

A Comprehensive Sample Preparation Scheme for Accelerants in Suspect Arson Cases

REFERENCES: Ren QL, Bertsch W. A comprehensive sample preparation scheme for accelerants in suspect arson cases. *J Forensic Sci* 1999;44(3):504–515.

ABSTRACT: This study represents a critical comparison of adsorbent based heated headspace methods for the enrichment of volatiles from fire debris. A dynamic and a static method, based on charcoal adsorption and solvent extraction are compared to the solid phase micro extraction (SPME) procedure. The SPME method has been optimized in respect to fiber type, sampling time, sampling temperature, analyte concentration and the effects of water. Collection efficiencies were evaluated for a variety of accelerant types, ranging from methanol to diesel fuel. The minimum detectable quantity for each of the methods is within an order of magnitude for most accelerant types. We propose a two step method based on SPME with two different fibers. Polar and water soluble accelerants such as ethanol and light petroleum distillates are most effectively enriched at low temperature on Carboxen™, a newly developed high capacity fiber which contains a carbon based adsorbent. Low volatility accelerants such as diesel fuel can be recovered on a methylpolysiloxane type fiber at elevated temperature. Limitations of currently used sample preparation methods are discussed.

KEYWORDS: forensic science, arson, fire debris, sample preparation, solid phase micro extraction, accelerants, gas chromatography/mass spectrometry

Arson is one of the oldest crimes committed by mankind. Fires are often examined to determine whether they result from natural causes or are incendiary in nature. After suppression of a fire, trained investigators usually examine a fire scene to determine its origin and cause. Guidelines for fire scene investigation have recently been formulated by the National Fire Protection Association (NFPA) (1). The laboratory examination of fire debris may involve both physical and chemical measurements. The vast majority of all cases, however, is limited to the search for residual volatile accelerants which may be commonly available fuels such as gasoline or kerosene (2), or off the shelf flammables such as paint thinners, charcoal lighter fuels, etc. The process is usually referred to as “arson analysis.” This term is a misnomer over because the word “arson” has a legal foundation. The laboratory does not determine if arson has been committed. It merely analyzes for ignitable liquids.

The forensic chemist attempts to identify the presence of residual flammable liquids which are sometimes referred to as accelerants in the presence of a vast amount of other volatiles. The bulk of these volatiles is derived from the pyrolyzed matrix or constitute other sources of interference. Most common flammable liquids

used as accelerants are derived from petroleum distillates that consist of a complex mixture of mostly hydrocarbon type substances. Liquids that are not based on petroleum feedstock, such as alcohols, acetone, or turpentine, can also be used as accelerants and therefore should also be considered. The analysis of flammables starts with a sample preparation step which is almost always followed by gas chromatography. The resulting gas chromatogram can be considered as a fingerprint-like depiction of the sample content. The chromatogram of the sample is compared to a series of chromatograms from accelerant standards. This process is usually referred to as pattern recognition. It relies on similarities in the composition of petroleum based distillates which produce characteristic patterns. The principle of pattern matching in fire debris was first demonstrated in 1959, within a few years after the introduction of the first commercial gas chromatographs (3). Meanwhile, a variety of methods and instruments have become available which can overcome some of the problems associated with background interferences. The sample can be subjected to a cleanup step (4) or undergo examination with a selective detector (5). Mass spectrometry (6) is especially useful to enhance the response of the target analytes. Whatever techniques are applied for the characterization of potential accelerant volatiles, one fundamental requirement stands out: the sample preparation method must be at least partially effective in isolating the target volatiles from the matrix. Poor sample recovery can, in many cases be compensated by efficient chromatography and sensitive detection but some material must be available to work with.

A wide variety of sample preparation methods have been introduced since about 1960 when sophisticated instrumental characterization methods, such as gas chromatography and various forms of spectroscopy became routinely available. Classical procedures such as distillation (7) and solvent extraction (8) were used primarily in the early years. More recent methods focus around the principles of heated headspace enrichment. These methods are based on adsorbents such as porous polymers (9) and especially carbon (10). The latter provides relatively effective solute retention which, on the other hand, necessitates the use of a solvent to recover the volatiles. Two variations, the so-called dynamic (or purge and trap) and static (or carbon strip) methods evolved. The dynamic version, the older of the two techniques, was originally adapted from environmental monitoring applications. Heated headspace from a container of debris is pulled through a bed of granular charcoal. This is followed by a solvent extraction step, usually using carbon disulfide (11). Interesting hardware capable of rapid thermal desorption was also developed but has not been widely adopted (12). The static method, which is conceptually simpler than the dynamic method, centered around a carbon strip which is simply suspended in the heated headspace over the debris

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(13). Solute recovery is also accomplished by solvent extraction. Recently, another version of the static method has been introduced. This procedure is called SPME (for Solid Phase Micro Extraction) (14). It differs from the conventional static method in the way the volatiles are collected and released. In SPME, the adsorbent is a thin polymer coated silica fiber which can be extended and retracted into a syringe type needle. The major advantage of SPME over its alternatives is its simplicity. It avoids solvents altogether and can be very rapid.

The heated headspace above a sample can also be sampled and injected into the GC without adsorbent based enrichment. This technique, referred to as direct headspace analysis is simple but lacks the necessary sensitivity since sample enrichment does not take place. Ignitable liquids have a wide range of physical and chemical properties. This makes it difficult, if not impossible, to find a single sample preparation method to encompass all potential materials. The liquids have been initially classified into 5 classes by ASTM 1287, for comparison. The classes were defined by chemical composition as well as physical properties such as boiling point ranges. The classification system has recently been expanded to accommodate accelerants which do not readily fit into any of the original 5 categories (15). Sample preparation technology has been periodically reviewed (16–19). Questions about the “sensitivity” of individual sample preparation methods are raised frequently. Direct comparisons have been made between conventional methods (20–22), but the results are inconclusive because these studies did not attempt to optimize the individual techniques. Recently, several studies have appeared on the optimization of the static (carbon strip) method (23,24). The performance of SPME based methods has also been critically evaluated (25,26). The data show that SPME is indeed an attractive alternative to carbon based enrichment methods but significant discrimination against high volatility compounds, i.e., light and medium range distillates, is evident (27). The problem of inadequate retention of low boiling point substances has recently been overcome with the introduction of new fiber technology (28). It appears that SPME sensitivity can compare favorably to the carbon strip method (25–30). Detection limits in the low ppm range have been reported for some accelerants (26).

Most analysts agree that the recovery of an ignitable liquid is strongly dependent on the properties of the analyte, i.e., conditions suitable for a diesel fuel are inadequate for ethanol and vice versa. The successful outcome of an analytical procedure is thus critically dependent on the selection of an appropriate sample preparation method and the conditions under which it is applied. Many forensic chemists participate voluntarily in a series of round robin tests. Proficiency testing is a requirement for laboratory accreditation by the American Society of Crime Laboratory Directors and by the American Board of Criminalistics. The tests are designed to let each laboratory examine its strengths or weaknesses and compare its performance to other laboratories (31). Participants freely select analytical methodologies and report their findings from the simulated arson samples. Some results from the last nine years have recently been summarized (32). In general, analysts performed best for samples containing common medium boiling range distillates, such as gasoline or kerosene. In cases where the recovery of mixtures of accelerants containing both low and high boiling point range distillates was required, laboratories fared worse. The 1995 test which involved the analysis of a mixture of gasoline and diesel fuel is a good example. Participants were provided with four samples: two liquids and two solids. One of the solids was a simulated arson sample consisting of a mixture of gasoline and diesel fuel on

a cloth matrix. The liquids were aliquots taken from “two cans found in the suspect’s apartment.” One of them, the gasoline/diesel fuel mixture was used to prepare the simulated arson sample. The task was to (1) determine whether the matrices contained an accelerant, (2) provide a classification, if positive for an accelerant, and (3) look for a possible match to one or both liquids. Eighty-eight percent of the analysts had no trouble with the neat mixture from the container but more than half could not identify the same accelerant mixture after recovery from the matrix. The problems were clearly due to discrimination in the sample preparation step.

