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Developments in Arson Analysis: A Comparison of Charcoal Adsorption and Direct Headspace Injection Techniques Using Fused Silica Capillary Gas Chromatography

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ABSTRACT: Procedures that have been explored for the extraction or concentration or both of fire accelerant materials from arson residues include direct headspace injection, steam distillation, charcoal adsorption followed by thermal or solvent elution, and on-column headspace injection of vapor samples, combined with cryogenic focusing. Because of the advantages to be gained from improved separations and increased sensitivity, it seemed advisable to use capillary column gas chromatography with whatever method was ultimately selected. The results of previous studies led to a decision to compare (1) a modified carbon wire adsorption technique and (2) cryogenic focused vapor samples directly injected on-column. Based on our experiences with the charcoal and cryogenic focusing techniques (in presence of water), the cryogenic method is an appropriate and satisfactory technique. Concentration methods (for example, distillation and adsorption) have been faulted for engendering quantitative and qualitative changes in the sample. Direct headspace injections of the type investigated here exercise less effects. They are simple to perform, require minimum sample preparation, and result in superior case sensitivity.

KEYWORDS: criminalistics, arson, accelerants, chromatographic analysis

California State Fire Marshal arson investigators currently employ a broad spectrum Nalguchi detection device whose sensitivity has been purported to exceed that of conventional analytical methods for the detection of volatile fire accelerants. The latter generally use the gas chromatographic (GC) separation of a vapor sample, directly injected onto a packed column, with flame ionization detection. There is considerable interest in the development of an alternative technique that would provide the sensitivity necessary for these marginal samples (that is, detection to at least 1-ppm level).

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tion, charcoal adsorption followed by thermal or solvent elution, and on-column headspace injection of vapor samples, combined with cryogenic focusing.

Because of the advantages to be gained from improved separations and increased sensitivity, it seemed advisable to employ capillary column gas chromatography with whatever method was ultimately selected. The results of previous studies [1-3] led to a decision to compare (1) a modified carbon wire adsorption technique and (2) cryogenic focused vapor samples directly injected on-column [4].

Experimental Procedure

Apparatus

Gas chromatographic analyses were done with a Varian 6000 gas chromatograph,³ connected to a Varian 401 Data Terminal, equipped with dual flame ionization detectors, and modified further as described below. The primary functions of the data terminal included acquisition and plotting of the gas chromatographic data and control of the chromatograph via the keyboard. The data were stored on individual floppy discs, which permitted replotting at different attenuations.

The chromatograph was adapted to a retractable on-column injector⁴ containing a glass alignment device which permitted the injection of vapor samples as large as 500 μL directly inside the fused silica column via a gastight syringe fitted with a fused silica needle.⁴ The 30-m by 320- μm fused silica column, coated with a 1.0- μm film of DB-5,⁴ was supplied with ultrapure hydrogen carrier⁵ at an average linear gas velocity of 70 cm/s (250°C). The initial oven temperature of 35°C was held for 3 min, and then programmed at a rate of 8°C/min to a final temperature of 250°C for a final 10-min hold.

Preparation of Charcoal Wires

Twenty-gauge copper wire in 76.2-mm (3-in.) lengths were brought to a red heat in a gas flame and immediately dipped into a sodium silicate solution. They were then reheated, and the sodium silicate allowed to spread over about half the length of the wire. The wires were then reimmersed in sodium silicate, rolled in activated charcoal (>180 μm [>80 mesh], Fisher Scientific #5690A), and stored in a dry airtight container until used.

Experimental Samples

Sealable, 0.95-L (1-qt) bare metal "paint cans," normally used to collect arson samples from fire debris in the field, were used as containers in these studies. The accelerant mixtures investigated included (1) unleaded gasoline (Arco Regular) as obtained from the pump; and after evaporation (see below) to (2) 46%; and to (3) 20% of its original volume; (4) kerosene (Fisher Odorless); and (5) diesel fuel. These represent a wide range of flammable hydrocarbons commonly associated with arson.

Triplicate samples were run for both the charcoal wire and for the headspace techniques for each determination. Three of the container lids were fitted with a rubber septum insertion, to provide syringe access to the headspace. In the other three cans, a 76.2-mm (3-in.) wire (prepared as above) was suspended from the lid. A small piece (about 25.4 mm [1 in.] square) of white butcher paper, which served as a substrate for the sample of liquid accelerant, was placed in each of six sample containers. Of the appropriate accelerant, 0.5 μL was

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added to the container, and the can was sealed. The sealed cans were placed in an oven at 60°C for 1 h, and replicate samples analyzed as described below.

