TECHNICAL NOTE

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Extraction and Analysis of Low Molecular Weight Alcohols and Acetone From Fire Debris Using Passive Headspace Concentration

ABSTRACT: Passive headspace concentration was utilized for recovering methanol, ethanol, isopropanol and acetone from materials commonly found in fire debris. Gas Chromatography/Flame Ionization Detection was used for screening the extracts, followed by Gas Chromatography/Ion Trap Detection to confirm the presence of an alcohol or acetone with mass spectra.

KEYWORDS: forensic science, acetone, alcohol, fire debris, chromatographic analysis

Passive diffusion recovery of flammable liquids from fire debris using carbon membranes (carbon strips) was introduced in 1991 by William Dietz [1]. The method has been widely adopted by arson analysts because of its sensitivity, simplicity and reproducibility [2,3]. The carbon strip method has been used to recover all classes of petroleum products and works consistently for light petroleum distillates as well as heavier products such as diesel fuel. However there has been no discussion concerning the use of the carbon strip to recover alcohols from fire debris.

Many laboratories screen for alcohols using direct headspace injection, which is less sensitive than carbon strip recovery [4]. This then requires subjecting the evidence to a second procedure to recover petroleum products [5]. A third procedure would be necessary for positive samples since alcohols and acetone are a single chromatographic peak which must be verified by a second column or preferably by a mass spectra.

Some may question the necessity of routine screening for alcohols and acetone. Commercial products are readily available: methanol and acetone are sold as solvents, ethanol is available as a beverage and isopropanol is sold as rubbing alcohol. The State of Ohio

TABLE 1—*GC/FID parameters.*

Column	SGE, 0.32-mm × 25 M, 0.5-μM methyl silicone bonded phase
Carrier gas	helium, 42 cm/s linear velocity at 50°C
Injector	300°C, split/splitless in split mode, 30:1 split ratio, 2 μL injection
Detector	300°C
Temperature program	
initial temperature	50°C
initial hold	1 minute
ramp	20°C/minute
final temperature	300°C
final hold	2 minutes

Arson Crime Laboratory published statistics in 1988 which reported 3.3% of the accelerants detected at that facility were alcohols [6]. Since the Florida State Fire Marshal's Fire and Arson Laboratory began routine screening for alcohols 1.4% of the accelerants detected were alcohols.

It has been argued that the volatility of alcohols and of acetone is likely to preclude their recovery from a fire scene. Both the State of Ohio's Arson Crime Laboratory and the Florida State Fire Marshal's Fire and Arson Laboratory have conducted controlled house burns using ethanol and isopropanol as accelerants [7]. In both circumstances the alcohols were readily recovered from the fire debris.

The carbon strip method is the primary method of recovery at the Florida State Fire Marshal's Fire and Arson Laboratory, which analyzes more than 3000 fire debris samples per year. Headspace screening for each sample would significantly increase the sample turn around time. A method of screening for alcohols without subjecting the evidence to a second procedure was needed. Development of this procedure required validation of the carbon strip method for extraction of methanol, ethanol, acetone, and isopropanol; and confirmation that the established chromatographic conditions for petroleum product analysis could serve as a screening method. Finally the chromatographic conditions to be used for mass spectrometric analysis had to be established.

Methods and Materials

Separation Technique

The carbon strips were prepared from charcoal membranes purchased from Pro-Tek Systems Inc. The membranes were cut into four sections, inserted through the outside