Sample discrimination is undoubtedly a major problem in all heated headspace methods. Discrimination effects of this type can, in principle, be overcome but there are practical limitations. If a sample is heated too strongly, pyrolysis of partially combusted matrices will start to compete with the thermal desorption of the adsorbed accelerant volatiles (19). Solvent extraction and supercritical fluid extraction do not subject the sample to thermal stress but cause other complications (33). The solvents remove unrelated soluble constituents from matrices and unnecessarily complicate chromatographic patterns. Solvent evaporation which is frequently used to counteract dilution effects can also be detrimental. It is necessary to obtain adequate sensitivity but there is always some loss of low boiling range compounds.

The analysis of water soluble ignitables such as ethanol and acetone is particularly difficult because of the similarity of these solvents to the major interference in fire debris, water. Another problem with the recovery of oxygenated solvents is their high volatility. Little information is available on the isolation of these potential accelerants and their occurrence in suspect arson cases. Some data from the state arson laboratories from the States of Ohio (34) and Florida (35) indicate that 1 to 3% of all detected accelerants are based on such low molecular weight alcohols and ketones. A Swedish study reported that ethanol accounted for almost 10% of all positive cases (36). One may ask whether the general lack of reporting for these fluids reflects infrequent use or is due to a lack of suitable sample preparation techniques. There is, of course also the possibility that they are washed away in the course of fire fighting. Direct headspace analysis is feasible for these highly volatile water soluble components but it lacks sensitivity because no solute enrichment takes place. It is surprising that the static (carbon strip) method is effective even though the enrichment yield seems to be rather modest (37). The development of routine methods for alcohols is clearly an area where improvement is needed.

Materials and Methods

Volatiles were recovered from a fire debris sample using static headspace, dynamic headspace and SPME. Gas chromatography and gas chromatography/mass spectrometry were used to evaluate accelerant recovery. The SPME method was optimized. The effects of fiber type, sample collection interval, sample collection temperature, analyte concentration and presence of water on the recovery of individual accelerants were determined.

Materials

A stock solution of a wide range accelerant standard was prepared by mixing equal volumes of six liquids representing accelerants from class 0 to class 5.

- Class 0: Miscellaneous, ((1:1:1) methanol, ethanol, acetone)
- Class 1: Light Petroleum Distillate (Coleman fuel)
- Class 2: Gasoline (40% evaporated gasoline)
- Class 3: Medium Petroleum Distillate (mineral spirits)

TABLE 1—SPME fibers.

Stationary Phase	Film Thickness (d_f)
Polyacrylate (PA)	85 μm
Carbowax®/Divinylbenzene (CW/DVB)	65 μm
Polydimethylsiloxane (PDMS)	100 μm
Divinylbenzene/Polydimethylsiloxane (DVB/PDMS)	65 μm
Carboxen™/Polydimethylsiloxane (Carboxen/PDMS)	75 μm
Carboxen™/Divinylbenzene/Polydimethylsiloxane (Carboxen/DVB/PDMS)	85 μm

Class 4: Kerosene

Class 5: Heavy Petroleum Distillate (diesel fuel)

The oxygenated solvents of class 0 were purchased from Fisher Scientific (Fairlow, NJ). All other liquids in the standard were obtained from local gasoline service stations or stores. The weathered gasoline was prepared by evaporation of the liquid to the desired volume in a fume hood. Typically, 10 μL aliquots of the neat standard were spotted onto Kimwipes® (Kimberly-Clark, Roswell, GA) and introduced into quart size paint cans equipped with modified lids. The cans were obtained from a local paint store. The actual fire debris sample containing burnt carpet and carpet pad was received from a certified fire investigator. The stock standard was diluted from 5 μL to 1 mL with carbon disulfide (J. T. Baker, Inc., Phillipsburg, NJ) for direct injection by GC. Distilled water was used to study the effect of water on recovery.

The SPME holders and fibers for manual operations were obtained from Supelco (Bellefonte, PA). The fibers are listed in Table 1. A 100 μL Luer tip syringe, obtained from Hamilton Co. (Reno, NV) was used to prepare the micro charcoal trap for the dynamic headspace enrichment method (11). DFLEX® (Diffusive Flammable Liquid Extraction) carbon strips (Albrayco Laboratories, Inc., Cromwell, CT) were used for the static enrichment experiments.

Methods

Sample Preparation

Each individual quart size can was placed into a heating mantle. A hole was drilled into the lid to accommodate the micro charcoal trap (11). The micro charcoal trap consisted of a 100 μL glass syringe which was loaded with 5 mg of granular charcoal. The charcoal was held in place by two small plugs of silanized glass wool. A thermocouple probe (Omega Engineering, Inc., Stamford, CT) was inserted through a second opening in the lid to monitor the temperature. The trap was connected via a rubber hose to a source of vacuum. A metering valve was set to regulate the headspace withdrawal rate. Typical collection volume, time and temperature were 2 L, 15 min and 80°C, respectively. The air, drawn over the trap was continuously replaced by laboratory air. Blank checks were carried out periodically to verify that the background remained acceptable. The release of the adsorbed volatiles was effected by addition of 20 μL of carbon disulfide. The extract was saved in a sample vial and a 1 μL aliquot was injected into the GC.

Static Headspace Enrichment

One half of the size of the carbon-strip form each DFLEX® device, i.e., a strip of about 10 mm \times 8 mm was hung in the

headspace above the sample by a paper clip attached to a string (13). The can was sealed and placed in an oven at 90°C for an overnight period. Care was taken to ensure that the lid was firmly attached to counteract the effect of pressure buildup. The can was then allowed to cool to room temperature for 30 min. The carbon strip was divided into 4 slices and placed into a tipped narrow bore glass vial. After the adsorbent was soaked in 100 μL of carbon disulfide for 10 min, a 1- μL aliquot of the carbon disulfide extract was introduced into the GC.

SPME Headspace Enrichment

The samples, placed inside quart size cans were also heated in a heating mantle. The lid was modified with a GC type septum to accommodate SPME needle insertion. Headspace temperature was measured with the thermocouple at the heating mantle/can interface. The fibers were exposed to the sample headspace for a variable period of time and then inserted into the GC injector port for the desorption of the analytes. The fibers were initially conditioned in the injector port according to the manufacturer's recommendation before first use and thermally cleaned for 10 min between consecutive uses. Sample temperature, sampling time, sample concentration and water content were varied.

Gas Chromatography and Gas Chromatography/Mass Spectrometry

Two GC-FID instruments were used. Instrument 1, Table 2 was a model HP 5890 GC (Hewlett Packard, Wilmington, DE) with a 15 m \times 0.25 mm \times 1 μm DB-5 column (J&W Scientific, Inc., Folsom, CA). The data obtained was analyzed using Chrom Perfect software (Justice Innovations, Inc., Palo Alto, CA). Instrument 2, Table 3 was a HP 6890 GC (Hewlett Packard, Wilmington, DE)

TABLE 2—Instrument 1 HP 5890 GC/FID parameters.

