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The Application of a Simple and Inexpensive Modified Carbon Wire Adsorption/Solvent Extraction Technique to the Analysis of Accelerants and Volatile Organic Compounds in Arson Debris

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ABSTRACT: A simple, inexpensive carbon wire adsorption/solvent extraction (CWSE) technique that allows for sensitive and reproducible analysis of organic volatiles from arson debris is described. The technique requires a minimum of expensive equipment and is particularly suited to those laboratories without a thermal desorption unit or pyrolyzer. The technique combines static headspace sampling with solvent extraction and analysis by capillary column gas chromatography.

KEYWORDS: criminalistics, arson, accelerants, volatile organic compounds, solvent extraction, chromatographic analysis, automation

As arson caseloads have increased, forensic science laboratories have sought suitable methods that allow fast, accurate, and reproducible analysis of fire debris samples.

The use of adsorption/solvent elution techniques for the collection and separation of accelerants from fire debris has been described in a number of publications [1-3].

These methods are sensitive and accurate in reproducing chromatograms of collected headspace of similar composition to the accelerants contained in fire debris. They are however time-consuming and cumbersome because of the complicated sample manipulations that are involved.

A carbon wire adsorption/solvent elution technique, reported by Juhala [4] and modified by Reeve [5], has been examined. Since Reeve achieved only limited success, the modified carbon wire/solvent elution technique was further investigated. A method has been developed which provides a simple, low-cost recovery technique that allows the recovered organic volatiles to be presented in a form suitable for automated analysis by gas chromatography (GC).

A carbon-coated wire was chosen as the means of adsorbing headspace volatiles because it was inexpensive and easily prepared. Strips of aluminum or copper (5.0 by 70.0 by 0.15 mm) may also be used as a support for the activated carbon. The wire is easily

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exposed to headspace volatiles, allowing for uncomplicated sample preparation. The wire is easily manipulated for solvent extraction. The technique adopted at this laboratory differed to that of Reeve [5] in that (1) headspace samples were collected at 70 or 80°C and (2) the adsorbed volatiles were extracted from the wire using *n*-pentane and ultrasonic vibration, whereas Reeve [5] relied solely on solvent elution using carbon disulphide to displace preferentially accelerant vapors adsorbed onto a carbon wire.

Experimental Procedure

Materials and Methods

Preparation of Activated Carbon—The charcoal (Ajax Chemicals, "charcoal, activated decolourising powder") was cleaned and activated by heating in an oven overnight at 250°C, then cooled and stored in a dessicator.

Preparation of Purified Solvent—Ajax analytical grade *n*-pentane (boiling point 36°C) was purified by refluxing with concentrated sulphuric acid (5% by volume) for 3 h followed by fractional distillation.

Preparation of Carbon-Coated Wires—Pye Curie-point pyrolysis wires (358°C) were flattened to a width of 2 mm, over 50 mm in length. The flattened section was brought to red heat in a Bunsen flame, then dipped into a saturated sodium silicate solution. The wire was reheated, then reimmersed in sodium silicate, then dipped into a glass vial containing activated charcoal. The charcoal-coated wires were stored in a dessicator until required.

Sample Containers—Cryovac® barrier bags were purchased from W. R. Grace, Australia Limited. Clean metal cans (1-L volume) were purchased from J. Gadsen Pty. Ltd., Western Australia.

Preparation and Analysis of Fire Debris Samples—The analytical technique developed consisted of three parts: (1) heated headspace adsorption, (2) desorption by solvent extraction, and (3) analysis by gas chromatography.

Heated headspace adsorption—The carbon-coated wire (in a protective open glass vial) was placed into the sample container, generally a Cryovac plastic bag or metal can. The sample container was placed in an oven and heated for 2 h at a temperature of 70 (Cryovac plastic bag) or 80°C (metal can), then removed and allowed to cool to room temperature.

Desorption by solvent extraction—The carbon-coated wire was removed from the glass vial and placed into a small (1.0- by 5.0-cm) glass test tube to which was added 4 mL of purified *n*-pentane.

The test tube was placed in an ultrasonic bath and treated to ultrasonic extraction for 1 min. The solvent was removed and dried by passing through anhydrous sodium sulphate (1 cm in a pasteur pipette). The solvent was evaporated (under nitrogen) to a final volume of 180 to 200 μ L.

