

Moske Frenkel,¹ Ph.D.; Shalom Tsaroom,² M.Sc.; Zeev Aizenshtat,³ Ph.D.; Shmuel Kraus,² Ph.D.; and Dalia Daphna²

Enhanced Sensitivity in Analysis of Arson Residues: An Adsorption-Tube/Gas Chromatograph Method

REFERENCE: Frenkel, M., Tsaroom, S., Aizenshtat, Z., Kraus, S., and Daphna, D., "Enhanced Sensitivity in Analysis of Arson Residues: An Adsorption-Tube/Gas Chromatograph Method," *Journal of Forensic Sciences*, JFSCA, Vol. 29, No. 3, July 1984, pp. 723-731.

ABSTRACT: The headspace of samples taken from fire scenes were passed through a tube packed with active charcoal granules. Desorption of the compounds by either pyrolysis or carbon disulfide (CS₂) and subsequent analysis by gas chromatography showed enhanced sensitivity over the headspace method. Both methods were evaluated for the analysis of gasoline, kerosene, and diesel oil. Interference caused by the presence of water was eliminated by the use of 0.4-nm molecular sieve. Case study of samples was followed by both headspace and adsorption tube methods, the latter has been found to be of a higher sensitivity.

KEYWORDS: criminalistics, arson, accelerants, chemical analysis, fire debris, hydrocarbons, gas chromatography, active charcoal

Arson appears to have become a significant crime in today's society [1], and new approaches are needed for quicker and more sensitive analysis of debris from suspected arson cases [2,3]. Various analytical methods have been suggested in the past for this purpose, for example, infrared spectroscopy, X-ray, and mass spectroscopy [4] as well as nuclear magnetic resonance [5].

One of the most popular analytical methods to date for the identification of fire residues is gas chromatography (GC). The headspace method requires a few millilitres of preheated fire residue that are directly injected into a gas chromatograph (GC) [6]. The use of both packed and capillary columns for the analysis of the complex mixtures of gasoline, kerosene, and diesel oil has been suggested [7]. Sampling of hydrocarbon vapors, mainly in air pollution studies, is routinely carried out by adsorption on active charcoal [8]; on various polymers, for example, Tenax[®] [9]; or other phases [10]. Desorption and analysis of the adsorbed compounds is achieved by either liquid extraction [8,10] or thermal desorption from the solid phase. One technique for the analysis of arson samples is the Curie point thermal desorption which is performed by introducing ferromagnetic wires, coated with a thin layer of highly active charcoal, for 1 to 2 h into the atmosphere under test, followed by inductive heating for desorption of the hydrocarbons [11,12].

Received for publication 31 May 1983; revised manuscript 19 Sept. 1983; accepted for publication 20 Sept. 1983.

¹Researcher in formulation center, Casali Institute of Applied Chemistry, The Hebrew University of Jerusalem, Jerusalem, Israel.

²Analytical laboratory, head of laboratories division, and analytical laboratory, respectively, Criminal Identification Division, Israel National Police Headquarters, Jerusalem, Israel.

³Chairman of studies and head of instrumentation division, Casali Institute of Applied Chemistry, The Hebrew University of Jerusalem, Jerusalem, Israel.

Two recent papers deal with dynamic headspace analysis of fire debris. One uses a special adsorption-desorption setup in which the sample is heated in an empty can and the headspace collected on a charcoal tube [13]. The hydrocarbons are gas chromatographically identified by computer assistance. Tenax is used in another work [14] to trap the volatiles by flushing a heated headspace produced over fire debris with nitrogen. The hydrocarbons were then thermally desorbed into a gas chromatograph. A similar method was used for the collection of accelerants vapors at fire scenes.

The present work is a study of various parameters that affect the sensitivity of the adsorption-tube method when used for the detection of gasoline, kerosene, or diesel oil residues. Special attention is given to the problem of water interference. Thermal desorption is compared to solvent extraction for each of the accelerants and best conditions for sampling are suggested. The proposed method is suitable for automatic analyses of samples.

Experimental Procedure

Apparatus

Gas chromatographic analyses were carried out on a Varian 2400 GC equipped with a flame ionization detector (FID) (Varian Co., Palo Alto, CA).

Air samples were pumped by Personal Air Sampling pumps, Model 7107 (Xonics Inc., Los Angeles, CA). The pyrolyzer used in this study was pyroprobe 150 (Chemical Data Systems Inc.)

Chemicals

Hydrocarbon mixtures, gasoline, kerosene, and fuel oil were regular fuels purchased from gas stations.