Weathered Gasoline Samples

Two separate lots of the Arco regular unleaded gasoline were evaporated under a stream of nitrogen at room temperature, one to 46%, and one to 20% of the original volumes. These evaporated samples served as weathered arson samples. Heat generated by the fire may lead to a preferential evaporation of the more volatile components of these complex hydrocarbon mixtures; weathered arson samples possess higher concentrations of the less volatile components. Most forensic characterizations of these materials are based on pattern recognition. Laboratory weathering is useful in producing hydrocarbon mixtures that are more nearly comparable to those recovered from fire debris [5].

Charcoal Wire Analysis Procedure

Each can containing a sample and a charcoal-coated copper wire was opened, the wire was placed in a 1-mL round bottom glass test tube, and immediately washed with 150 μL of carbon disulfide (CS_2). The on-column injector was retracted (Fig. 1a), and a 2- μL aliquot of this solution was subjected to on-column injection for gas chromatographic analysis by means of a 10- μL gastight syringe fitted with a fused silica needle.⁴ The cryogenic focus described below was not used with the charcoal wire analyses.

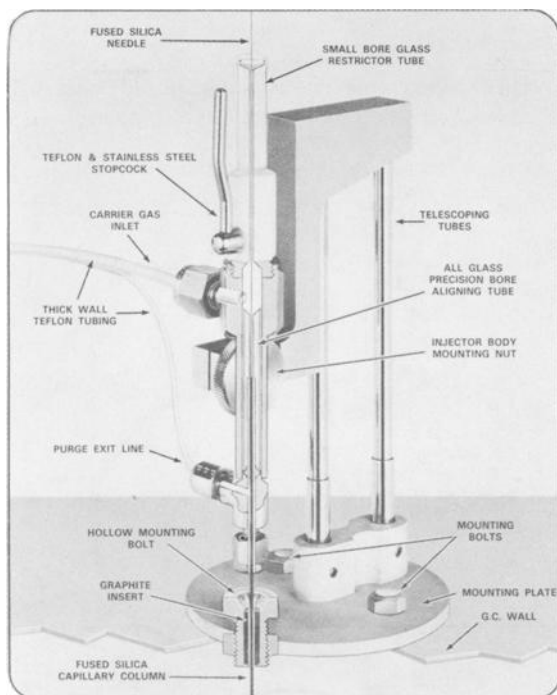


FIG. 1a—On-column injector; anatomical diagram. (Portions of this figure were reproduced with the permission of J. & W. Scientific, Inc.)

Headspace Analysis Procedure

The procedure was essentially that described by Takeoka and Jennings [4]. With the GC oven fan on and the oven temperature at its initial setting (35°C), the oven door was opened and a loop of the flexible fused silica column just below the inlet was thrust into a 6-cm inside diameter (ID) by 10-cm Dewar flask filled with liquid nitrogen (LN₂), so that about 25 cm of the column was immersed in the coolant (Fig. 1*b*). A short 18-gauge hypodermic needle was inserted through the septum in the sample can to serve as an entrance and guide for the fused silica needle on the sampling syringe. A 500- μ L sample was withdrawn, and the fused silica needle introduced into the glass restrictor forming the entrance to the on-column injector (Fig. 1). The valve was opened, the needle was inserted into the column, and 500 μ L injected (at a point well upstream from the cooled portion of the column) over a period of about 15 s. The needle was then withdrawn until the end was visible in the restrictor tube, and the valve was closed. The LN₂-filled Dewar flask was removed 10 s after the injection, the oven door was closed, and the program commenced.

Controls, Blanks, and Standards

Control runs were conducted on (1) laboratory air, via injection of 500 μ L; (2) CS₂ reagent, via injection of 2 μ L; (3) single charcoal wires randomly selected from each batch, via injection of the CS₂ eluant; and (4) empty cans, via both charcoal wire adsorption, and direct headspace sampling. Blank runs on the column and carrier were conducted by programming the system through an analysis without first making an injection. To permit indexing the analytical chromatograms, a set of standards containing the homologous *n*-alkanes C₆ through C₂₄ was also subjected to analysis by both techniques. Blank runs in 1 through 4 did not produce detectable background.

Analysis of High Moisture Samples

Arson samples are often obtained some time after the fire and under high moisture conditions. To evaluate the effects exercised by moisture on these procedures, the entire experi-

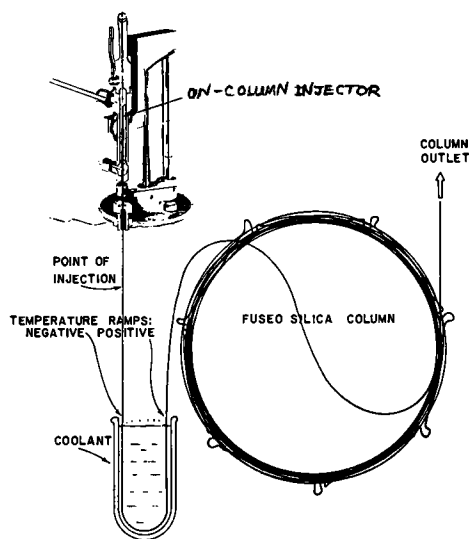


FIG. 1*b*—Cryogenic focusing in GC oven: diagram. (Portions of this figure were reproduced with the permission of J. & W. Scientific, Inc.)

mental design was reproduced, except that instead of the small piece of paper formerly placed in each sample container, 100 mL of water were substituted. All other conditions and procedures were the same.