Gas chromatographic analysis—A 5- or 1- μ L aliquot was injected into the gas chromatograph either manually or by using an autosampler.

Accelerant standards (petrol, kerosene, diesoline) were prepared by placing a 1- μ L aliquot of fuel onto a section of tissue paper in a 1-L metal can.

A carbon-coated wire was placed in the can which was sealed and placed in an oven for 2 h. The wire was treated as previously described and the solvent analyzed by gas chromatography.

Instrumentation

Gas chromatographic analyses were carried out with a Hewlett Packard 5890 model GC, fitted with capillary column, split/splitless injector, and flame ionization detector.

A Shimadzu CR3A recorder was used for data acquisition and production of chromatograms (hard copy). The CR3A includes storage and replot facilities which facilitate the presentation of chromatograms in a form suitable for examination.

The chromatography was carried out on a bonded methyl silicone capillary column (25 m by 0.25 mm, 0.25- μ m film thickness, model S.G.E., B.P. 1). The carrier gas was helium at a head pressure of 120 kPa. The chromatograph was operated in the splitless mode (purge off for 0.41 min). The initial oven temperature of 30°C was held for 2 min, then programmed at a rate of 8°C/min to a final temperature of 215°C with a 5-min hold at that temperature. Automatic sample injection was carried out using a Hewlett Packard 7673A injection turret.

Mass spectral data was obtained by computerized gas chromatography/mass spectrometry (GC/MS) using a Hewlett Packard 5890 GC coupled to a 5970 mass selective detector. Mass spectrometer control, data acquisition, and manipulation were carried out with a Hewlett Packard 5997C chemstation. Helium carrier gas was used with a head pressure of 35 kPa. Mass spectral detection (EI) was carried out with 70-eV ionization voltage.

Results and Discussion

Pentane was used as the extracting solvent in preference to carbon disulphide [6] as it showed similar displacement properties without the offensive smell or danger [7].

The modified carbon wire adsorption/solvent extraction (CWSE) technique has been applied, with success, to routine casework over the past two years. The method has been used as a check for the normally used technique of Curie-point thermal desorption of collected volatiles from carbon- or Tenax GC-coated pyrolysis wires [8]. The method has proved to be accurate and reliable in producing recovered accelerant profiles. There has been no indication of any interference from water vapor, differing from the findings of Frenkel [3] and Reeve [5]. The modified CWSE technique is not suitable for the detection of low molecular weight alcohols or ketones as these are masked by the solvent. Where such accelerants are suspected, steam distillation or thermal desorption are the preferred recovery techniques.

The following examples illustrate that the modified CWSE technique offers an alternative to (1) headspace desorption techniques using thermal desorbers or (2) direct headspace injection. The technique accurately reproduces the composition of an accelerant contained in arson debris. This is extremely important because pattern recognition is the most widely used technique for accelerant identification. The recovered accelerant is also presented in a manner suitable for automatic injection into a gas chromatograph.

Case Examples

Figures 1a and b show chromatograms of volatile organic compounds recovered from fire scene debris (burnt carpet). The volatile organic compounds from the solvent extract were identified by mass spectrometry as ethyl benzene and xylenes.

The volatiles recovered from the debris sample (Figs. 1a and b) were of similar composition to an accelerant (Taubmans Series 2000 thinners) contained in a metal can (Fig. 1c), which was located at the fire scene.

Figure 2a shows chromatographic confirmation of a petrol/ kerosene mixture found in debris from a fire scene. This is compared with the composition of a petrol/kerosene mixture sampled from a drum located at the fire scene (Fig. 2b). There is good agreement between the two samples.

These results indicate that the modified CWSE technique is suitable for the recovery