Active charcoal, 400 (400-m²/gm) granules of 2 mm in diameter were packed into glass tubes (20 by 2 mm) to make the adsorption tubes. Carbon disulfide (CS₂) used was the analytical reagent grade (Merck). Chromatographic column was 6-m by 3.175-mm (1/2-in.) stainless steel tubing packed with 5% OV 101 on Chromosorb P.

Water vapors were adsorbed by Zeolite 4A (0.4-nm pores) molecular sieves (Linde).

Procedures

Hydrocarbons samples from the various fuels were prepared by placing 1 μ L of the fuel on filter paper, the paper was then sealed in a heat resistant nylon bag at about 300 mL in volume. The bag was oven heated to 130°C for 15 min before sampling.

Two sampling methods were compared:

1. Headspace analysis (HS)—a disposable syringe was used to collect 2 mL of headspace from the heated bag. The air sample was immediately injected into the GC and chromatographed.

2. Adsorption tube analysis (AT)—adsorption tubes were used in two different models:

- a. The adsorption tube packed with charcoal was placed in the sealed bag with the sample and left there at room temperature for periods of time ranging from 15 min to 48 h.

- b. The whole volume of the bag was passed at a rate of 80 mL/min through the adsorption tube using the "Personal Air Sampler."

The hydrocarbons trapped on the charcoal were desorbed by either thermal desorption or by solvent extraction:

1. Thermal desorption was achieved by placing the adsorption tube in the pyroprobe and

setting the pyrolysis temperature to 950°C for 20 s. The interface was held at 300°C to prevent condensation of heavy hydrocarbons.

2. The hydrocarbons on the active charcoal granules were extracted with 50 to 60 μL of CS_2 and injected into the GC.

Effects of water on the process were studied by introducing 1 to 5 mL of water to the nylon bags containing the samples and sampled as described above.

Exhibits from real cases of fire investigations were put in nylon bags, heated to 130° for 15 min and then sampled by HS as well as AT methods.

Results and Discussion

Gasoline, kerosene, and diesel oil are the most common fire accelerants used by arsonists. The analytical method was, therefore, adapted to these solvents. Since each of the hydrocarbon mixtures has its characteristics problems the sampling technique of each of them was separately discussed.

Sampling Technique

Gasoline—Some chromatograms obtained using various methods are presented in Fig. 1: liquid gasoline directly injected (Fig. 1a); HS analysis of gasoline sample (1 μL) in preheated nylon bag (Fig. 1b); the AT and pyrolysis where the tube equilibrated in the bag for 2 h (Fig. 1c), and for 48 h (Fig. 1d). The chromatogram obtained after passing the total headspace through the glass tube over the active charcoal and desorption by pyrolysis is presented in Fig. 1e. It is clear that active charcoal can absorb the amount of gasoline present in the bag (1 μL) but this process is lengthy. Passing the headspace over the active charcoal takes only several minutes and its sensitivity is about 350 times greater than that of the direct headspace analysis method (Fig. 1b) as indicated by peak's height and attenuation. The comparison of 1a and 1e chromatograms (and the corresponding attenuations) reveals that the amount of gasoline detected by the AT method is about 0.5 μL of the sample that was introduced into the bag.

Liquid extraction for desorption of hydrocarbons has several advantages over pyrolysis since it is much simpler, time-saving, and it is one step towards an automatic gas chromatographic analysis of the desorbed sample. CS_2 was chosen as the solvent since it dissolves very well all the hydrocarbons and itself is poorly detected by FID. As can be seen from Fig. 1f some of the light hydrocarbons are not recorded by the detector since they are masked by elution of CS_2 which "blocks" the detector. Apart from this the desorption by CS_2 leads to the same sensitivity as the pyrolysis.

Kerosene—Figure 2 presents the gas chromatograms obtained for kerosene (Fig. 2a). The HS analysis was found in the case of kerosene, as with gasoline, to be of low sensitivity. On application of the AT method for kerosene sample in a nylon bag, the pyrolysis of the tube containing the charcoal for 20 s at 950°C gave rise to several light hydrocarbons derived from cracking on the charcoal surface (Fig. 2b). Slower pyrolysis at a rate of 0.1°C per milliseconds up to 850°C produced only slight cracking (Fig. 2c) and sensitivity equivalent to the detection of 25% of the kerosene, which was introduced into the bag. Desorption of the adsorbed kerosene by CS_2 yields in high sensitivity (equivalent to detection of about 50% of the initial amount of kerosene in the bag) and no cracking products were detected (Fig. 2d).

