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The AAN solicits contributions from forensic scientists, arson investigators, attorneys, and interested parties who have some unique or routine analysis which helps in the identification of flammable liquid or explosive residues. Articles herein express the views and opinions of the authors, which are not necessarily those of the AAN or Systems Engineering Associates.

# The Use of Wide Bore Capillary Columns for Gas Chromatographic Analysis of Arson Samples

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The resolution of the components of petroleum hydrocarbon mixtures may be accomplished to satisfactory levels for identification purposes by gas chromatography. The efficiency of the resolution depends upon the type column used as well as the detector and the operating conditions. Even with relatively crude systems one can obtain chromatograms which can be recognized as unique commercial mixtures such as gasoline or kerosene and the like. The recognition of these chromatographic patterns is basis for the first proposals to use gas chromatography as an analytical tool for identifying flammable liquids in fire debris.[1,2]

If the flammable liquids maintained their composition through a fire, and many times they do, the identity of these substances from fire debris would be a simple problem in qualitative analysis. However, these mixtures burn off and evaporate off the more volatile components and differentially adsorb on to the developing char and thus the compositions often are altered drastically from that before the fire. The identity of these altered compositions can be confusing even with a good library of chromatograms of evaporated samples because hydrocarbon mixtures do not just evaporate or burn in the fire. There are differential adsorption phenomena, there are various catalytic surfaces which alter burning rates, there are differential burnings and there are substrate background patterns from wood and plastics, all of which alter the patterns. The identification problem then becomes difficult when the chromatograph is operated at very high sensitivity. Furthermore, we often find that the patterns are poorly resolved when the hydrocarbon mixture has been burned off to the extent of say 99.99% and instrumental sensitivity must be increased greatly to see the patterns. Substantial improvement in the gas chromatographic patterns can be achieved by capillary column chromatography and a number of workers have recommended the adoption of these systems.[3,4]

We strongly urge that workers in the forensic science field give serious consideration to the use of wide bore capillary columns which are available from Supelco.[5] These wide bore columns put one in the capillary business without the associated problems and expense of the narrow bore capillary systems.

We were introduced to these columns because of a serious separation problem we experienced with the four anomers of fructose in water solution by silylation and gas chromatographic methods. While success was claimed in the literature for this system, we found the techniques to be non-reproducible. To improve on the resolution we tried the wide bore capillary system from Supelco. This column provided excellent resolution of all four anomers. Because of the availability of the column we evaluated its use on hydrocarbon mixtures. The results were so good that we now use the wide-bore capillary system on a routine basis with arson samples.

We will first describe our experiences with the SPB-1 column from Supelco for the separation of hydrocarbon mixtures. Then we will contrast its use to packed columns and end with some general comments about wide bore capillary columns. In a subsequent article we will give a detailed contrast of packed column chromatography to the wide bore capillary chromatography for a series of hydrocarbon mixtures used to formulate paint thinners. The column we have used is a 60m x 0.75mm. borosilicate glass with a 1.0 μm methyl silicone layer bonded to the glass. Supelco calls this column the SPB-1 column and is designed to replace OV-101, the SE-30 or the SP-2100 packed columns.[5] A schematic of its installation in a chromatographic system is shown in Figure 1.

The capillary column comes installed in a cage with the ends attached to a butt connector with fused silica leads for connection to the injector and to the detector. Notice in Figure 1, the presence of a fine metering valve leading from carrier gas to the detector. This valve is required to furnish make-up carrier gas to the detector. The wide bore capillary columns can be operated with as little as 1 to 2 ml/min. carrier gas flow but the FID requires 25 to 35 ml/min. flow for efficient operation. Otherwise the wide bore capillary columns are operated very much like packed column systems.

To optimize operating conditions for a Varian 3700 instrument with FID we evaluated the capillary column for (1) sample size (2) carrier gas flow rate, (3) initial temperature and hold-time, (4) program rate and final temperature. The conditions we have selected are: Injector temperature 220°, detector temperature 290°, column oven program, initial temperature 50°, 2 min. hold, 8°/min to 230° or 290° depending upon the hydrocarbon mixtures; flow rates: 15 ml/min He, 15 ml/min make up He to detector, 30 ml/min $H_2$ and 300 ml/min air to FID. The samples were 1 $\mu\ell$. $CS_2$ solution containing 2-5 $\mu\ell$. of hydrocarbon mixture per ml of $CS_2$. If neat samples are used they must be 0.1 $\mu\ell$. or less. The recorder was a Fisher Recordall with a 0.5 sec. full-scale response and a chart speed of 0.5 inch/min.

For comparison we also ran the same mixtures on the same instrument with a 2m x 1/8" OV-101 S.S. packed column. For the packed column work our standard program is: Injector temperature of 220°, detector temperature of 290°; column oven program of 70°, 2 min hold, 16°/min to 230-250°; flowrates: 30 ml/min He, 30 ml/min $H_2$ and 300 ml/min air to FID. The chart speed was 1.0 inch/min.

