furnace. The cartridges were reused approximately 75 times.

The collection and concentration of organic vapors at fire scenes were also accomplished with a Tenax-GC cartridge. A battery-operated, hand-held pump drew air through the cartridge at a fixed rate of 1 L/min. The collection time was 30 min. The cartridge was stored in a clean screw-capped test tube (16 by 125 mm). The mouth of the tube was covered with aluminum foil before the tube was closed with a Teflon®-coated screw cap. Prior to use, the cap was boiled in distilled water for 30 min to ensure that the cartridge remain free of GC-detectable contaminants for 90 days.

Results and Discussion

Tenax-GC was selected as the chemical adsorbent to trap and concentrate accelerant vapors. Nonpolar hydrocarbons common to accelerants (for example, benzene, toluene, xylenes, and trimethylbenzenes) are effectively retained by Tenax as demonstrated by their high "breakthrough" volumes. Breakthrough can be defined as the volume of gas that must be passed through an adsorbent before the compound of interest begins to be eluted off the adsorbent. High breakthrough volumes reflect the high retentive power of an adsorbent towards a particular substance. For example, toluene, xylenes, and trimethylbenzenes have breakthrough volumes of 25, 200, and 900 L, respectively [9]. Additionally, Tenax is insensitive to the presence of water vapor, for which it has an extremely low affinity. Obviously, this aspect is extremely important because of the copious quantities of water normally associated with fire evidence.

Our initial efforts in examining the concentration of samples in arson analysis dealt with the formulation of a chromatogram library for common accelerants. Figures 1 to 4 illustrate examples of such chromatograms. Interestingly, as shown, the chromatographic patterns formed by a conventional headspace sampling do, in some instances, differ from those formed after concentration on Tenax. These distinctions can be attributed to the varied trapping and desorption efficiencies of Tenax-GC toward hydrocarbons; however, other than the altered GC patterns necessitating a separate reference library, no difficulties were encountered in interpreting and comparing the GC patterns.

The major expectation in implementing a concentration step for arson evidence analysis is its enhanced sensitivity over a normal headspace analysis. This expectation proved justified. Relative sensitivities between the two procedures were established by spiking a tissue paper with a known volume of accelerant and enclosing the material in a 3.8-L (1-gal) paint can. The contents were then tested via concentration on Tenax (see Experimental Procedure) or with a 2-cm³ headspace sample. On the basis of the results contained in Table 1, one can ex-

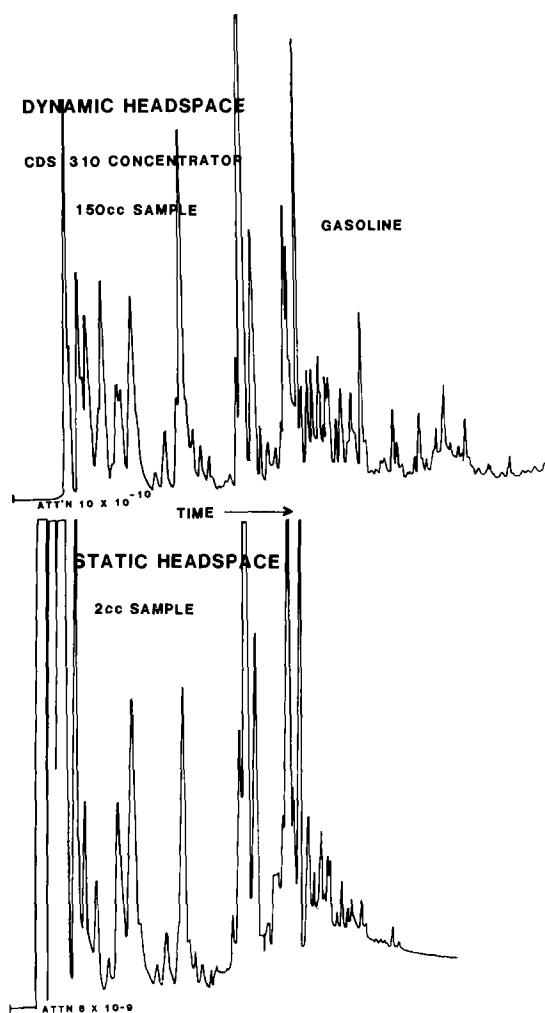


FIG. 1—A comparison of dynamic and static headspace chromatograms for gasoline (column, 3% SP-2100).