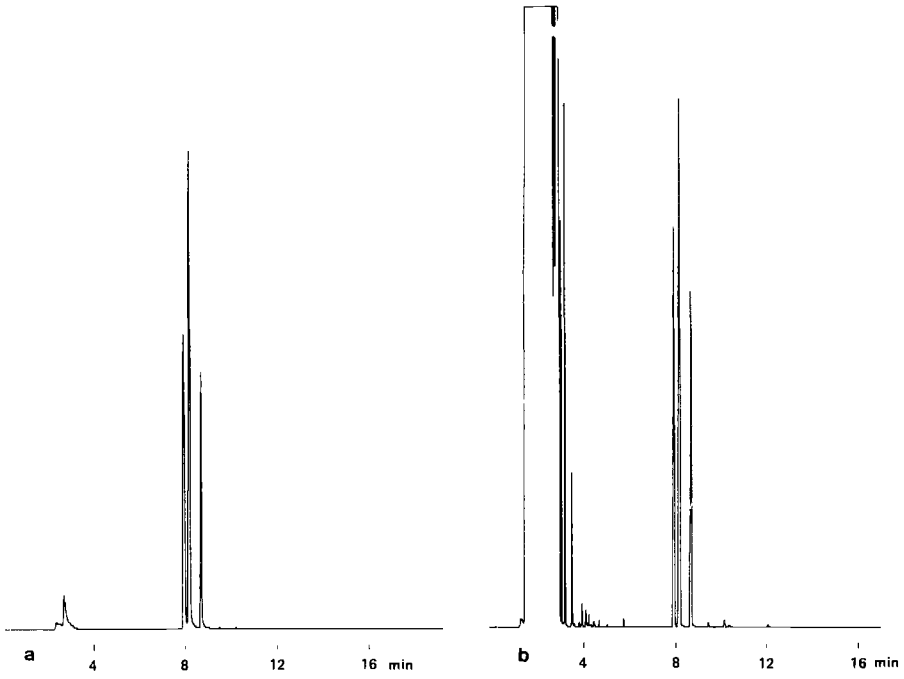


FIG. 1a and b—Chromatograms of recovered accelerant from arson debris by (a) thermal desorption (carbon-coated Curie-point pyrolysis wire) and (b) modified CWSE technique.

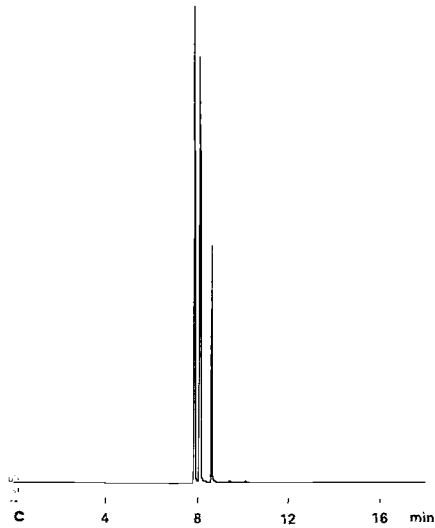


FIG. 1c—Chromatogram of a liquid accelerant (Taubmans Series 2000 thinners, direct injection, split mode) found at a fire scene.