Injector and detector temperature	260°C
Oven program for the actual arson sample	Initial 40°C, 1 min, ramp 10°C/min, to 270°C, 5 min.
Oven program for the simulated arson samples spiked with the wide range accelerant standard	Initial 30°C, 1 min, ramp 15°C/min to 270°C, 4 min.
Split/splitless mode	All liquid injections used the split mode, split ratio 20:1. SPME method used splitless mode: The purge was turned on 1 min after injection.
Column	15 m \times 0.25 mm \times 1 μm , DB5.
Column gas flow	He, 1 mL/min.

TABLE 3—Instrument 2-HP 6890 GC/FID parameters.

Injector and detector temperature	260°C
Oven program	Initial 40°C, ramp 30°C/min, to 280°C.
Split/splitless mode	All liquid injections used the split mode split ratio 20:1. SPME method used splitless mode except where stated otherwise: The purge was turned on 1 min after injection.
Column	5.5 m \times 0.25 mm \times 0.25 μm , HP1.
Column gas flow	He, 1 mL/min.

equipped with a short $5.5 \text{ m} \times 0.25 \text{ mm} \times 0.25 \text{ }\mu\text{m}$ column (HP-1, same manufacturer). The GC conditions for both instruments are listed in Tables 2 and 3, respectively. The identities of some of the peaks were confirmed by GC/MS under similar conditions. The instrument used was a bench top instrument (GCD, Hewlett Packard, Wilmington, DE). The column and chromatographic conditions were similar to those of instrument 1.

Results and Discussion

The selection of optimal sample preparation methodology is often considered the most critical step in the analysis of fire debris for flammables. Currently used procedures which have been formulated into several ASTM documents rely on a variety of different principles, including direct (heated) headspace, dynamic headspace concentration, passive headspace concentration, steam distillation and solvent extraction. Every sample preparation method has inherent weaknesses, depending on accelerant volatility and polarity. At present, enrichment methods based on carbon adsorbents are most widely used (32). They work particularly well for intermediate volatility accelerants such as medium petroleum distillates (MPD), gasoline, and kerosene, but show a marked deficiency toward low boiling distillates and polar, water soluble ac-

celerants. Little is known about recovery yields of the methods. Meaningful comparison of the relative sensitivities of individual methods requires that each procedure is reasonably optimized.

Many of the methods reported in the literature are based on the use of relatively large amounts of adsorbent and extraction solvent. It is not uncommon to read that as much as one milliliter of solvent is used for recovery of adsorbed volatiles. Solvents, especially those of low molecular weight expand significantly when vaporized. Most common GC inlets do not accept more than about one microliter of the extract. Sample utilization is therefore often unnecessarily low. Some efforts have been made to adapt fire debris sample preparation procedures to the requirements of capillary GC. Static (24) and dynamic (11) enrichment methods have been developed that end up with only a few microliters of the extract. Figure 1 compares the profiles of a fire debris sample containing partially evaporated gasoline. The sample was prepared by SPME, static, and dynamic enrichment, respectively. Detector sensitivity is identical in each run. It is apparent that the recovery of the volatiles is comparable under the conditions of these experiments. The primary purpose of this demonstration is to show that similar chromatograms can be obtained for different sample preparation procedures. It does not necessarily indicate the best sensitivity which can be achieved for each individual method. The definition

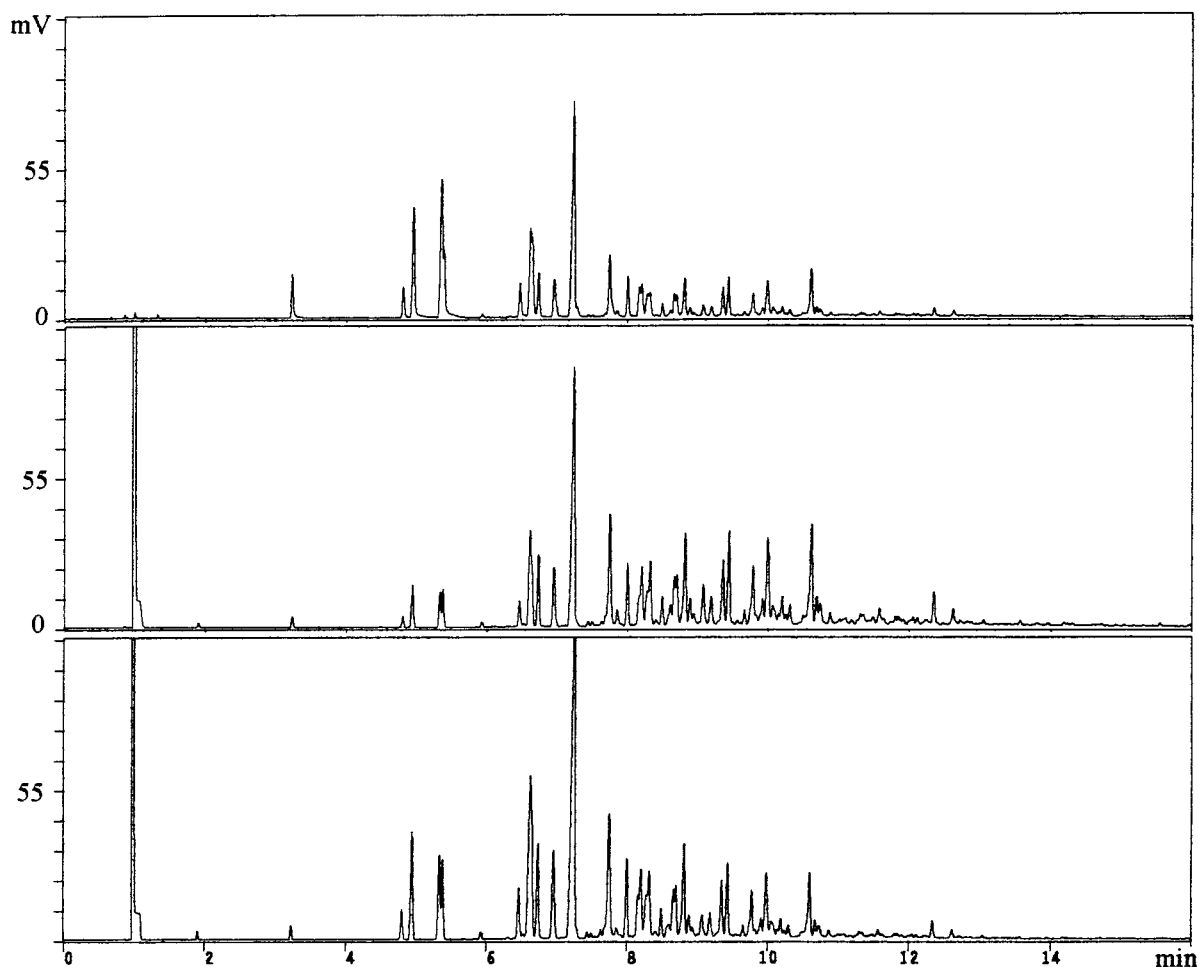


FIG. 1—Comparison of recovery by 3 heated headspace enrichment methods. Sample: Fire debris sample, gasoline on a charred matrix of carpet and carpet padding. (Instrument 1). Top: SPME, Carboxen/PDMS fiber (70°C , 3 min extraction), Middle: Static headspace enrichment (90°C , 16 h extraction), and Bottom: Dynamic headspace enrichment (80°C , 15 min extraction).