pect the concentration technique to be two orders of magnitude more sensitive than conventional headspace analysis for most common accelerants. However, a word of caution is necessary. Interpretation of resultant GC patterns must be approached with the knowledge that heated, clean, empty paint cans will produce a chromatographic pattern when their enclosed airspace is subject to concentration on Tenax (see Fig. 5). The source of these peaks has not yet been identified, but it is probably machine oil or an antioxidant coated onto the can's interior surface. Examination of cans available to our laboratory showed this GC pattern to be consistently reproducible.

While the presence of these "background" peaks were at first a cause for concern, continued experience with the concentration procedure has alleviated our apprehensions. For reasons that cannot yet be explained, paint cans filled to at least one-third capacity with debris do not exhibit any "background" peaks. In fact, a GC pattern from a blank can is infrequent with case evidence. However, the analyst must be aware that this situation can arise

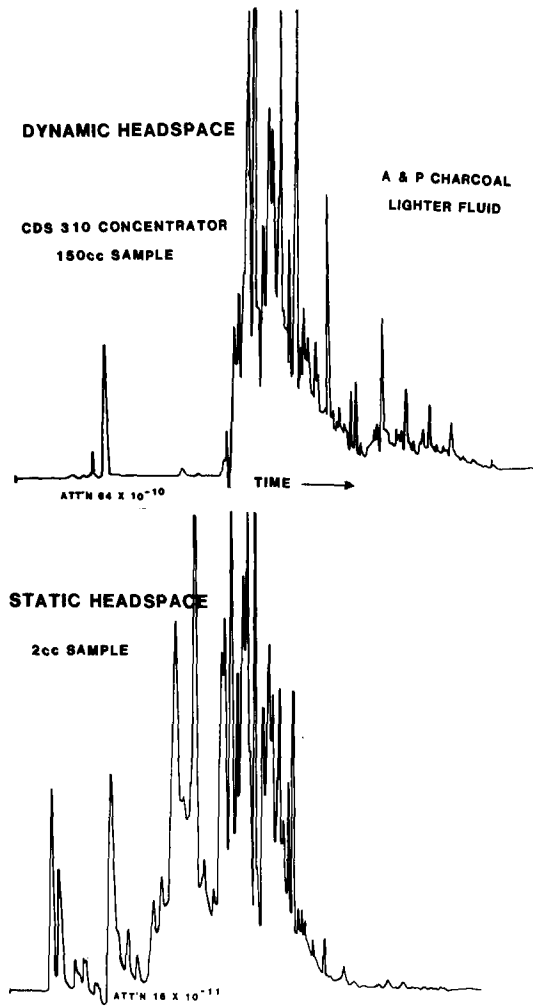


FIG. 2—A comparison of dynamic and static headspace chromatograms for charcoal lighter fluid (column, 3% SP-2100).

TABLE 1—Minimum detectable amounts of accelerant in a 3.8-L container.

Accelerant	Heated Headspace, ^a μL	Concentration on Tenax GC, ^b μL	Relative Sensitivity of Concentration to Headspace
Gasoline	5	0.025	200
Kerosine	5	0.025	200
Fuel oil #1	5	0.025	200
Fuel oil #2	10	0.050	200
Charcoal lighter fluid	1.2	0.012	100

^a2 cm³ of headspace air sampled with GC attenuation set at 4 to 8 $\times 10^{-12}$.

^b150 cm³ of nitrogen passed through the adsorbent. The GC attenuation was set at 4 to 8 $\times 10^{-11}$.