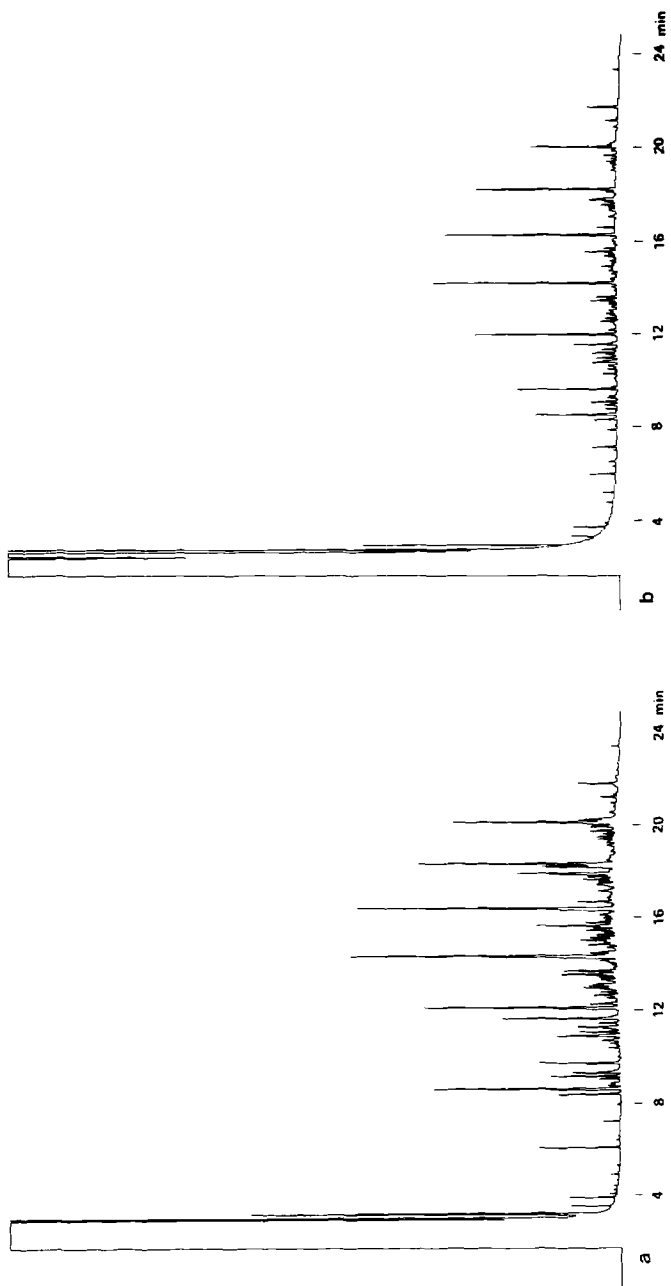


FIG. 2a and b—Chromatograms of (a) accelerant recovered from fire debris by the modified CWSE technique and (b) liquid accelerant from a drum at the fire scene (pentane dilution).

of petrol and kerosene which are the most common accelerants used by arsonists in Western Australia (Table 1).

Limits of detection were not determined but petrol and kerosene (0.1 μL) could be detected in the headspace of a 1-L metal can. For diesoline, the level was 0.5 μL .

The technique has proved invaluable in a number of cases in which the volatile organic compound profiles from arson debris have not corresponded to common accelerants or have shown an accelerant profile with additional components that make pattern recognition difficult. The solvent extract is suitable for GC/MS analysis allowing for accelerant confirmation and identification of unknown compounds. Figure 3 shows a chromatogram

TABLE 1—Types and frequency of accelerants detected in arson/fire cases (all exhibits) 1981–1987.^a

Accelerant	Year						
	1981	1982	1983	1984	1985	1986	1987
Petrol	15	19	54	40	40	70	99
Kerosene	7	11	39	24	18	49	39
M/Turpentine	...	1	3	3	2	20	2
L/Thinners	1	1	1	3	2	7	24
Diesoline	4	1	13	7	11	9	2
Ethanol	2	3	...	6	3	2	2
Toluene	5	1
Xylene	3

^aValues are the number of exhibits in which an accelerant was detected during the indicated year.

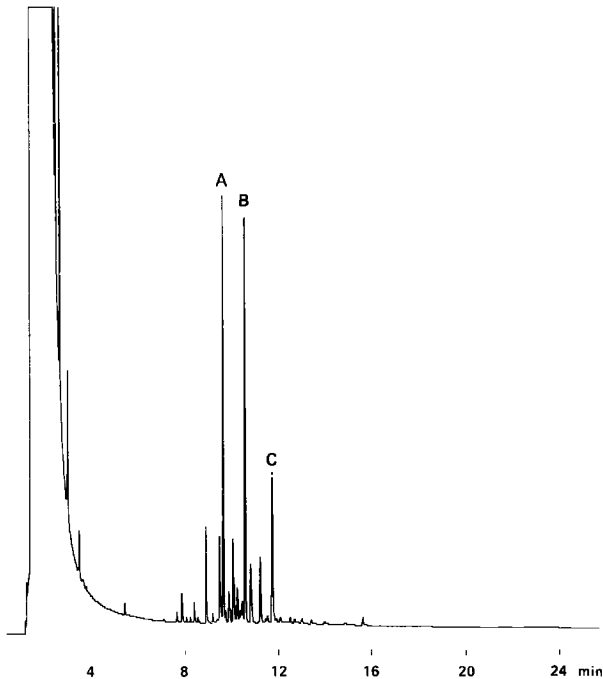


FIG. 3—Chromatogram of volatile organic compounds recovered from partly burnt pine chips by the modified CWSE technique.

of organic volatiles obtained from pine chips that were used to set a fire trail at the scene of an attempted arson. The major components (A, B, C) were identified by GC/MS as terpenes (Fig. 4) having a base peak of M^+93 .

Mineral turpentine of similar composition to that from a drum located at the scene was detected in three other samples of pine chips.