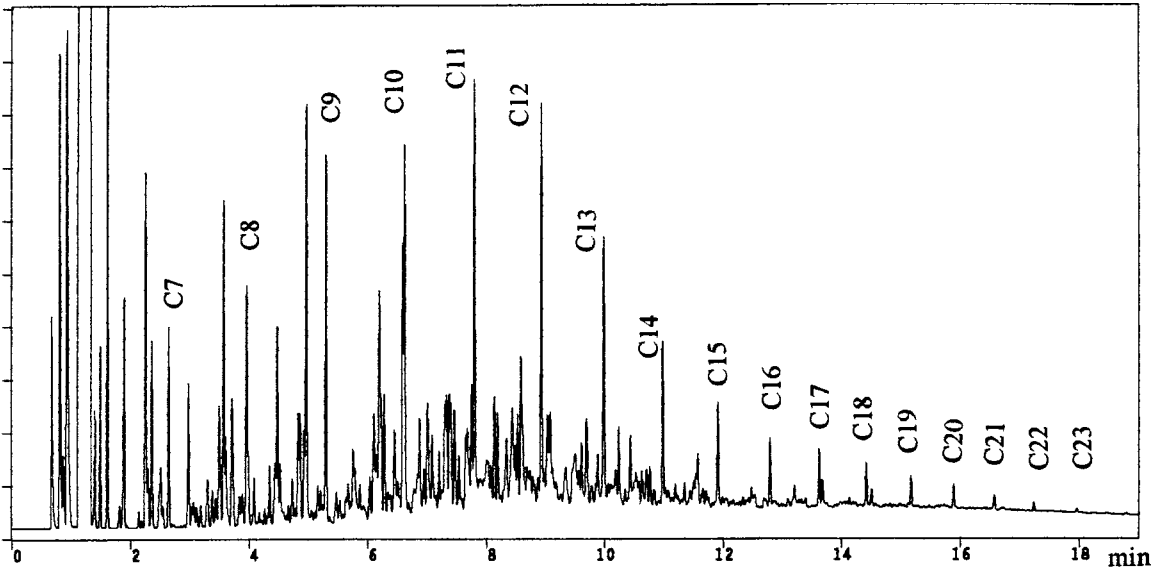
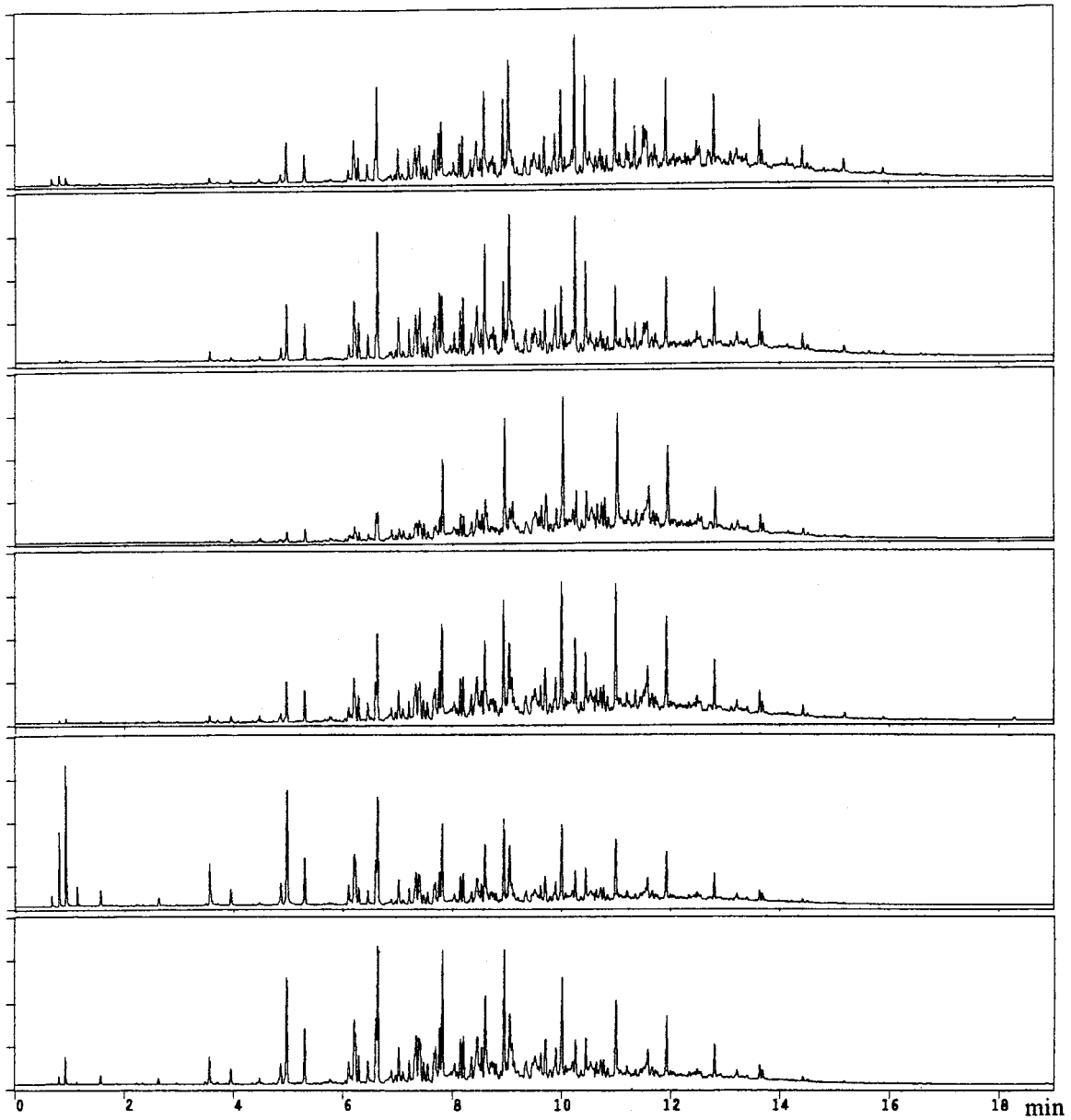


FIG. 2—Chromatogram of the wide range accelerant standard. (Instrument 1).