Diesel Oil—With diesel oil (Fig. 3a) the phenomena of cracking during pyrolysis was again observed at high temperatures (950°C; 20 s) while at lower temperatures (700°C, 20 s) no cracking was observed. However, only a small fraction of the hydrocarbons was desorbed (about 30% of the initial amount adsorbed). When CS_2 was used for desorption a partial chromatogram was obtained (Fig. 3b). The proportions of original quantities of the various

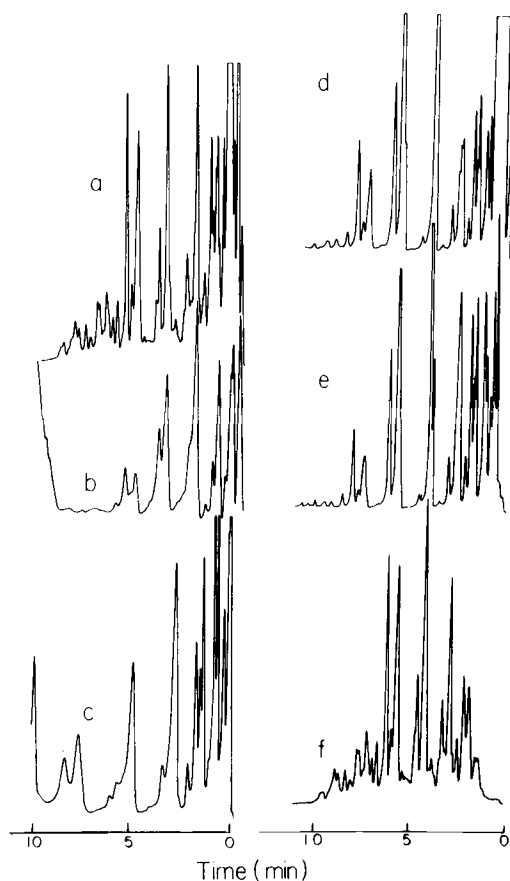


FIG. 1—Gas chromatograms of gasoline obtained by various sampling techniques. Attenuation values are given, for each sample, in brackets: (a) $1 \mu\text{L}$ of liquid gasoline (256×10^{-10}), (b) HS analysis of $1 \mu\text{L}$ gasoline in the bag (8×10^{-11}), (c) tube equilibrated in the bag for 2 h (8×10^{-11}), (d) tube equilibrated in the bag for 48 h (128×10^{-10}), (e) AT analysis-pyrolysis (128×10^{-10}), and (f) AT sampling- CS_2 desorption (128×10^{-10}).

hydrocarbons were changed, the amount of the higher molecular weights hydrocarbons being reduced, the chromatogram being no more typical of diesel oil. Two obvious reasons could cause this change in the relative amount of the hydrocarbons:

- (1) selective adsorption of the various constituents on the charcoal surface and
- (2) selective desorption from the charcoal as high molecular weight compounds are known to adsorb more strongly on charcoal surfaces.

To determine which of these possibilities was responsible for this phenomenon two additional experiments were carried out: $1 \mu\text{L}$ of diesel oil was dissolved in $50 \mu\text{L}$ of CS_2 and six granules of the active charcoal were added. After equilibration for 1 h the solution was injected into the gas chromatograph. The chromatogram obtained was identical to that of liquid diesel oil. No selective adsorption was observed, a fact that eliminates the second possibility mentioned above.

In the second experiment six granules of the active charcoal were introduced into a nylon bag containing filter paper and $1 \mu\text{L}$ of diesel oil. The bag was heated for 1 h at 130°C ,