The modified CWSE technique was extremely sensitive, and it is not uncommon to detect combustion and pyrolysis products from carpet underlays, carpet adhesives, and other polymeric materials which are encountered in fire debris. Figure 5 shows a chromatogram of volatile organic compounds collected from a piece of burnt carpet obtained from a fire scene. Analysis by GC/MS revealed that no accelerants were present. The major component was identified as styrene which is derived from the styrene-butadiene rubber carpet adhesive (Fig. 6). Pyrolysis products (three isomers of 2,4,6,8-tetramethyl-1-undecene) from polypropylene primary backing material were also identified. These results are in agreement with the findings of Howard [9] and Sousa Pessoa De Amorim [10].

These results highlight the major advantage of the modified CWSE technique over thermal desorption techniques, namely the ability to reinject the solvent extract for GC/MS analysis, allowing for unequivocal identification of organic volatiles and identification of accelerants [11].

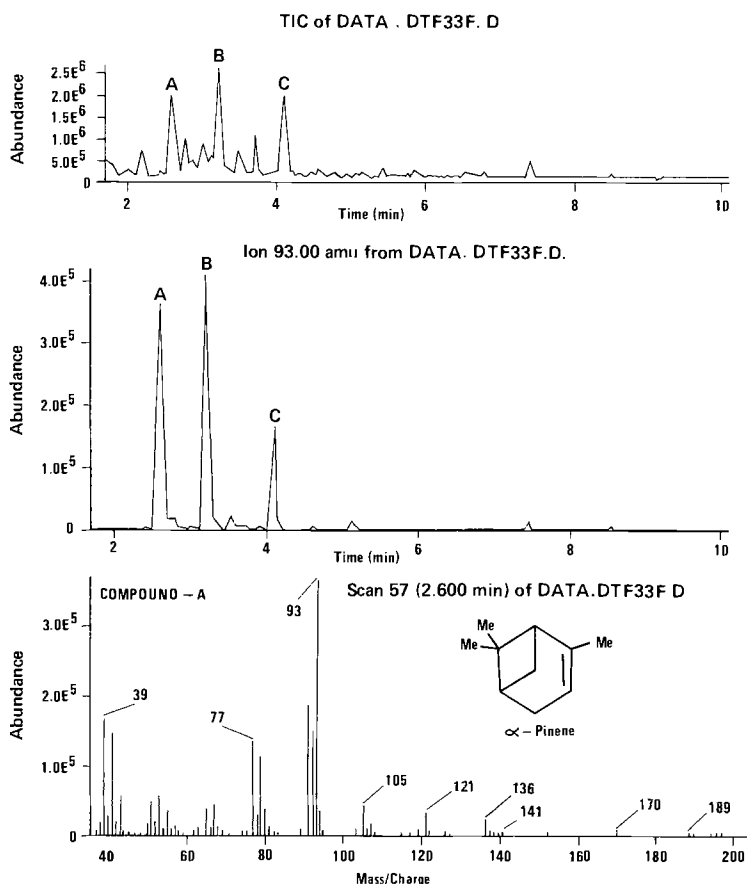


FIG. 4—Total ion, selected ion chromatograms and mass spectra of volatile organic compounds (terpenes) recovered from pine chips by the modified CWSE technique.

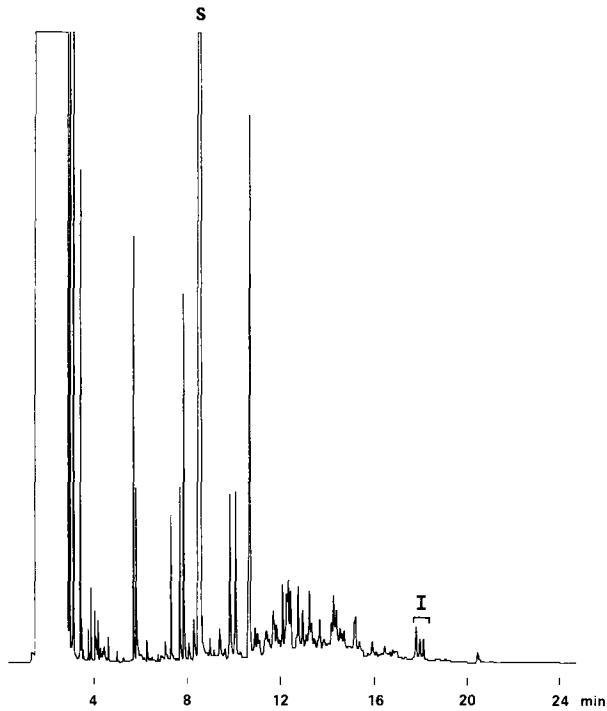


FIG. 5—Chromatogram of volatile organic compounds recovered from fire debris (burnt carpet) by the modified CWSE technique. Key: S = styrene and I = isomers of 2,4,6,8-tetramethyl-1-undecene.