Results and Discussion

There is a real need for a more simple, sensitive, rapid, and reliable analytical procedure applicable to arson samples. This study used state-of-the-art gas chromatography, employing fused silica open tubular capillary columns. Two sampling methods were compared: (1) charcoal adsorption, followed by CS₂ elution, and (2) a simple, direct injection of headspace samples, combined with cryogenic focusing. Some preliminary discussion over the essential points of the two methods follows.

Charcoal Adsorption

The efficacy of activated charcoal as an adsorbent for a wide variety of volatiles has long been recognized: most volatile materials exhibit high heats of adsorption on charcoal. On the other hand, this high trapping efficiency can lead to difficulties in the recovery of the adsorbed materials. Thermal desorption has been used, but solvent elution is more widespread among forensic scientists. Recovery of the adsorbed materials is enhanced if they undergo preferential displacement by the eluant. The higher the heat of adsorption that the eluant exhibits on charcoal, the smaller the volume that can be used, and the more recovery (and sensitivity) is enhanced. An early evaluation of common solvents as charcoal eluants established that CS₂ was most effective [6]. It generates minimal flame ionization detection (FID) response, and its use has been generally adopted.

Direct Headspace Analysis

The use of this particular retrofit on-column injector permitted the injection of up to 500 μ L of headspace sample from a fused silica needle directly inside the fused silica column, without requiring that the sample undergo further dilution to be transported to the column. Under the impetus of the carrier gas flow, the sample band moves toward that portion of the column immersed in LN₂. Because of the negative temperature gradient, the velocity of the volatile solutes in the front of the band is abruptly decreased and the rear of the band momentarily continues at the higher velocity, and the band is focused. Because the solutes still possess positive (albeit slight) vapor pressures, they continue to chromatograph, but very slowly. Before they traverse the cooled section and begin warming up (which would result in defocusing the band), the thermal gradients are cancelled by physical removal of the trap [4].

In general, direct headspace injections by the above procedure resulted in good sensitivity, reproducibility, and resolution. Figure 2 illustrates chromatograms obtained from (top) fresh gasoline and gasoline at two stages of weathering. Many of the solutes whose retention times are less than 3 min (and which emerge during the initial 35°C hold) are off-scale. Comparison of the three chromatograms demonstrates that weathered gasoline possesses, per unit volume, a greater concentration of the higher boiling components. Major losses of the lower boiling components are evident in the more severely weathered sample. The sensitivity and resolution are obviously sufficient to distinguish clearly between these samples. Volatile artifacts are present in these samples. The components may have resulted from trace impurities in the carrier gas being concentrated under cryogenic conditions and then evaporating rapidly once the coolant is removed.

Comparison of Fig. 3 (diesel fuel, dry sample) with the chromatograms of Fig. 2, illustrates that under these sampling conditions (dry, 60°C), the sensitivity of the method for