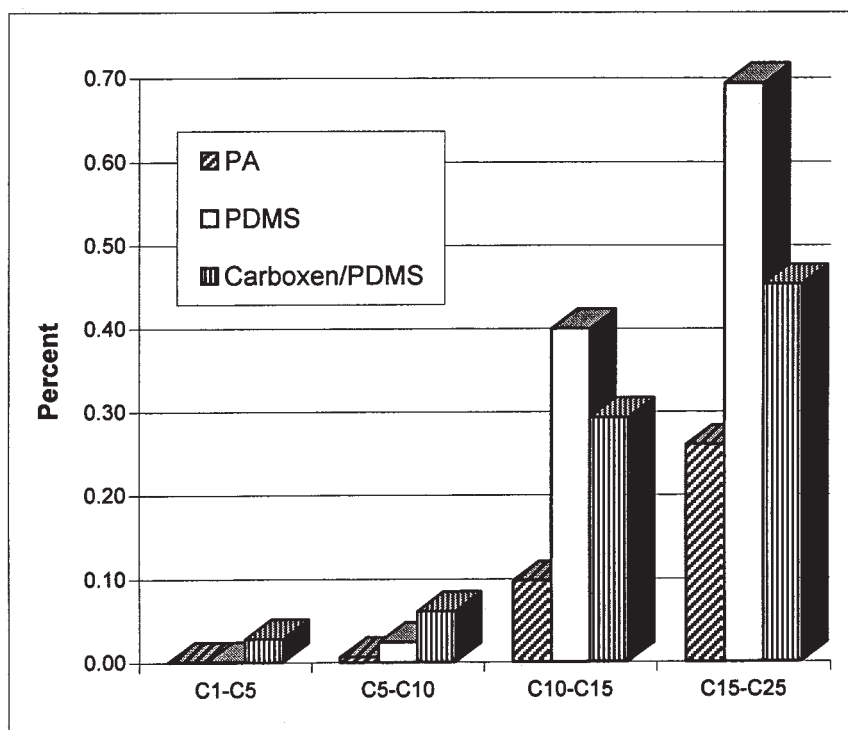


FIG. 3b—Comparison of recovery efficiency as a function of volatility for different fiber types. Headspace temperature 80°C. Collection time 3 min. Data from instrument 2.

of the term sensitivity is more complicated in fire debris analysis than in most other analytical applications. The identification of an accelerant is seldom limited by detector sensitivity. The chemical noise introduced by background interferences is usually much more serious. Inadequacies in representative collection of the volatiles from the debris sample presents another major problem. It is not surprising that different adsorbents selectively enrich components depending on accelerant volatility and polarity. Figure 2 represents the chromatographic profile of the composite wide boiling range standard. The three peaks preceding the solvent peak in Fig. 2 correspond to methanol, ethanol and acetone, respectively. All major accelerants listed in ASTM E-1387-95 (15) are included.

Figure 3a compares the recovery of compounds on 6 different SPME fibers at 80°C. The chromatographic envelopes of the four fibers shown in the top chromatograms are similar in appearance. Some peaks are selectively enhanced with the polar fibers. These components have been identified by mass spectrometry as naphthalene and alkylnaphthalenes. All fibers show a weakness for the recovery of high volatility compounds. There is quite a difference between the fiber generated chromatograms and the standard. This can be explained by the low temperature of the sample. The volatility of the carbon 20 to 25 range is too low for effective recovery at a temperature of only 80°C. The water soluble compounds in the sample, methanol, ethanol and acetone, are barely visible using the top four fibers. It is apparent that these substances, as well as low to medium range accelerants are not effectively enriched. Only the Carboxen™ fibers, in particular the Carboxen/PDMS fiber show acceptable enrichment for high volatility compounds. This is due to

the porous structure of the carbon particles embedded in the fiber (28). Carboxen™ however, also has specific drawbacks. Elution of components higher than about C₁₈ is incomplete. This situation does not change much at higher extraction temperatures. It is clearly unsuitable for the enrichment of a high boiling range distillate such as diesel fuel.

The solution to the dilemma is obvious. Recovery of the high volatility end of the accelerant spectrum, i.e., water solubles to medium range distillates is effective on Carboxen™ fibers at a relatively low temperature. Any one of the other fibers can be used to enrich medium to high molecular weight accelerants. A temperature of around 100°C is required (38). PDMS should be preferred over the other fibers because it produces the lowest distortion of the profile. The PDMS chromatogram is most comparable to the chromatogram from the liquid standard. The chromatogram is also the most intense because the large film thickness of the fiber provides high sample capacity. Fortunately, there is considerable overlap between the fibers for medium volatility accelerants. Figure 3b provides another picture of recovery as a function of volatility. Only three fibers are shown, for simplicity. The five basic accelerant classes have been broken down into four ranges. C₁–C₅ corresponds to the water soluble accelerants. C₅–C₁₀ is representative for accelerants up to and including light petroleum distillates. C₁₀–C₁₅ is indicative of medium boiling range distillates, such as gasoline and kerosene. C₁₅–C₂₅ reflects the properties of high boiling range distillates such as diesel fuel. As discussed earlier, SPME methods show discrimination of high volatility components. Carboxen™ is the only fiber capable of acceptable re-

FIG. 3a—Comparison of recoveries for 10 μL of the wide range accelerant standard by different SPME fibers. From top to bottom: PA, CW/DVB, PDMS, DVB/PDMS, Carboxen/PDMS, Carboxen/DVB/PDMS, refer to Table 1. Headspace temperature 80°C. Collection time 3 min. (Instrument 1, response normalized). Note: The Carboxen/DVB/PDMS fiber is experimental.