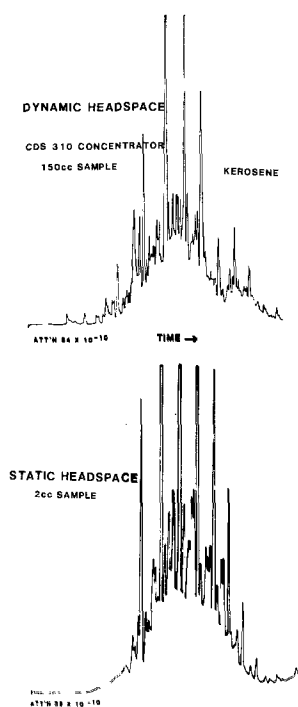


FIG. 3—A comparison of dynamic and static headspace chromatograms for kerosine (column, 3% SP-2100).

and must therefore check for background peaks. When necessary, their contribution to the questioned specimen's chromatogram must be taken into account before a final conclusion is drawn. Another matter for consideration is the potential contribution to the chromatogram from pyrolysis products of wood, synthetic fabrics, and plastics. While the study did not include a systematic evaluation of this problem, there is encouraging evidence to indicate that this contribution is probably minimal. After analyzing nearly 300 specimens recovered from fire scenes, we have not observed consistent chromatographic peaks that could be associated with the combustion of wood or synthetics. For the most part, there is little difficulty in matching chromatographic patterns from questioned specimens with those of known accelerants. Furthermore, we have reviewed chromatograms obtained with 10% SP-2100 column for burned wood and various synthetic materials [10]. Prior to GC analysis, the volatile combustion products of these materials were concentrated on and thermally desorbed from silica gel. Generally, these GC patterns are relatively simple and none would be mistaken for any accelerant material known to us.

Chromatograms arising from the analysis of fire evidence can normally be classified as giving either positive, inconclusive, or negative results. Positive results occur with a peak-for-peak match of the questioned and known accelerant chromatograms; the inconclusive find arises when a sample chromatogram shows a series of significant peaks that do not correspond to a known accelerant pattern; and a negative conclusion is drawn with the absence of any significant chromatographic peaks from the questioned sample. A logical analytical scheme for evaluating fire evidence would be to first subject the evidence to heated headspace analysis. This step would quickly isolate those materials containing a high concentration of accelerant. Specimens found to be either inconclusive or negative would then

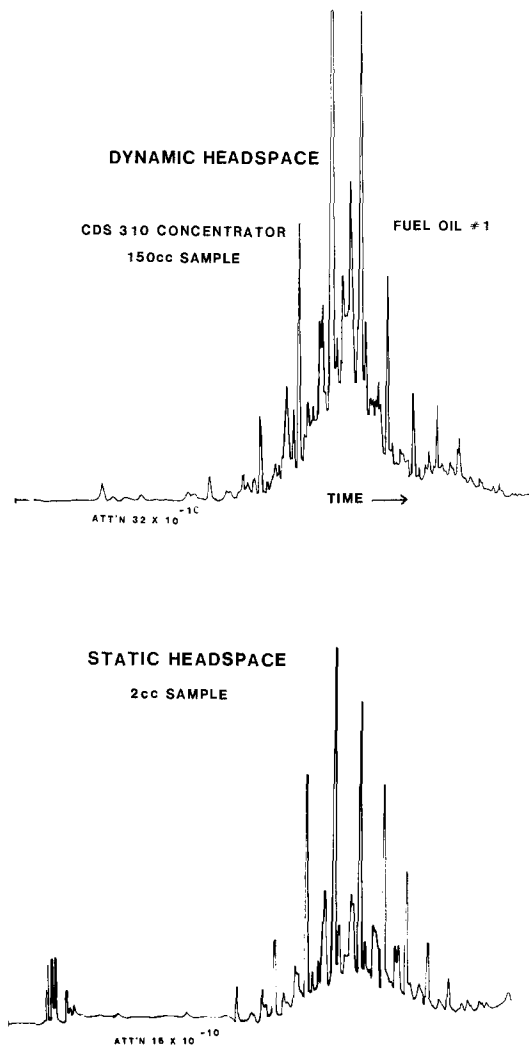


FIG. 4—A comparison of dynamic and static headspace chromatograms for fuel oil #1 (column, 3% SP-2100).

be tested by the more time-consuming and sensitive concentration technique. A number of examples contrasting heated headspace and Tenax concentration for actual case specimens are illustrated in Figs. 6 to 8. The results of such an analytical scheme during a recent twelve-month period in the New Jersey State Police Laboratories are summarized in Table 2. Concentrating 275 specimens (one specimen was weakly positive by heated headspace, the others either inconclusive or negative) resulted in a 38% decline in negative findings and a 60% reduction in inconclusive determinations. Clearly, this trend has had a significant impact on the forensic science laboratory's contribution to arson investigation in New Jersey.