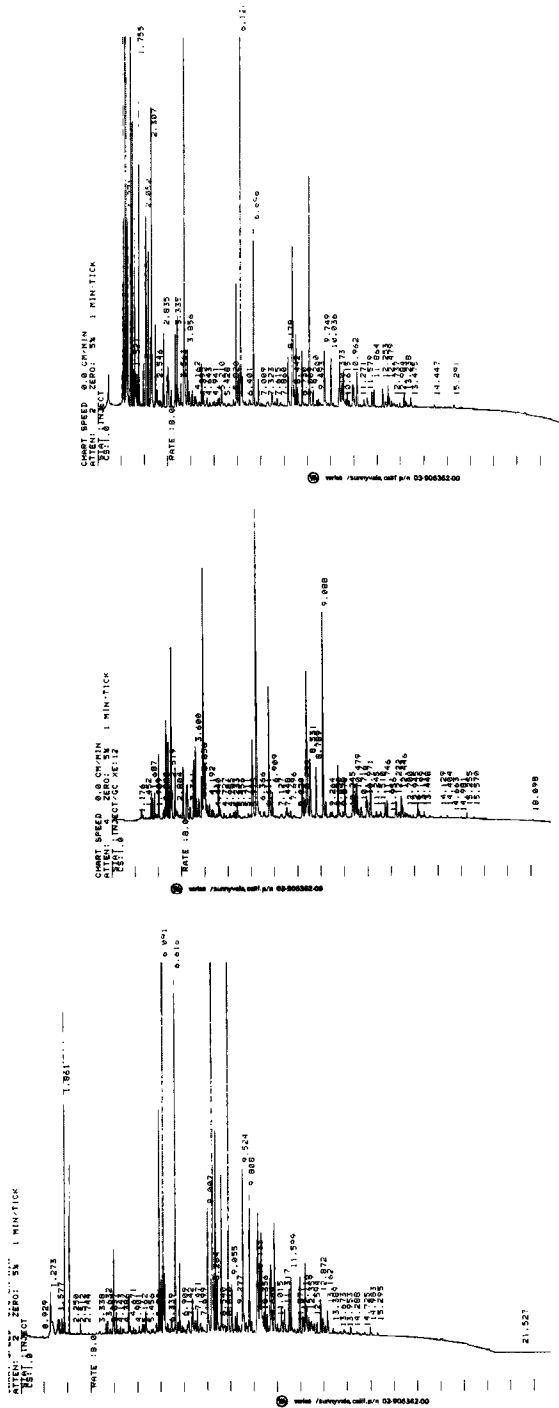


FIG. 2—Cryogenically focused headspace chromatograms: 1-ppm Arco unleaded regular gasoline. Top, fresh gasoline, Attenuation 2; center, 54% evaporated gasoline, Attenuation 4; and bottom, 80% evaporated gasoline, Attenuation 2.

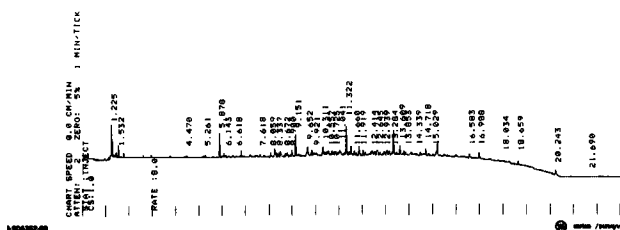


FIG. 3—Diesel fuel (dry); cryogenically focused headspace chromatogram, ~1 ppm. Attenuation 2.

diesel fuel is limited. At this temperature and these low concentrations, the materials making up diesel fuel exhibit restricted vapor pressures, and their concentrations in the volume of that vapor injected are in many cases below the limits of detectability. At higher concentrations in the vapor space, this limitation can be overcome (Fig. 4).

Effects of Water on Direct Headspace Analysis

As contrasted with the results observed by the charcoal wire technique, the apparent sensitivity of direct headspace injections increased in the presence of water (see Figs. 5 through 8). Figures 5 and 6 demonstrate that the cryogenically focused headspace of weathered gasoline is more sensitive than the eluted charcoal adsorbed sample. Although the headspace method does not have as great a sensitivity with respect to diesel fuel, it detects this petroleum fraction in the presence of water. This is not the situation regarding the adsorption technique (Figs. 7 and 8).

One possible explanation for this result is a concentration effect: the 100-mL water addition occupies about 10% of the sample can volume, effectively confining the hydrocarbon vapors to a smaller volume. It is also possible that some hydrocarbons adsorbed to active sites on the can surface are preferentially displaced by water, or that azeotrope formation enhances the contribution of the hydrocarbons. Water may also be preferentially adsorbed

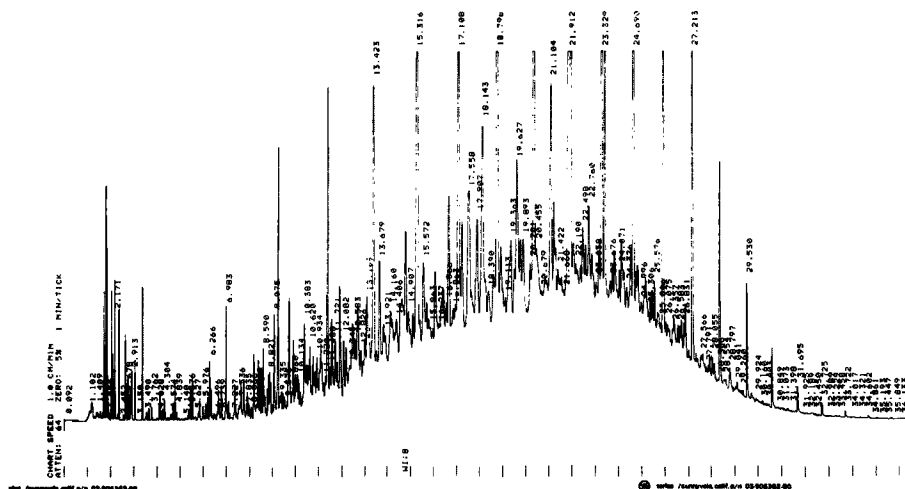


FIG. 4—Diesel fuel (dry); cryogenically focused headspace chromatogram (greater amount of diesel fuel in headspace). Attenuation 2.

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