TABLE 2—*GC/ITD parameters.*

| Column	SGE, 0.32-mm × 50 M, 0.5-μM methyl silicone bonded phase
Carrier gas	helium, 19 cm/s linear velocity at 35°C
Injector	200°C, split/splitless in split mode, 30:1 split ratio, 2 μL injection
Transfer line	200°C
Temperature program	
initial temperature	35°C
hold	6 minutes
ramp	30°C/minute
final temperature	300°C
Mass spectrometer	
scan range	30–70 amu
scan cycle	1.0 second/scan
start time	0.0 minute
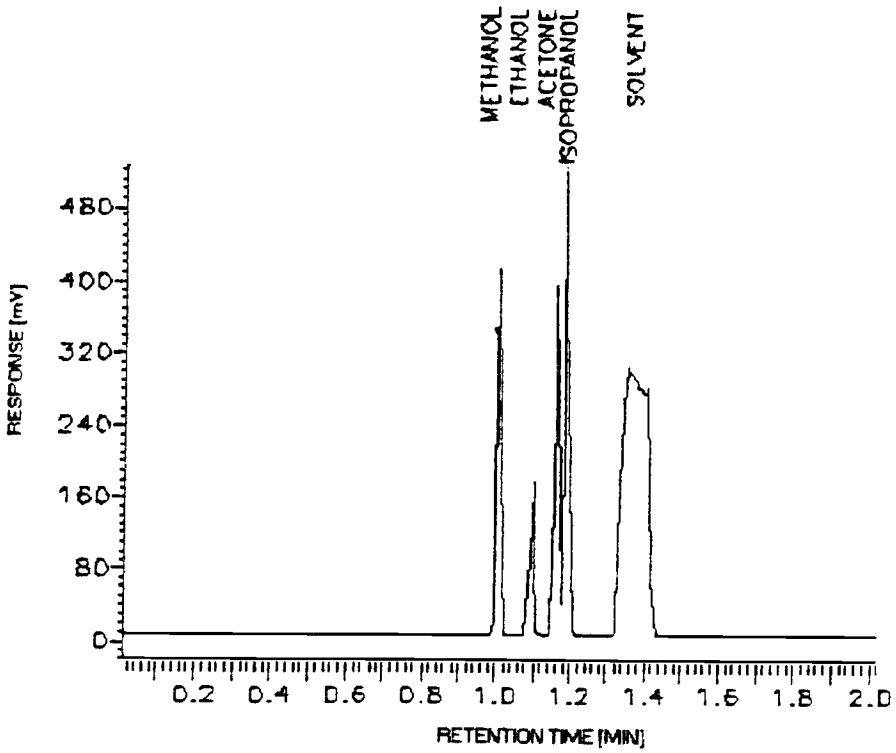
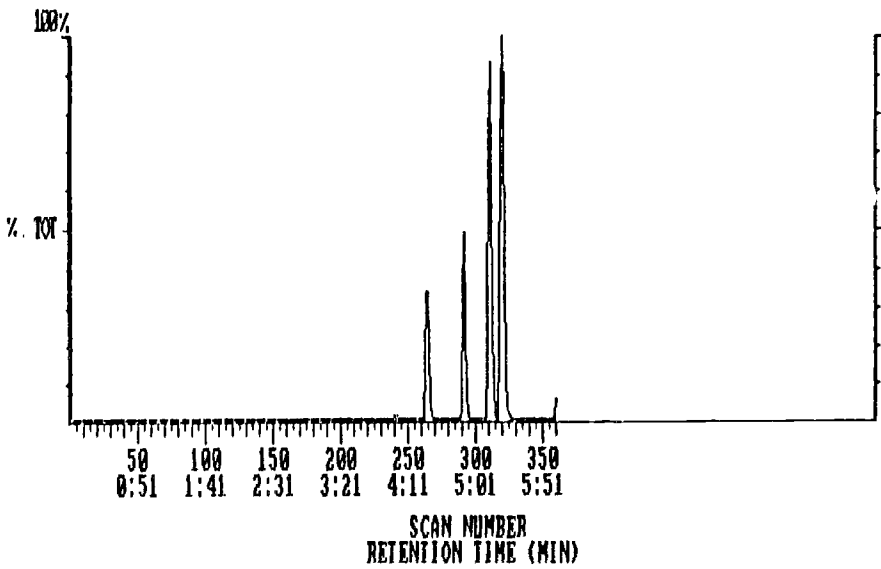FIG. 1—*Alcohol/acetone standard chromatogram, 25 meter column.*

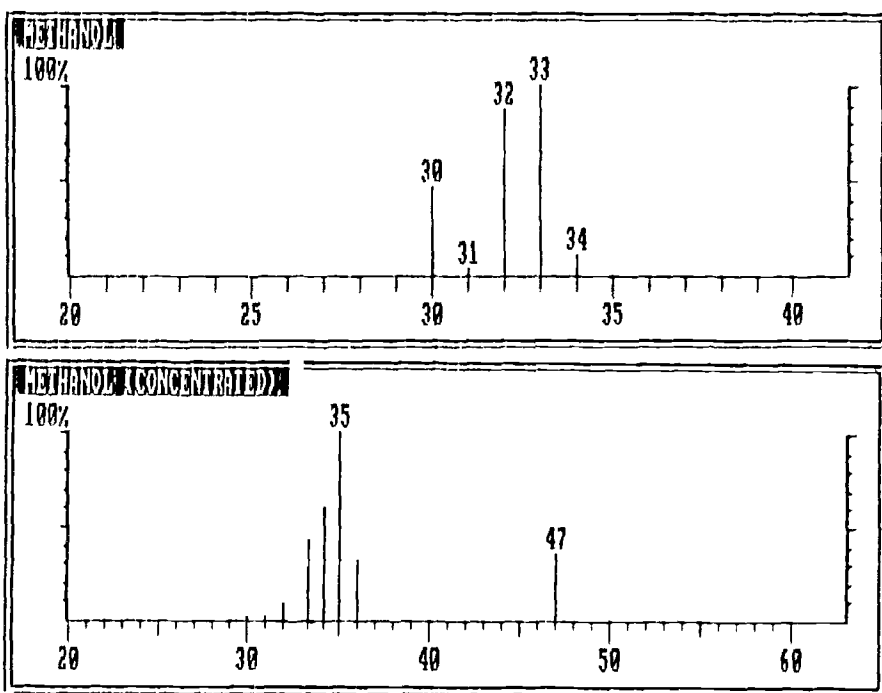FIG. 2—*Alcohol/acetone standard chromatogram, 50 meter column.*