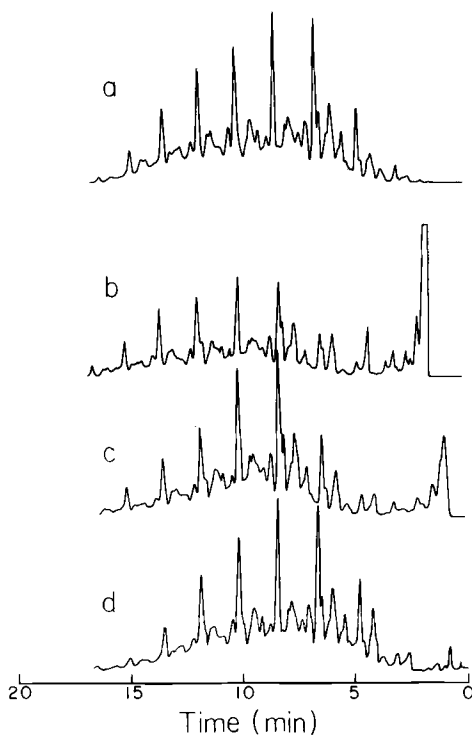


FIG. 2—Gas chromatograms of kerosene obtained by various sampling techniques. Attenuation values are given in brackets: (a) 1 μL of liquid kerosene (256×10^{-10}), (b) AT analysis-pyrolysis at 950°C (64×10^{-10}), (c) AT analysis-pyrolysis up to 850°C (64×10^{-10}), and (d) AT analysis- CS_2 desorption (128×10^{-10}).

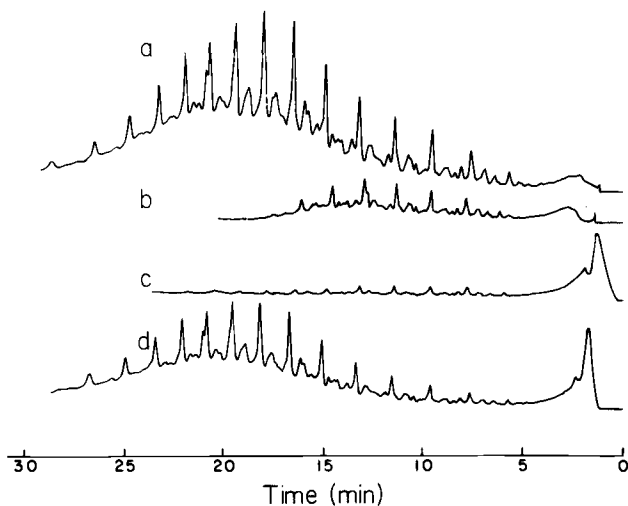


FIG. 3—Gas chromatograms of diesel oil obtained by various sampling techniques. Attenuation, in all cases, is (256×10^{-10}): (a) 1 μL liquid diesel oil, (b) AT analysis- CS_2 desorption, (c) AT sampling of cooled bag- CS_2 desorption, and (d) AT of hot bag- CS_2 desorption.

cooled, and the charcoal was treated with 50 μL of CS_2 to desorb the diesel oil. The gas chromatogram obtained was typical of diesel oil! Since adsorption as well as desorption could be achieved without any distortion of the chromatogram, it must be the sampling method used which causes this problem. As already mentioned, the sampling method included heating of the sampling bag at 130°C for 15 min, taking it out of the oven, and passing the whole headspace through the adsorption tube. During the sampling, the bag is cooled down and diesel oil vapors may condense on the bag. The higher molecular weight constituents condense first and therefore will not be absorbed on the charcoal. To emphasize this effect, the sampling bag, after being heated in the oven, was cooled at room temperature for 15 min and sampled. The gas chromatogram obtained is shown in Fig. 3c. The further distortion of the typical diesel oil chromatogram proves that it is the sampling method which causes this phenomenon and this step has to be improved. This was done by pumping the content of the bag, over the adsorption tube, in the oven itself. The bag is sampled hot and the chromatogram obtained under these conditions is presented in Fig. 3d. This chromatogram is a typical one for diesel oil. About 50% of the amount of diesel oil which was originally introduced to the bag was detected by this method.

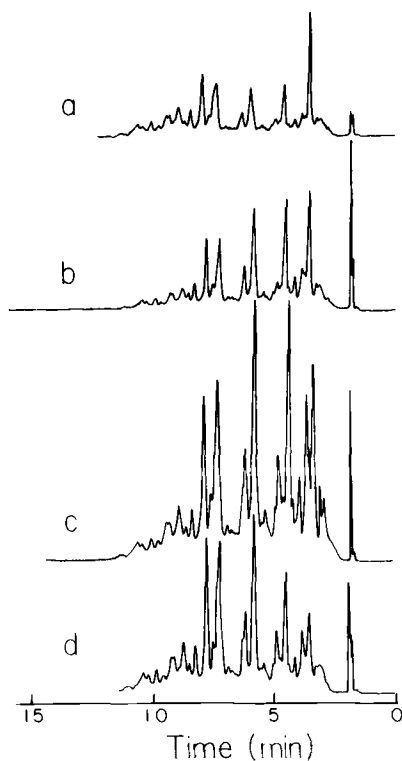


FIG. 4—Gas chromatograms of gasoline analyzed by the AT method- CS_2 desorption in presence of water (5 mL in the bag) and zeolite 0.4 nm as adsorbant for the water: (a) zeolite present in the bag for 1 h before sampling, (b) zeolite present in the bag for 5 h before sampling, (c) zeolite left in the bag overnight, and (d) zeolite left in the bag for 5 h and taken out before heating the bag. Attenuation, in all chromatograms: 64×10^{-10} .