With existing techniques of charcoal adsorption/solvent elution (purge and trap), all volatiles are removed from the fire debris. Some forensic scientists have shown concern that a failure to preserve fire debris evidence for reanalysis may jeopardize such evidence in court proceedings [5,12]. The modified CWSE technique, which is nonintrusive and in which the sample is not damaged or altered in any way, allows further examination at a later date if required and should allay these concerns.

Conclusion

The modified CWSE technique described here has been found to be comparable in sensitivity to thermal desorption methods. It requires a minimum of expensive equipment and is particularly suitable for laboratories without a thermal desorption unit or pyrolyzer. It is suitable for automation using standard GC autoinjection devices and allows for reanalysis if necessary. Reanalysis of samples using GC/MS has proved invaluable in identifying accelerants and natural and pyrolysis products from fire debris samples. The move to automation should result in a more efficient use of instrumentation with the potential to improve reporting times significantly in those situations where a lack of chromatography time causes bottlenecks in sample throughput.

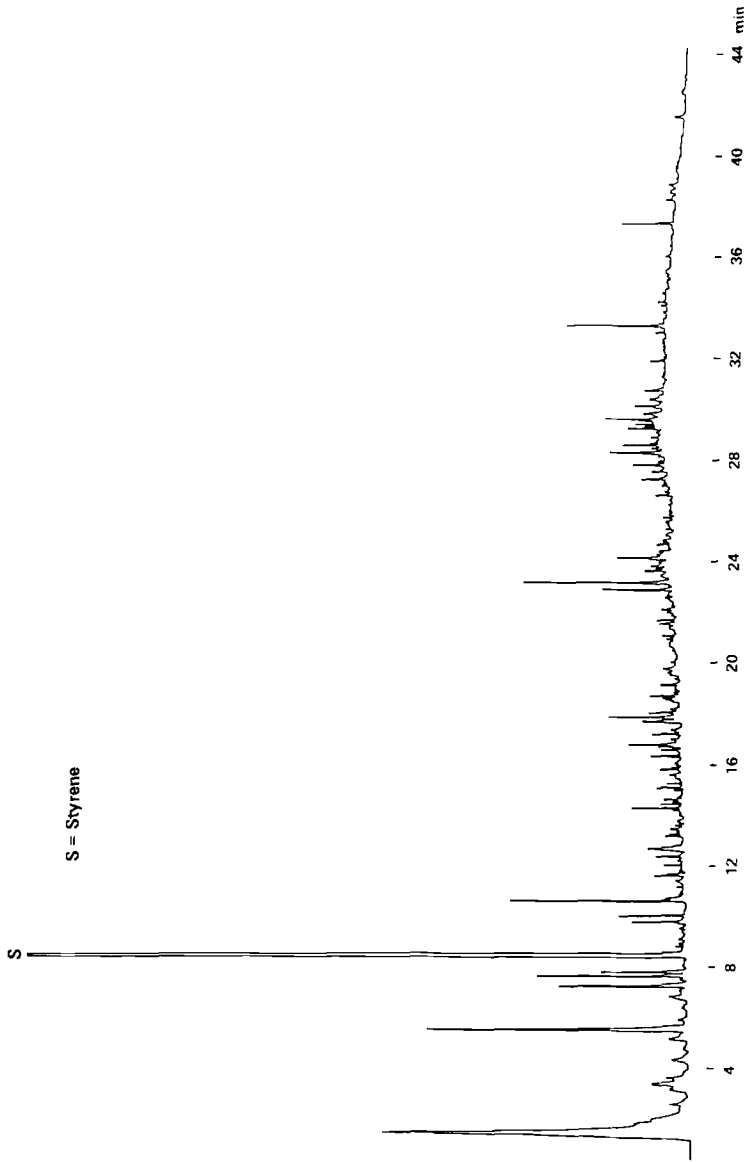


FIG. 6—Chromatogram of pyrolysis products from carpet adhesive (Curie-point pyrolyzer, 770°C pyrolysis wire). Key: S = styrene.

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