FIG. 3—*ITD spectra for methanol.*

leg of a paper clip tied to a piece of cotton cord and suspended in a gallon can. All of the extractions took place in sealed 1 gallon metal paint cans maintained at 70°C overnight. The strip was then placed in a sample vial and eluted with 0.5 mL of carbon disulfide. Carbon disulfide was Certified Spectral Analyzed from Fisher Scientific.

Standards

Methanol was purchased from Fisher Scientific. 95% ethanol was purchased from a liquor store. 70% isopropanol was a generic brand of rubbing alcohol. Acetone was purchased from Fisher Scientific.

An alcohol/acetone standard was prepared by diluting 0.5 μL each of ethanol, methanol, isopropanol and acetone (2 μL total) to 10 mL with carbon disulfide. A neat spiking standard was prepared by mixing equal quantities of ethanol, methanol, isopropanol and acetone.

Gas Chromatography

Analyses of the extracts were performed on a Perkin-Elmer 900 Autosystem with a computerized data acquisition system and either a flame ionization detector (FID) or an ion trap detector (ITD). Operating parameters are listed in Tables 1 and 2.
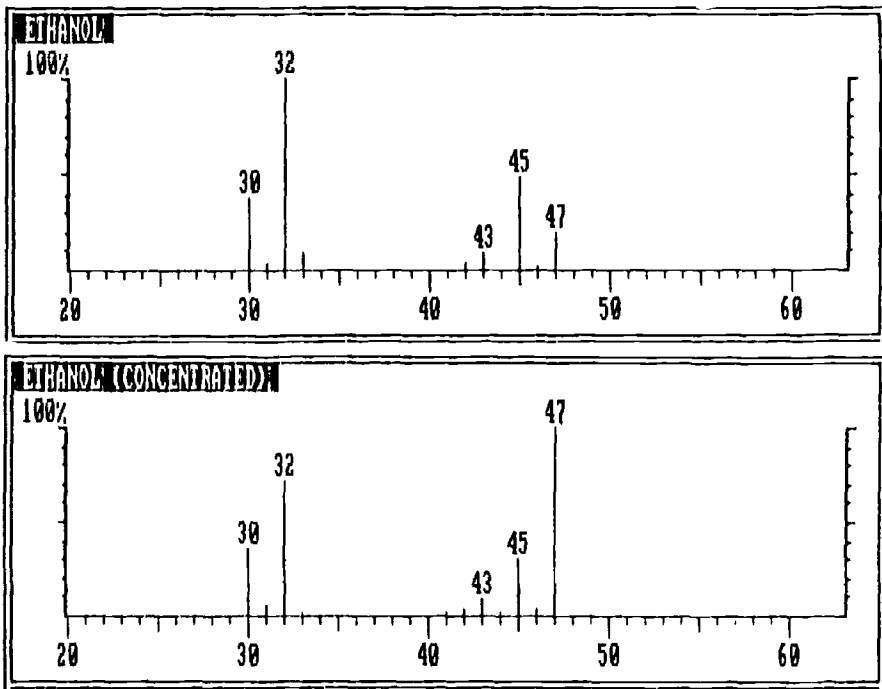
FIG. 4—*ITD spectra for ethanol.*

Burning of Matrix Spikes

In studies using common household materials and petroleum distillates, it was found that a 20 μL spike, burned for 30 seconds with a propane torch was recovered and detected using the carbon strip/GC-FID system. The 30 second time limit was based on the observation that 20 μL of flammable liquid burned independently for this amount of time. These conditions did not duplicate full scale fire environments and were not intended as such. The test design provided evaporation of the analyte under simulated fire conditions on materials typically found in a fire scene. This same procedure was applied to the tests using alcohols and acetone.

Results

Gas Chromatograph/Flame Ionization Detector

The alcohol/acetone standard was injected on the GC/FID. Methanol and ethanol achieved baseline separation from each other and from acetone and isopropanol. Acetone and isopropanol produced a split peak, which could not be resolved (Fig. 1). This less than ideal chromatography was sufficient to screen for volatile components eluting before carbon disulfide.