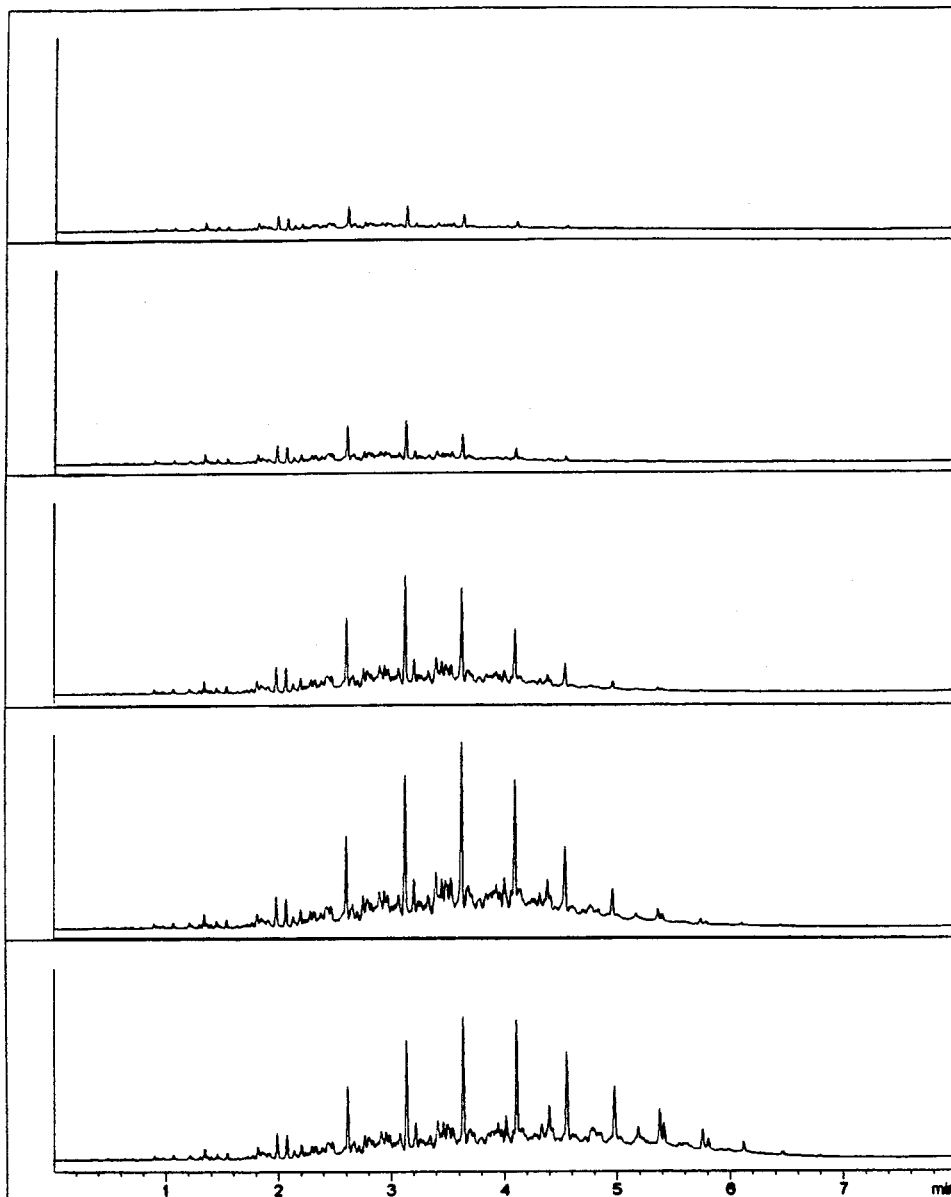


FIG. 4—Recovery as a function of fiber sampling time. From top to bottom: 1 s, 5 s, 50 s, 3 min and 20 min. 10 μ L wide range accelerant standard, PDMS fiber at 80°C (Instrument 2, split ratio 40:1).

covery in the high volatility range. Although the polyacrylate fiber has a relatively favorable recovery in the high boiling range, its absolute yield is low.

SPME is considered an equilibrium method. It is important to determine at what rate the equilibrium is established. Figure 4 shows the effect of different sampling times on the PDMS fiber. It appears that equilibrium is reached in approximately 3 min. Figure 5 amplifies an additional feature which may not be readily apparent in Fig. 4. There is a marked shift toward higher molecular weight compounds as the fiber exposure time increases. This observation can be explained by the displacement of lighter by heavier components. It should be noted that the chromatograms in Fig. 4 were generated in less than 8 min on a short column of only about 5 m. Chromatographic resolution is lower than in the chromatograms of Fig. 5 which was obtained on a longer column. Nev-

ertheless, the accelerant pattern remains easily recognizable on the short column. The chromatograms in Fig. 5 are normalized to emphasize the shift of the pattern. It should be noted that the intensity of the top chromatogram which corresponds to an exposure time of only 5 s is lower than that of the middle chromatogram by a factor of approximately 10. The data point out that collection of low molecular weight compounds is favored by a brief fiber exposure time.

The temperature of the headspace has a strong effect on both the sample profile and the amount of volatiles which can be retained on the fiber. Figure 6a compares recovery yields on the PDMS fiber for the wide range standard at temperatures of 80°C, 100°C and 120°C. Solute retention decreases markedly as temperature increases. Figure 6b demonstrates a subtle shift toward high molecular weight range substances, as temperature increases. The pattern

of the bottom chromatogram is extended by about four methylene units. The C₂₀ to C₂₄ n-alkane region which is diagnostic for diesel fuel is clearly visible. Obviously, both an increase in sample time and temperature result in a shift to higher masses. Figure 7 shows the recovery of different amounts of accelerant added to the matrix. The detection limit under the conditions of the experiment is around 0.1 μ L of the standard. As discussed previously, the minimum amount of an accelerant which has to be present for positive identification seldom depends on the quantity of the accelerant in the fire debris. It is usually determined by background interferences. Pyrolysate interferences cannot be avoided but they can be minimized. The hardware which is used to heat the sample also has some influence on the generation of artifact volatiles. Gradual heating in a heating mantle is preferred. Hot plates can cause local overheating of the bottom of the container, leading to increased artifacts.

The sensitivity of a method does not only depend on recovery efficiency but also on instrumental parameters, in particular detector sensitivity and details of sample introduction. The conditions under which the volatiles are desorbed from the fiber and introduced into the capillary column are also important. Thermal desorption from the fiber is essentially instantaneous. A reduction of the split ratio or use of splitless conditions obviously produces further improvement in sensitivity. Sample introduction by split injection is inher-

ently less complicated than the splitless mode. It was used for all liquid injections. The chromatograms shown do therefore not represent the best sensitivity which can be achieved.

Most fire debris samples contain copious amounts of water. It is of interest to examine how recovery of accelerants is affected by the presence of different quantities of water. Figure 8 shows that water has only a moderate influence. A slight shift occurs toward higher masses. One of the strengths of SPME based methods is that it can be applied to gas phase volatiles as well as to solutions. Accelerants can be directly recovered from water, if necessary (26).

Conclusion

At the present time, many analysts still rely on the use of a wide variety of sample preparation methods, depending on the ignitable fluid of interest. They may apply direct headspace sampling for alcohols and light boiling range distillates, an adsorbent based method for intermediate range volatiles, and solvent extraction for high boilers. The proposed two-step procedure greatly simplifies sample preparation for the full range of accelerants encountered in practice. SPME based sample preparation methods have not been widely explored by forensic chemists. Hopefully, further experimentation will lead to wider acceptance.

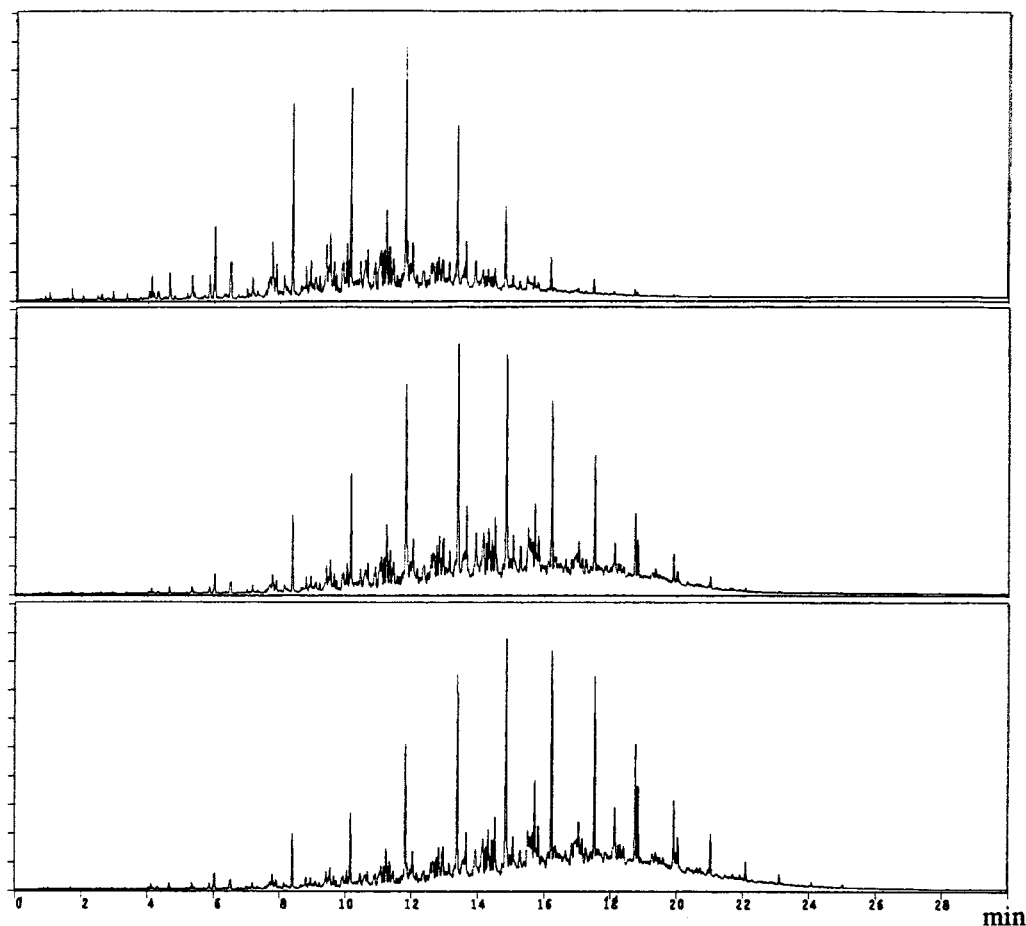


FIG. 5—Effect of sampling time. From top to bottom: 5 s, 3 min, 20 min. 10 μ L wide range accelerant standard, PDMS fiber at 80°C (Instrument 1, response normalized for each chromatogram).