Water Interference

Many of the field samples that reach the arson research laboratory contain water since usually an attempt is made to extinguish the fire at the site. Water might interfere in analyzing the hydrocarbons, since the concentration may be manifold that of the hydrocarbon traces and water may coat the surface of the charcoal. To examine this problem, 5 mL of water were introduced into a bag containing filter paper and 1 μL of gasoline. Under such conditions, no gasoline could be detected by the AT method. The use of Zeolite 4A proved to improve the situation since its 0.4-nm pores retain water and carbon dioxide but allow the hydrocarbons to pass (too large). Zeolite 4A (10 g per 5 mL of water) was introduced into the sampling bag which contained 1 μL of gasoline and left to equilibrate for various lengths of time before the bag was heated. Figure 4 presents the results obtained under these sampling conditions, when the Zeolite 4A was left in the bag for 1 and 5 h (Fig. 4a and b, respectively) and overnight (Fig. 4c). Further improvement was achieved by leaving the adsorbant in the bag for 5 h and taking it out (or isolating it) before the sampling bag is heated. Under such conditions, water interference is eliminated (Fig. 4d).

Water does not interfere in the analysis of kerosene or diesel oil, most probably because of their strong affinity to the charcoal surface.

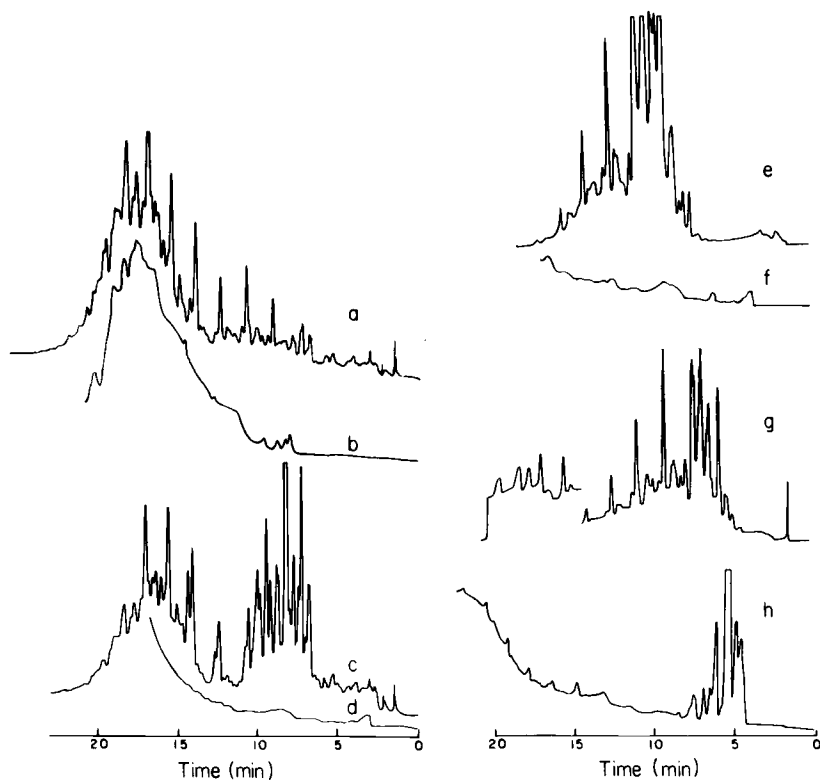


FIG. 5—Gas chromatograms of field samples collected by arson investigators and analyzed by HS versus AT methods. Attenuation values are given, for each case, in brackets. (a) and (b) Case 1—AT (64×10^{-10}) and HS (32×10^{-11}) methods, respectively. (c and d) Case 2—AT (64×10^{-10}) and HS (32×10^{-11}), respectively. (e and f) Case 3—AT (512×10^{-10}) and HS (32×10^{-11}), respectively. (g and h) Case 4—AT (128×10^{-10}) and HS (32×10^{-11}), respectively.