Gas Chromatography/Ion Trap Detector

The GC/ITD system differs from the GC/FID in several ways. The column is 50 meters in length and the linear velocity of the carrier gas is roughly half that of the GC/FID
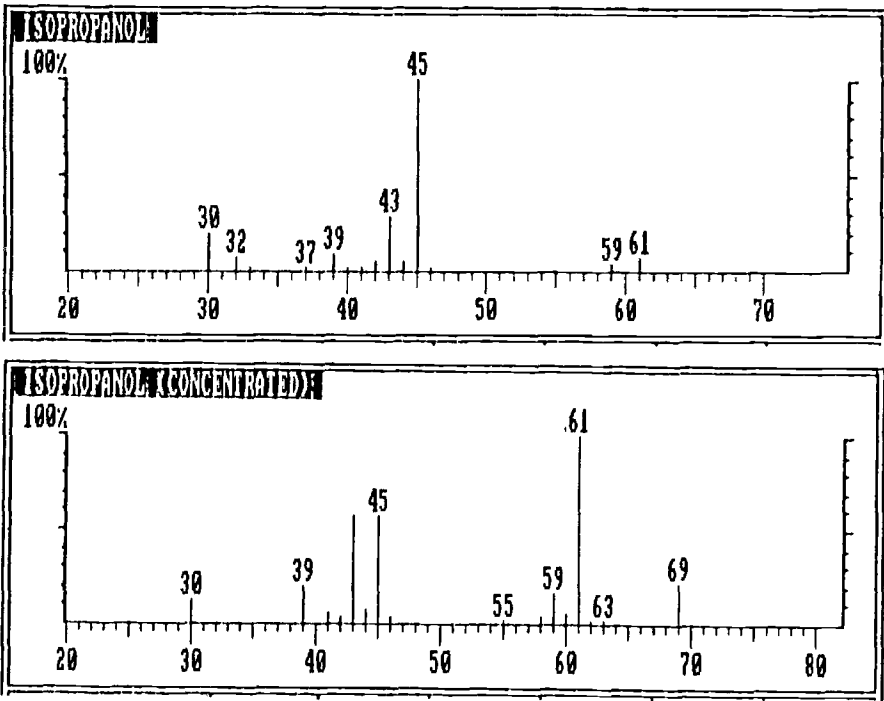
FIG. 5—*ITD spectra for isopropanol.*

system. The injector temperature and the column temperature are reduced. Baseline separation of isopropanol and acetone can be achieved with a 25 meter column using the same linear velocity, injector and oven temperatures, however the entire separation is complete in less than 3 minutes and the solvent peak may elute while the filament is on which would destroy the filament. The 50 meter column eliminated these problems and provided adequate separation (Fig. 2).

Samples enter the ion trap detector via a heated fused silica transfer line. The samples are then ionized by electron impact (EI) and all ions within the mass range of interest are stored. The ITD is then scanned sequentially from low to high mass causing the ions
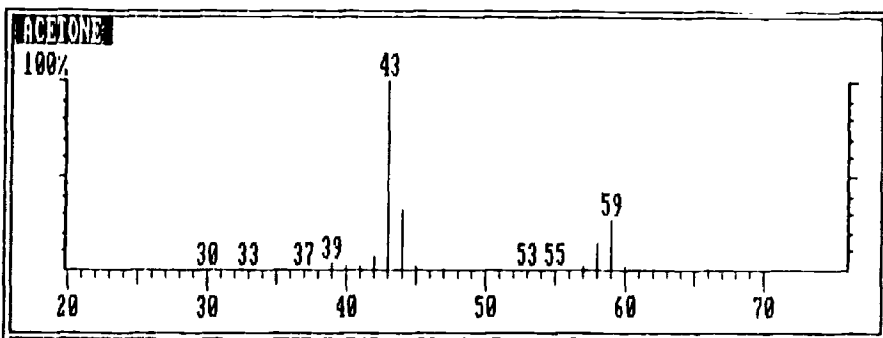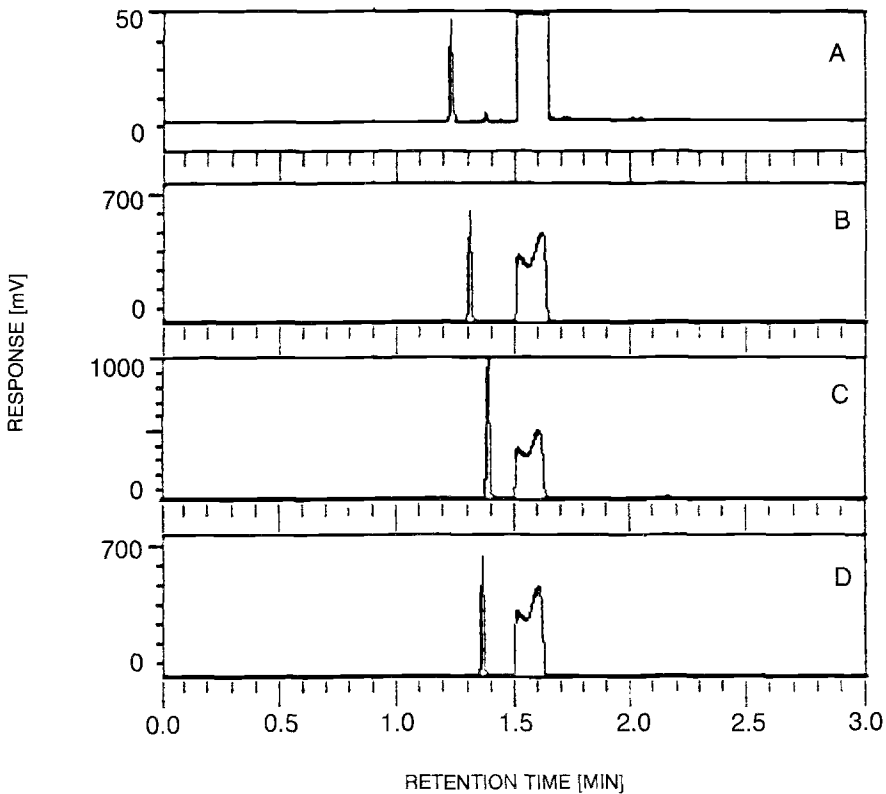