The concept of collecting and concentrating accelerant vapors onto a chemical adsorbent can be extended to the fire scene. With the aid of a pump, a known volume of air can be drawn through an adsorbent to collect and trap hydrocarbon components present in the atmosphere of the fire scene. The effectiveness of this collection procedure is subject to numerous variables such as the amount and type of accelerant used to initiate and support

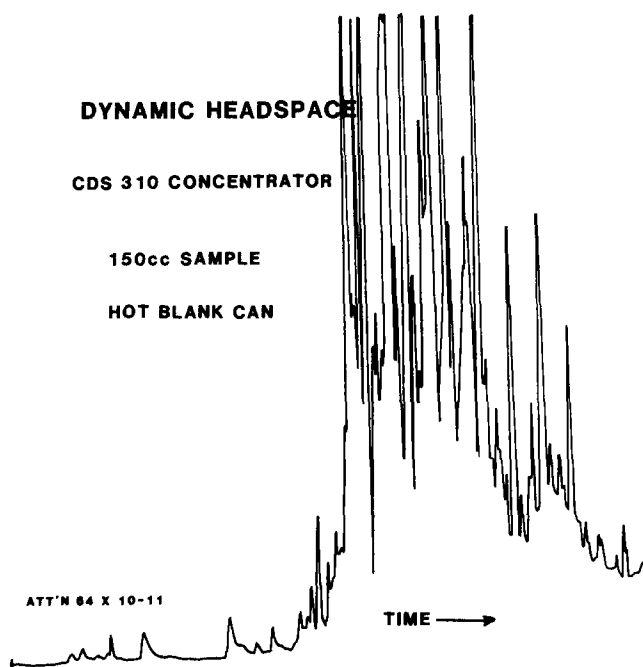


FIG. 5—The resultant chromatogram of the airspace of a clean, empty, 3.8-L (1-gal) paint can after concentration with Tenax (column, 3% SP-2100).

TABLE 2—A comparison of results obtained from headspace and concentration analysis of 275 arson specimens.^a

Analysis	Positive	Negative	Inconclusive
Headspace	1	181	93
Concentration	125	113	37

^aThese data were collected from February 1981 to January 1982 from case evidence submitted to the New Jersey State Police Laboratories.

the fire, the time interval between fire extinguishment and air sampling, air temperature, the design of the burned structure, and the nature of materials on which the accelerant was poured. From our experiences with a number of accelerant-assisted fires set with the cooperation of local fire department officials, it was estimated that at least 30 L of air had to be passed through a Tenax cartridge to detect the accelerant vapors present in a 55- to 75-m² (600- to 800-ft²) area 24 h after a fire was extinguished. This condition was achieved by drawing air through a Tenax cartridge at the rate of 1 L/min for a minimum of 30 min.

Field air sampling kits were prepared for selected arson investigators within the New Jersey State Police. The kit consisted of a battery-operated, hand-held pump, a recharger, four Tenax cartridges, and a 50-mm (2-in.) Teflon[®] tube to connect the Tenax cartridge to the pump. Each cartridge was enclosed in a screw-cap test tube as previously described. When stored in this type of container, the cartridges remained free of contamination for 90 days. Furthermore, no restrictions were placed on where an investigator could store the kit prior to use. Most kits were stored in automobiles without any detrimental effects.