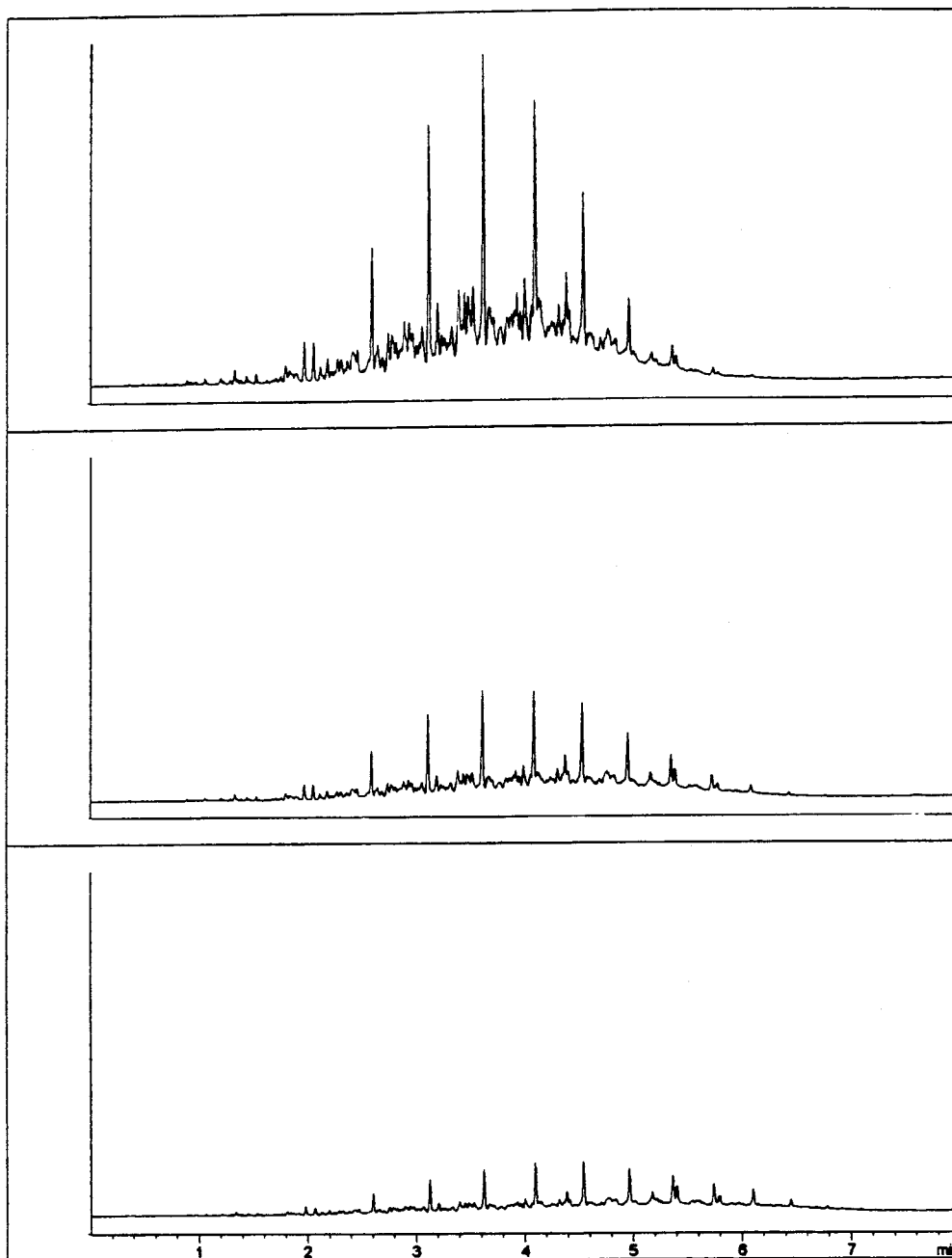


FIG. 6a—Effect of sampling temperature. From top to bottom: 80°C, 100°C, 120°C. 10- μ L wide range accelerant standard, PDMS fiber. Collection time 3 min (Instrument 2, split ratio 40:1).

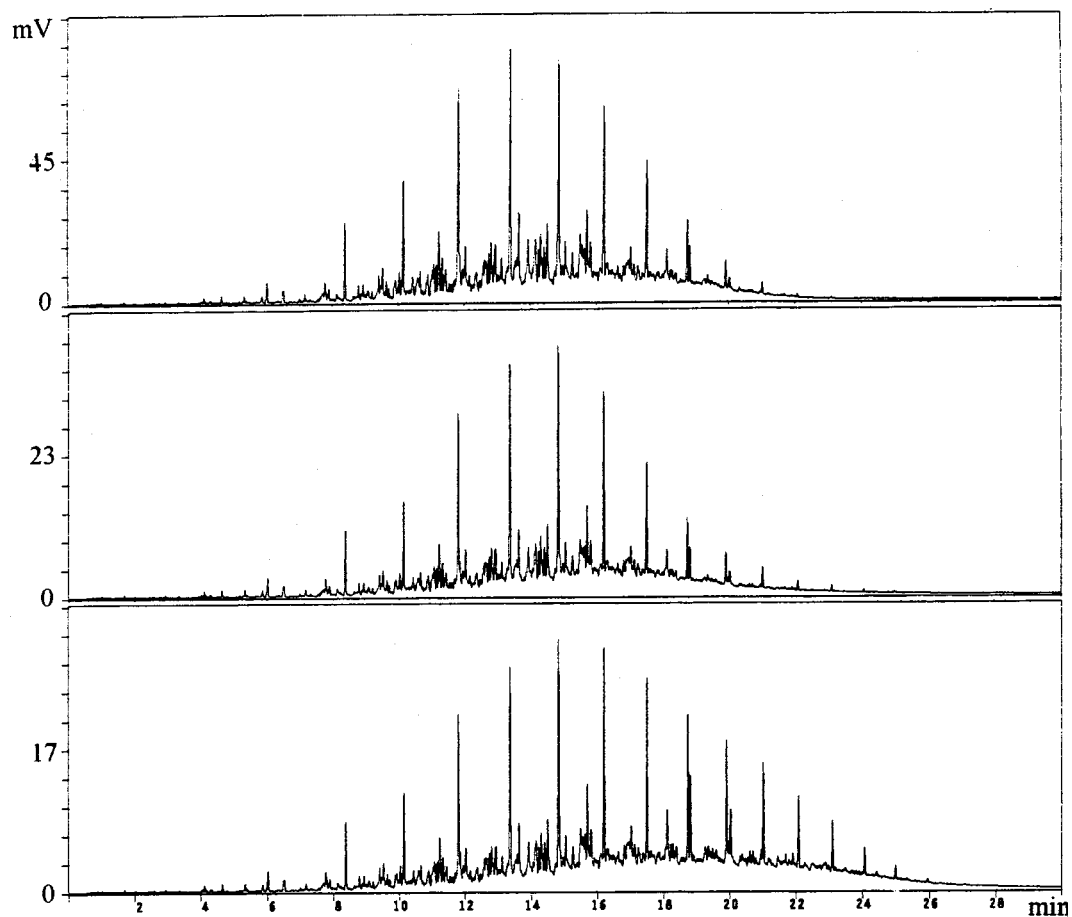


FIG. 6b—Effect of sampling temperature on boiling range of recovered solutes. From top to bottom: 80°C, 100°C, 120°C. 10- μ L wide range accelerant standard, PDMS fiber. Collection time 3 min (Instrument 1, response normalized).