FIG. 6—*ITD spectrum for acetone.*

FIG. 7—*GC/FID of Kimwipe™ spikes:* a) *methanol,* b) *ethanol,* c) *isopropanol and* d) *acetone.*

to be ejected from the ion storage region. The ejected ions are detected by a conventional electron multiplier [8,9].

Formation of $(M + 1)^+$ ions is commonly observed in electron impact mass spectrometry as sample pressure is raised. In mass spectrometers depending on ion storage, such as ion traps, the problem is magnified since long residence times result in collisions. In addition, large sample sizes can lead to the production of significant concentrations of the $(M + 1)^+$ species [10,11]. Since the concentration of analyte recovered from fire debris extracts may vary significantly, a library which contained the spectra for each of the alcohols under conditions of low and high concentrations was created. The spectra are unique and reliable for identification (Figs. 3 to 6).

Test Samples

Kimwipes™ spiked with 0.5 μL of the analyte were extracted and analyzed using GC/FID. Ethanol, Isopropanol and Acetone were recovered on approximately the same level. Methanol was recovered at a lower level, but still within this laboratory's limits of detection (Fig. 7). These tests using Kimwipes™ demonstrated that adsorption/elution for alcohols and acetone, using the carbon strip and carbon disulfide, was possible. The detection limits were well below 0.5 μL in a gallon can for a given alcohol or acetone.

Carpet was spiked with 20 μL of an alcohol or acetone. The carpet was burned for 30 seconds by slowly moving the flame from a propane torch over the sample. These
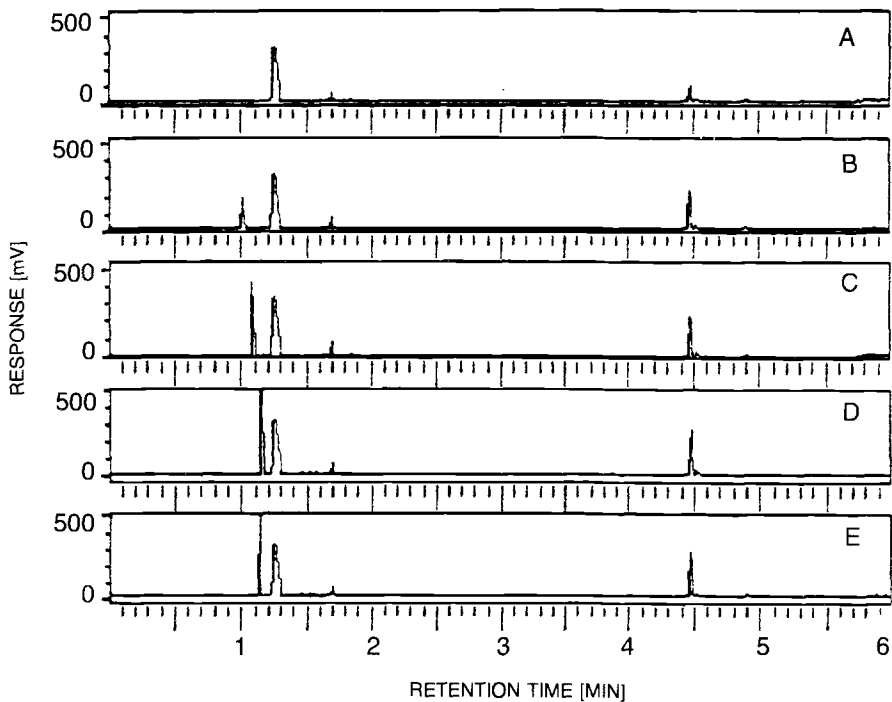
FIG. 8—*GC/FID of carpet spikes:* a) *blank,* b) *methanol,* c) *ethanol,* d) *isopropanol,* e) *acetone.*

samples were extracted and analyzed. The results were similar to the Kimwipe™ spikes with ethanol, isopropanol, and acetone yielding peaks off scale (over 1000 mV) and methanol being recovered at a lower level (Fig. 8).