Comparison of the HS and AT Methods in Field Cases

Since all the experiments that were carried out during this study were done under laboratory conditions, using filter paper as the "carrier" for the solvents, it was important to compare the suggested AT method with the HS one in actual samples which were collected by arson investigators. The debris included charcoaled remains of cloth and wood as well as empty bottles. Figure 5 shows gas chromatograms of some field samples that were sent to the arson investigation laboratory in the Israeli Police Headquarters and analyzed by both methods: HS versus the AT. As it can be seen in three of the four examples that are presented, nothing is detected by the HS method while the AT method detects various hydrocarbon mixtures. In the fourth case (Fig. 5 *g-h*) some light hydrocarbons are detected by the HS method but the chromatogram is not typical of any known hydrocarbon mixture. The chromatogram obtained by the AT method is clearly typical of kerosene, although detector sensitivity in the latter case is 40 times smaller than in the former.

Conclusion

The AT method for determining fire debris is found to be a most sensitive and useful method. It is suitable for light hydrocarbons (such as gasoline) as well as for higher molecular weights (kerosene or diesel oil). The experimental conditions overcome interferences caused by the presence of water in the sample and provide enhanced sensitivity as compared with the HS method which was used in the past. It has other advantages over the HS method: first, the need to store samples for prolonged periods of time is eliminated. The latter needs large spaces and requires efficient sealing in order to prevent contamination of one sample by others. The samples might be heated in the bags when accepted, sampled on the AT, and the tubes might be easily stored in small glass vessels. Solvent desorption of the hydrocarbons from the charcoal was found to be as sensitive as thermal desorption and offers an additional advantage since it enables an automatic injection of the samples into a gas chromatograph, an important step towards full automatization of analytical procedure.

References

- [1] Boudreau, J. F., *Arson and Arson Investigation*, National Institute of Law Enforcement and Criminal Justice, Washington, DC, 1977.
- [2] Kirk, P. L., *Fire Investigation*, John Wiley, Inc., New York, 1969.
- [3] Carroll, J. R., *Physical and Technical Aspects of Fire and Arson Investigation*, Charles C Thomas, Springfield, IL, 1979.
- [4] 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.
- [5] Bryce, K. L., Stone, I. C., and Daugherty, K. E., "Analysis of Fire Debris by Nuclear Magnetic Resonance Spectroscopy," *Journal of Forensic Sciences*, Vol. 26, No. 4, Oct. 1981, pp. 678-685.
- [6] Ettling, B. V., "Analysis of Paraffin Wax in Fire Remains," *Journal of Forensic Sciences*, Vol. 20, No. 3, July 1975, pp. 476-483.
- [7] Willson, D., "A Unified Scheme for the Analysis of Light Petroleum Products Used as Fire Accelerants," *Forensic Science*, Vol. 10, 1977, pp. 243-252.
- [8] Grob, K. and Grob G., "Gas-Liquid Chromatographic—Mass Spectrometric Investigation of C₆-C₂₀ Organic Compounds in an Urban Atmosphere," *Journal of Chromatography*, Vol. 62, No. 1, Oct. 1971, pp. 1-13.
- [9] Perry, R. and Twibell, J. D., "Time-Based Elution Technique for the Estimation of Specific Hydrocarbons in Air," *Atmospheric Environment*, Vol. 7, No. 10, Oct. 1973, pp. 929-937.
- [10] Aue, W. A. and Teli, P. M., "Sampling of Air Pollutants with Support Bonded Chromatographic Phases," *Journal of Chromatography*, Vol. 62, No. 1, Oct. 1971, pp. 15-27.
- [11] Twibell, J. D. and Home, J. M., "Novel Method for Direct Analysis of Hydrocarbons in Crime Investigation and Air Pollution Studies," *Nature*, Vol. 268, No. 5622, Aug. 1977, pp. 711-713.
- [12] 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," *Journal of Forensic Science Society*, Vol. 22, No. 2, April 1982, pp. 155-159.

- [13] Tontarski, R. E. and Strobel, B. S., "Automated Sampling and Computer Assisted Identification of Hydrocarbon Accelerants," *Journal of Forensic Sciences*, Vol. 27, No. 3, July 1982, pp. 710-714.
- [14] Saferstein, R. and Park, S. A., "Application of Dynamic Headspace Analysis to Laboratory and Field Arson Investigations," *Journal of Forensic Sciences*, Vol. 27, No. 3, July 1982, pp. 484-494.

Address requests for reprints or additional information to
Z. Aizenshtat
Casali Institute of Applied Chemistry
The Hebrew University of Jerusalem
Jerusalem 91904, Israel