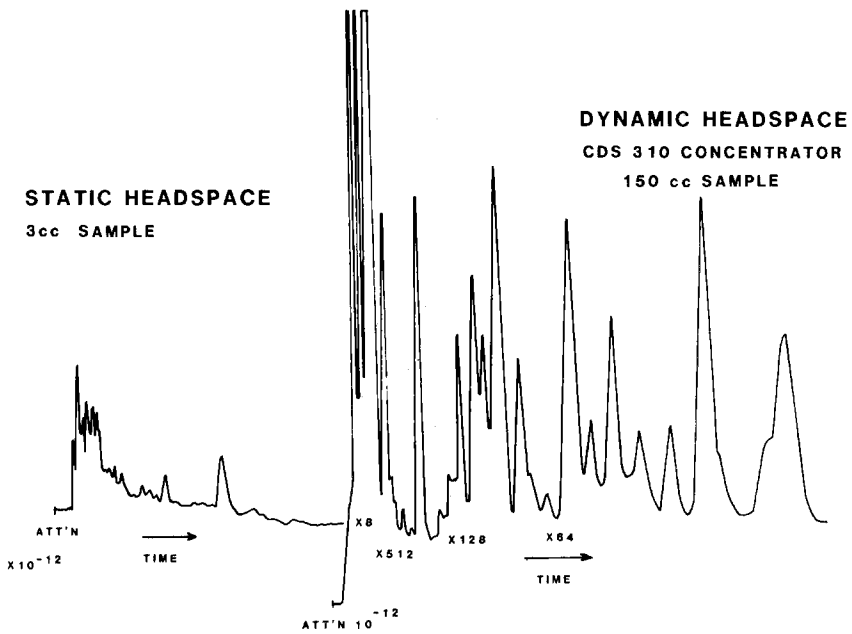


FIG. 6—Static and dynamic headspace chromatograms for a questioned specimen. The latter shows gasoline (column, 7% Bentone 34 plus 10% didecylphthalate).

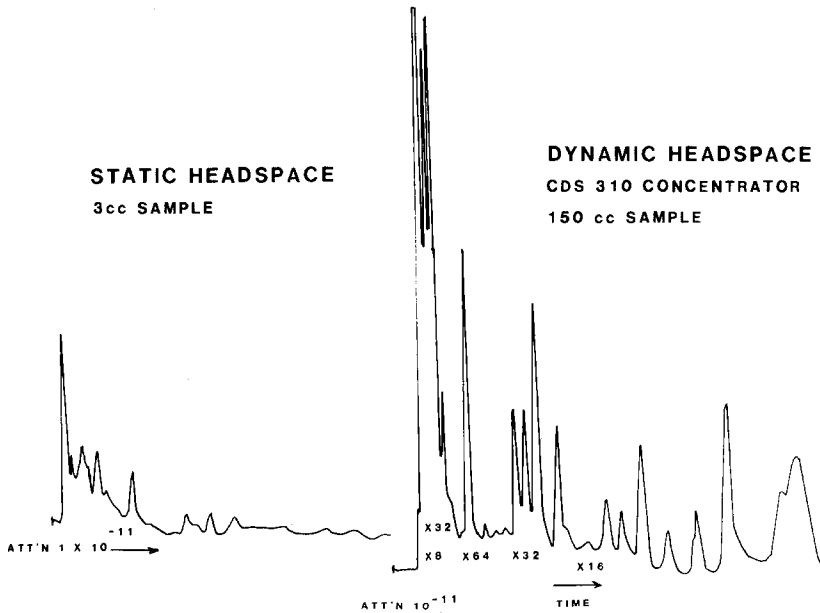


FIG. 7—Static and dynamic chromatograms for a questioned specimen. The latter shows gasoline (column, 7% Bentone plus 10% didecylphthalate).

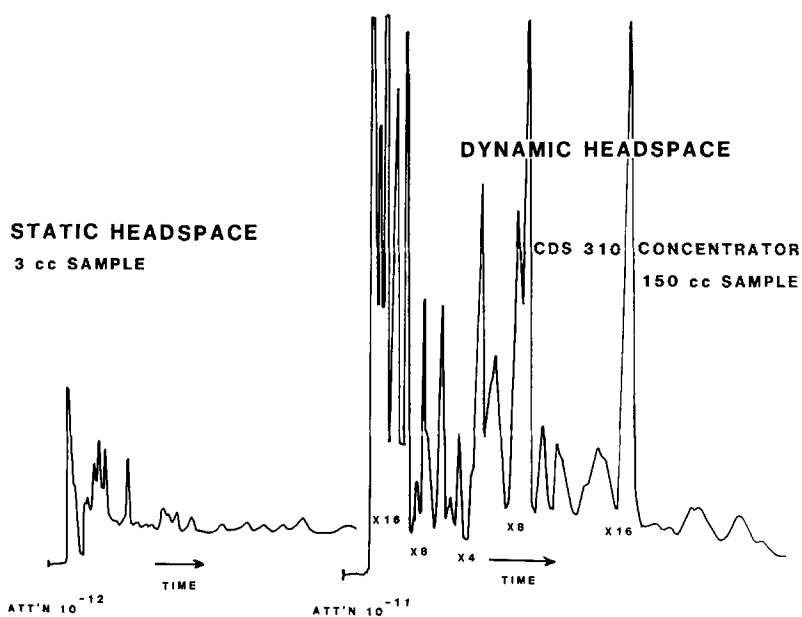


FIG. 8—Static and dynamic headspace chromatograms for a questioned specimen. The latter shows kerosine (column, 7% Bentone 34 plus 10% didecylphthalate).