The next set of carpet samples were spiked with 20 μL of kerosene and 20 μL of an alcohol or acetone. The carpet was burned, extracted and analyzed as described above (Fig. 9). The levels of alcohol and acetone recovered were reduced relative to the carpet spikes without kerosene.

Finally, different materials (carpet, wood, foam padding and vinyl flooring) were tested. Pieces of each of these materials were spiked with 100 μL of the spiking standard and burned for 30 seconds. Each set of 10 samples included a material blank and 9 spikes. In all cases the four analytes were recovered and confirmed with mass spectra.

Experimental House Fire

In an experimental house fire, conducted by the Florida State Fire Marshal's Fire and Arson Laboratory, a fire was set using 200 mL of commercial rubbing alcohol (70% isopropyl alcohol). The alcohol trail was approximately four feet long. The floor temperature directly beneath the carpet where the alcohol was poured was monitored by digital thermometers connected to thermocouple wire. At ignition the floor temperature was 22°C. This temperature rose to 123°C in 2.5 minutes and remained above 100°C for the next 2.5 minutes when the fire was extinguished with water.

Samples of the trailer areas and control samples were taken within two hours of burning, and secured in clean, unused metal paint cans for later analysis. The debris had
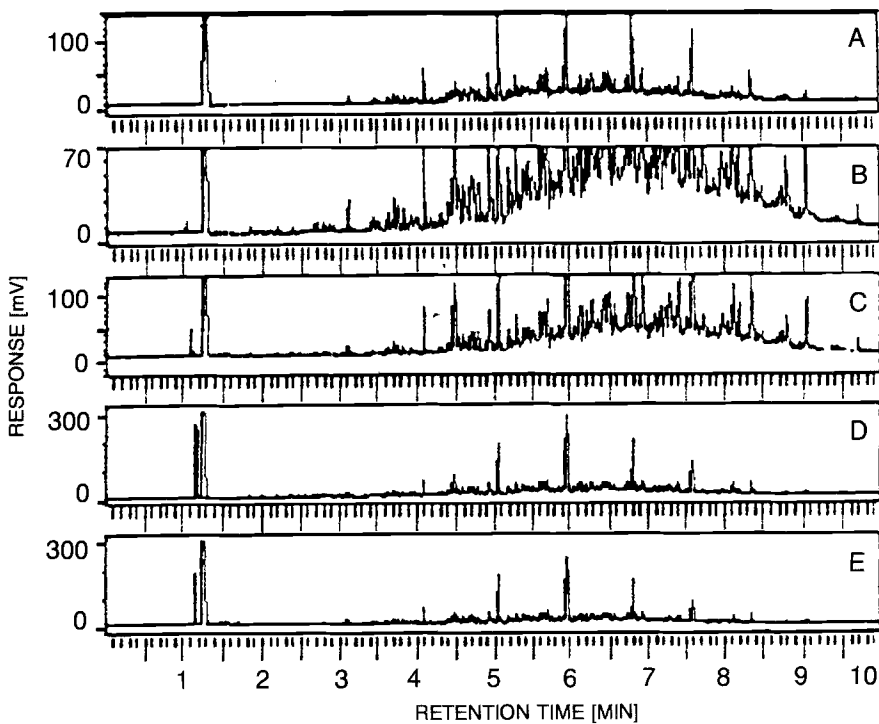
FIG. 9—*GC/FID of carpet/kerosene spikes:* a) *blank,* b) *methanol,* c) *ethanol,* d) *isopropanol,* e) *acetone.*

a significant odor of isopropyl alcohol, the presence of which was confirmed by GC/ITD analysis of the carbon strip extract (Figs. 10 to 12).

Discussion

In conjunction with this work, the Florida State Fire Marshal's Fire and Arson Laboratory has conducted a study of pyrolysis products. Pyrolysis products are chemical compounds recovered from a material matrix after burning. The actual chemicals produced by pyrolysis are dependent on the reaction conditions. These conditions vary from low temperature degradation to high temperature oxidation which may be further complicated by chemically active species containing sulphur, chlorine and nitrogen [12]. These conditions could readily produce low molecular weight alcohols and acetone.

The 30 second burn used on the test samples for this paper did not produce detectable levels of low molecular weight volatiles. However, low molecular weight alcohols and acetone have been detected from more extensive burning of laboratory samples and from samples taken at experimental house burns. Both the GC/FID of a carpet sample (Fig. 13) and the GC/ITD of a foam padding sample (Fig. 12) revealed the presence of acetone.

Comparison samples (similar substrate from the fire scene thought to be free of contamination) or reference samples (same substrate from a known source) may be used to identify the major pyrolysis products the sample produces in a fire. This information can be used to help interpret the results from questioned samples and to avoid reporting pyrolysis products as false positives.