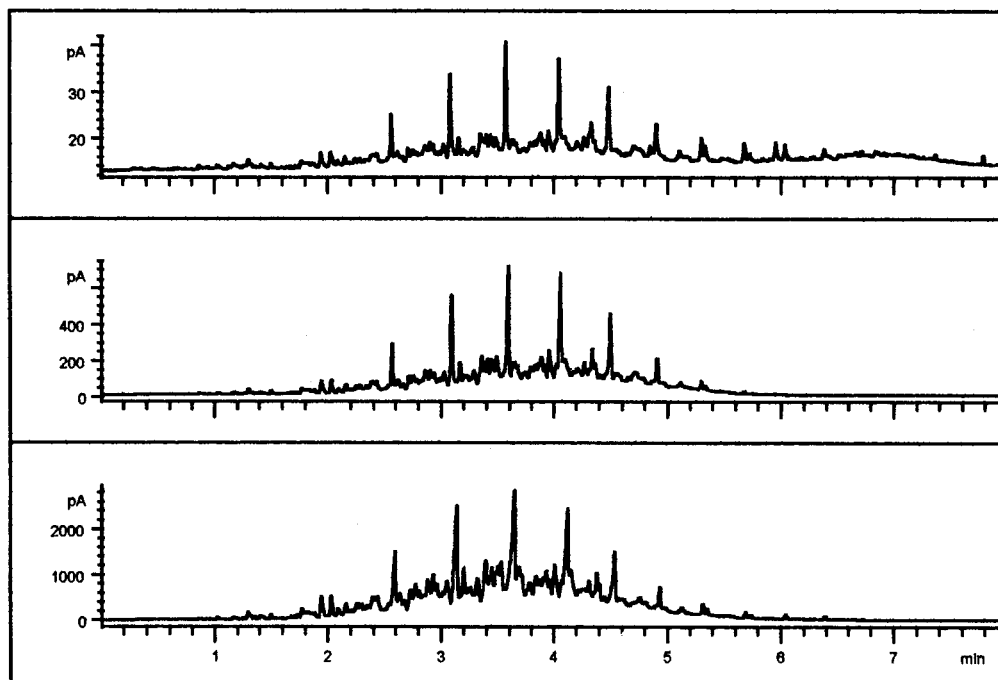


FIG. 7—Recovery of different amounts of accelerant. From top to bottom: 0.1 μ L, 1 μ L, 10 μ L, wide range accelerant standard, PDMS fiber at 80°C for 3 min (Instrument 2).

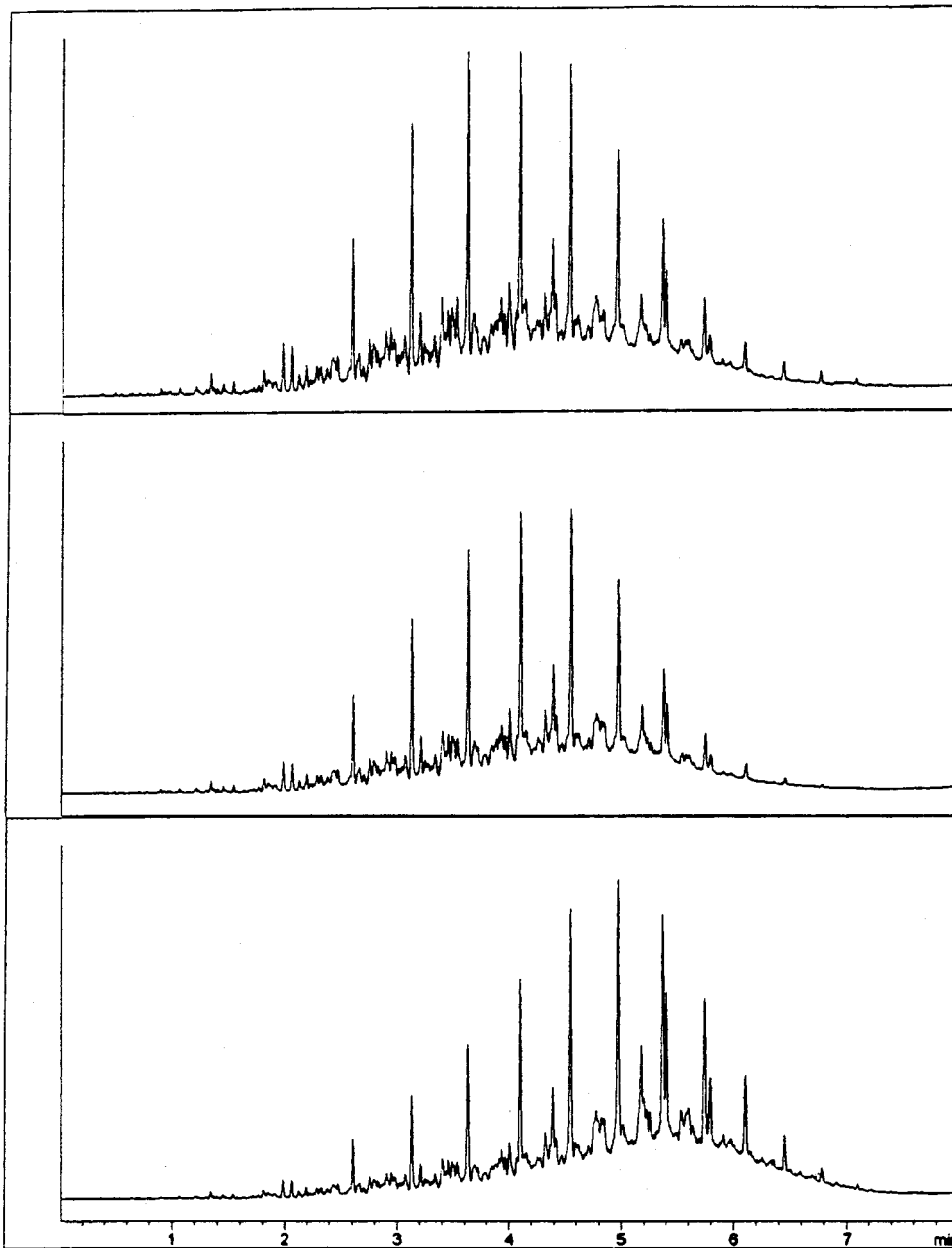


FIG. 8—Effect of water on recovery. From top to bottom: addition of no water, 1 mL, 10 mL water. 10 μ L wide range accelerant standard, PDMS fiber at 100°C for 3 min (Instrument 2, split ratio 40:1).

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