At the fire scene, one cartridge is used to collect a “control” air sample. The control is necessary to check both the integrity of the kit’s cartridges and the collection procedure, and hence it is collected in the same fashion as fire atmosphere samples. A control must be taken at a site at least 9 m (30 ft) away from the structure under investigation. As we employ the collection procedure, gasoline vapors that may be present in the air as a result of vehicular traffic have not been detectable. Hence, investigators are instructed not to take this factor into consideration when choosing a site for sampling a control specimen. The present air sampling kit allows for up to three air collections within the burned structure. When air sampling is complete, each cartridge is returned to its screw-cap tube and resealed. As a precaution, investigators are instructed to store the used cartridges at room temperature and not to store them in excessively warm areas (car trunks, or the interior of a car on a warm day). This precaution will preclude any accidental partial desorption of trapped materials from the adsorbent. Once in the laboratory, each cartridge is desorbed and chromatographed in the manner previously described.

As of this writing, the air at 15 fire scenes has been sampled by field investigators. Seven of the scenes have yielded positive results. Two scenes had accelerant vapors consistent with a charcoal lighter fluid, four with gasoline, and one with kerosine. The longest interval between fire extinguishment and a positive air sampling was 15 h.

The program for monitoring air at fire scenes for accelerant vapor is ongoing in New Jersey. As the number of sampled fire sites increases, so will our ability to evaluate its impact on arson investigation and physical evidence collection and analysis.

References

- [1] Loscalzo, P., De Forest, P., and Chao, J-M., *Arson Analysis Newsletter*, Vol. 1, No. 6, Sept. 1977, pp. 4-8.

- [2] Chrostowski, J. E. and Holmes, R. N., "Collection and Determination of Accelerant Vapors from Arson Debris," *Arson Analysis Newsletter*, Vol. 3, No. 5, Dec. 1979, pp. 1-17.
- [3] Baldwin, R. E., "Adsorption-Elution Techniques for Concentration of Hydrocarbon Vapors," *Arson Analysis Newsletter*, Vol. 1, No. 6, Sept. 1977, pp. 9-12.
- [4] Twibell, J. D. and Home, J. M., "Novel Method for Direct Analysis of Hydrocarbons in Crime Investigation and Air Pollution Studies," *Nature* (London), Vol. 268, Aug. 1977, pp. 711-713.
- [5] Twibell, J. D., Home, J. M., and Smalldon, K. W., "A Comparison of the Relative Sensitivities of the Adsorption Wire and Other Methods for the Detection of Accelerant Residues in Fire Debris," Report No. 368, Home Office Central Research Establishment, Aldermaston, United Kingdom, December 1980.
- [6] White, S. E., *Arson Analysis Newsletter*, Vol. 2, No. 7, Dec. 1978, pp. 1-15.
- [7] National Institute for Occupational Safety and Health, *Manual of Sampling Data Sheets*, Department of Health, Education, and Welfare (NIOSH) Publication, 77-159, Cincinnati, 1977.
- [8] Bruner, F., Bertoni, G., and Crescentini, G., "Critical Evaluation of Sampling and Gas Chromatography Analysis of Halocarbons and Other Organic Air Pollutants," *Journal of Chromatography*, Vol. 167, 1978, pp. 399-407.
- [9] Brown, R. H. and Purnell, C. J., "Collection and Analysis of Trace Organic Vapour Pollutants in Ambient Atmospheres," *Journal of Chromatography*, Vol. 178, 1979, pp. 79-90.
- [10] Clausen, C. A., "Early Detection and Entrapment of Accelerants in Fire Atmospheres," Final Report, Star 79-047 Grant, University of Central Florida, Orlando, FL, 1980.

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