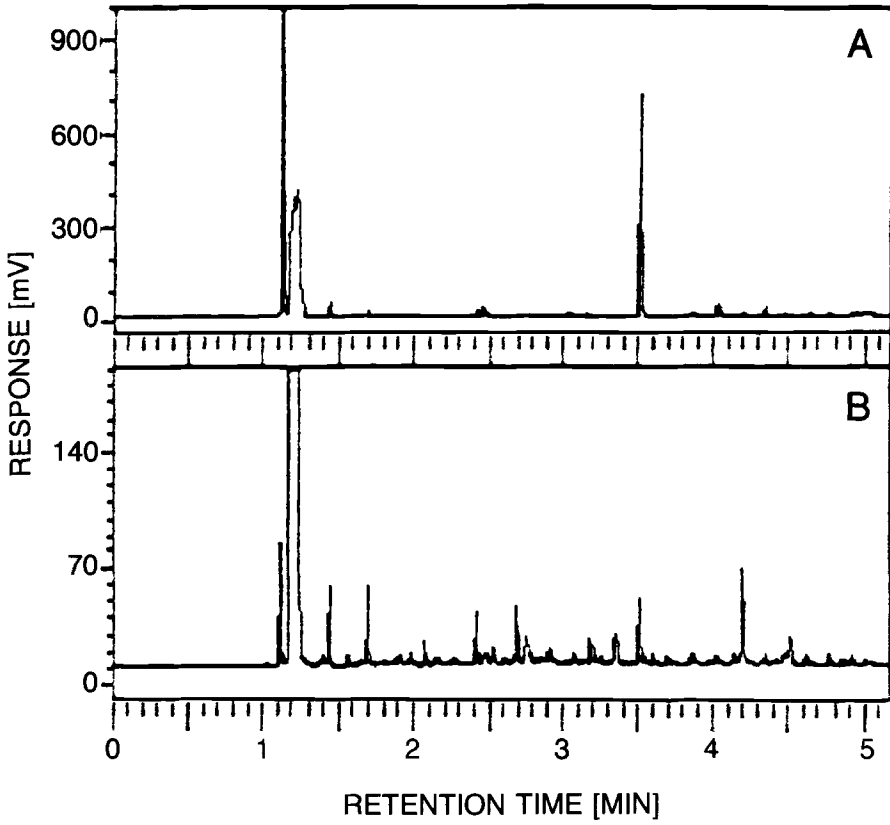The reduction in recovery of the alcohols and acetone in the presence of kerosene is

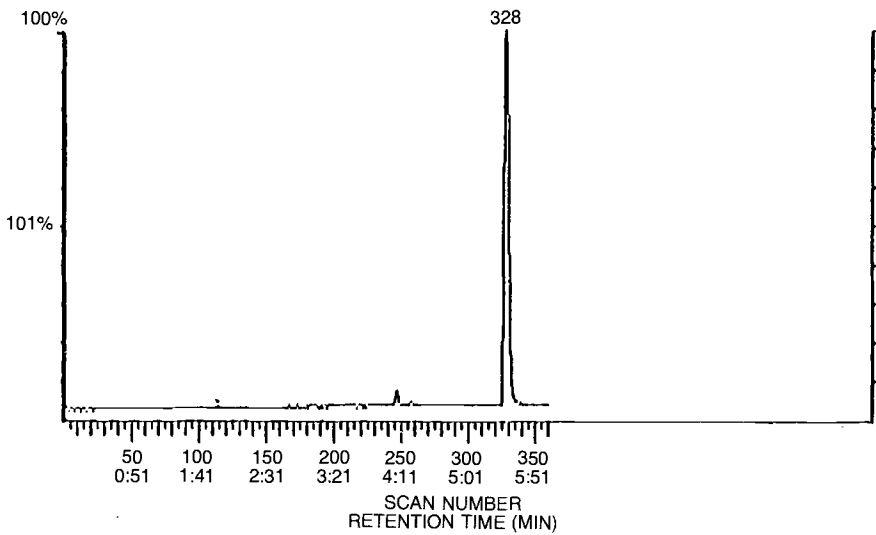FIG. 10—*GC/FID of control burn samples:* a) *carpet,* b) *foam padding.*

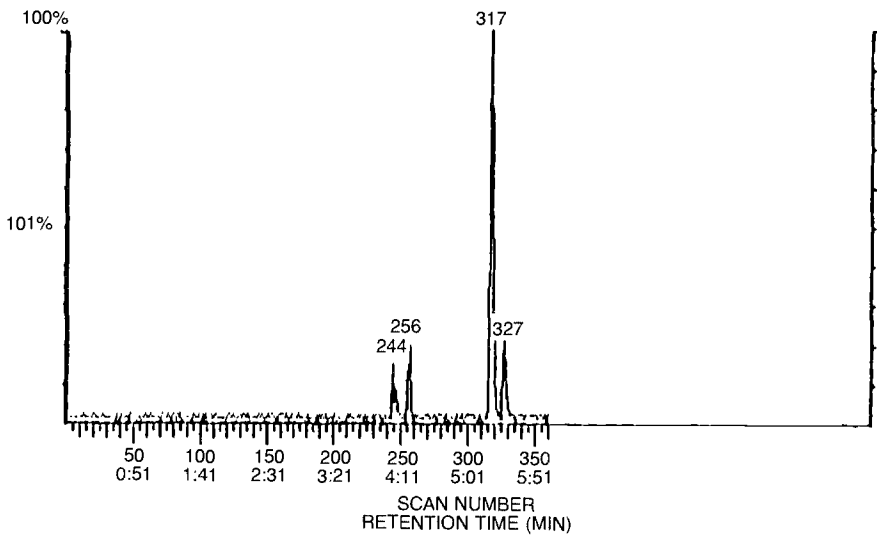FIG. 11—*GC/ITD of control burn sample A, carpet scan 328—isopropanol.*

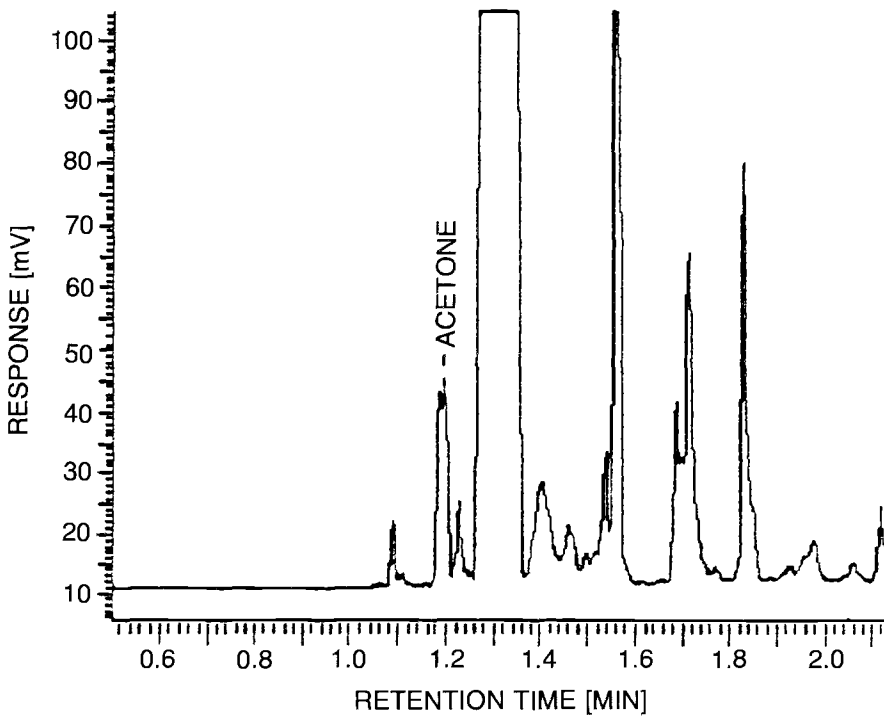FIG. 12—*GC/ITD of control burn sample B, foam padding scan 317—acetone and scan 327— isopropanol.*

FIG. 13—*GC/FID of burned carpet sample.*

a function of charcoal's greater affinity and efficiency for recovery of hydrocarbons over alcohols, and higher molecular weight compounds over lower molecular weight compounds. This phenomenon would occur with other petroleum products as well as pyrolyzates.

Adsorption is a function of the activity of the adsorbent material which may vary over a wide range of conditions and is not necessarily the same with different solutes [13]. In the case of activated carbon the amount of any one compound adsorbed is governed principally by its volatility or boiling point. The higher the boiling point the more strongly a compound is adsorbed. Other things being equal the boiling point rises with increasing molecular size [14]. Furthermore, activated charcoal is a nonpolar surface on which adsorption is the result primarily of London forces [15].

The Kimwipe™ spikes established the use of the carbon strip for recovery of trace levels of alcohol(s) and acetone. The carpet spikes with the kerosene standard established the potential for recovering a mixture of the more volatile alcohols and acetone combined with a petroleum product. It was established that the alcohols and acetone could be recovered from wood, vinyl flooring, foam padding and carpet which are common materials found in fire debris. Finally, isopropyl alcohol was readily recovered from a full scale fire environment where the temperature was in excess of 100°C.

The results from these tests provide clear methodology for routine screening and identification of methanol, ethanol, isopropanol and acetone from a single carbon strip extraction. This procedure is thus less time consuming and less invasive of the sample than multiple procedures, while providing adequate sensitivity.

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