Shown in Figures 2-6 are the separations of gasoline, kerosene, Varsol, Isopar G and a synthetic mixture of straight chain hydrocarbons from C-5 through C-20 on the Supelco SPB-1 wide bore capillary (60m x 0.75mm) compared to the separation on the 2m x 1/8" column packed with 3% OV-101 on C.W.H.P. The a chromatograms are for the wide bore capillary separations and the b chromatograms are for the packed column separations. As can be readily seen for Figure 2 (gasoline) Figure 3 (kerosene) Figure 4 (Varsol) and for Figure 5 (Isopar G) the separations are remarkably better with the wide bore capillary system compared to the packed column. On an average, approximately 2 to 3 times the number of peaks are seen for the capillary system as compared to the packed column. Inasmuch as the capillary program rate and recorder chart speeds are one half (fortuitously) that used for the packed column the peak envelopes appear at about the same places on the chromatograms which makes sample identification simpler between the two systems. The conditions used are not necessarily optimal as regards resolution for either system but on overall factors including time they are quite useful for the identification of hydrocarbon mixtures. Figure 6 is the chromatogram for the wide bore capillary column separation for a mixture of the straight chain hydrocarbons of C-5 through C-20.

Finally a clear advantage of the wide bore capillary over the packed column is seen in Figure 7 for the analysis of a severely evaporated gasoline (99+%). The packed column chromatogram shows poor resolution of the residual hydrocarbons with a nondescript recognition pattern while the wide bore capillary chromatogram shows excellent hydrocarbon resolution and the peaks are readily correlated with an unevaporated gasoline. Given the nature of samples from fires for which accelerants are often severely burned off and/or evaporated such improvement in the recognition pattern is one of the most important reasons for the utilization of capillary columns particularly the wide bore systems with their operational advantages over narrow bore capillary columns.[5,6]

Sample Analyses - The samples we receive from field investigators are treated by our gas purge and trap system to remove the volatile and flammable components from the fire debris.[7] The charcoal traps are eluted with carbon disulfide and the eluant analyzed by gas chromatography. The Varian 3700 instrument is equipped with dual FID detectors, a 2m x 1/8" S.S. OV-101 column on one side and a 60m x 0.75mm capillary column on the other side. We first analyze all samples by the use of the 2m packed column. If the sample is negative or cleanly identifiable we use those results. If the sample is not negative but cannot be identified by the chromatogram from the packed column we then use the wide bore capillary column. The advantages of this approach are that we save a great deal of time in adjusting the instrument sensitivity and sample size for a particular sample for the initial run and the reruns since we can recycle the packed column system in 15-16 mins whereas the wide bore system requires 28-30 mins. Once the proper sample size and attenuation is established for the packed column we can readily apply those conditions for use with the wide bore system. We now have established a library of commercial hydrocarbon mixtures which are unevaporated, 50% evaporated and 95% evaporated for both packed columns and wide bore capillary columns. By these procedures one can continue to operate with packed column systems while developing a library and experience with the wide bore capillary system all the while using the same basic techniques for both.

General Comments about Wide Bore Capillary Systems - Having described some typical results with the wide bore capillary column compared to the results for a packed column, we need to consider other reasons as to why the wide bore capillary columns represent such an important development for gas chromatographic analysis. It is obvious now that near ultimate separation of volatile mixtures can be achieved by techniques using narrow bore capillary columns.[8] One may then ask if this is true why should analysts convert from pack column techniques to wide bore capillary techniques? Why not go all the way over to narrow bore capillary techniques? The simple answer to the last question is that if one must have near the ultimate resolution of particular samples, the narrow bore system is the way one must go. It must be recognized, however, that the narrow bore capillary systems represent a totally different analytical system for those analysts trained and experienced in packed column chromatography. This fact requires expensive and specialized adaptation of equipment, it requires special training to effectively operate them, it requires special injection techniques (sample size and sample splitters) and may have serious limitations for detectors (e.g. one cannot use TC detectors) and for doing quantitative work due to splitter discrimination.[6]

In contrast the wide bore capillary columns are simple to install in most gas chromatographic instruments. We would tout the following:

1. With the capillary column mounted in a cage with flexible fused silica connectors the conversion is extremely simple, requires less than a day to install and test.
2. The operation of the narrow bore capillary system is nearly identical to that of the packed column systems.

3. While sample size must be somewhat smaller for wide bore capillaries than for packed columns, it may be substantially larger (up to 15 μg per component) than for narrow bore columns (up to 100 to 500 ng per component) to avoid column overloading.
4. The cost of the installation is about $1,000 for the column, the inlet and outlet hardware and make-up gas system. This compares to $2,500 or more for a narrow bore conversion system.
5. All standard detectors may be used.
6. Standard flow controllers can be used and the high flow rates minimize dead volume effects.
7. The analyst's past experience with reading chromatograms is utilized to the fullest without having to relearn new patterns. This fact makes the complete conversion to capillary systems very attractive.
8. By using two wide bore capillary columns - one polar and one nonpolar - one can handle with a single instrument nearly all of the kinds of samples analyzed by forensic laboratories from arson samples to blood alcohol to acid and basic drug samples.[9]

For complete details on the installation and operation of the wide bore capillary columns one should contact the technical service group at Supelco who developed this system.[5,6]

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7. D. G. Kubler, R. Given and C. Stackhouse, Arson Anal. Newsletter, 5 (6) 82 (1981).

8. W. Jennings, "Gas Chromatography with Glass Capillary Columns", Academic Press, 2nd ed., 1980.

9. The Supelco Reporter, Vol. III, No. 5, p. 8, 1984.

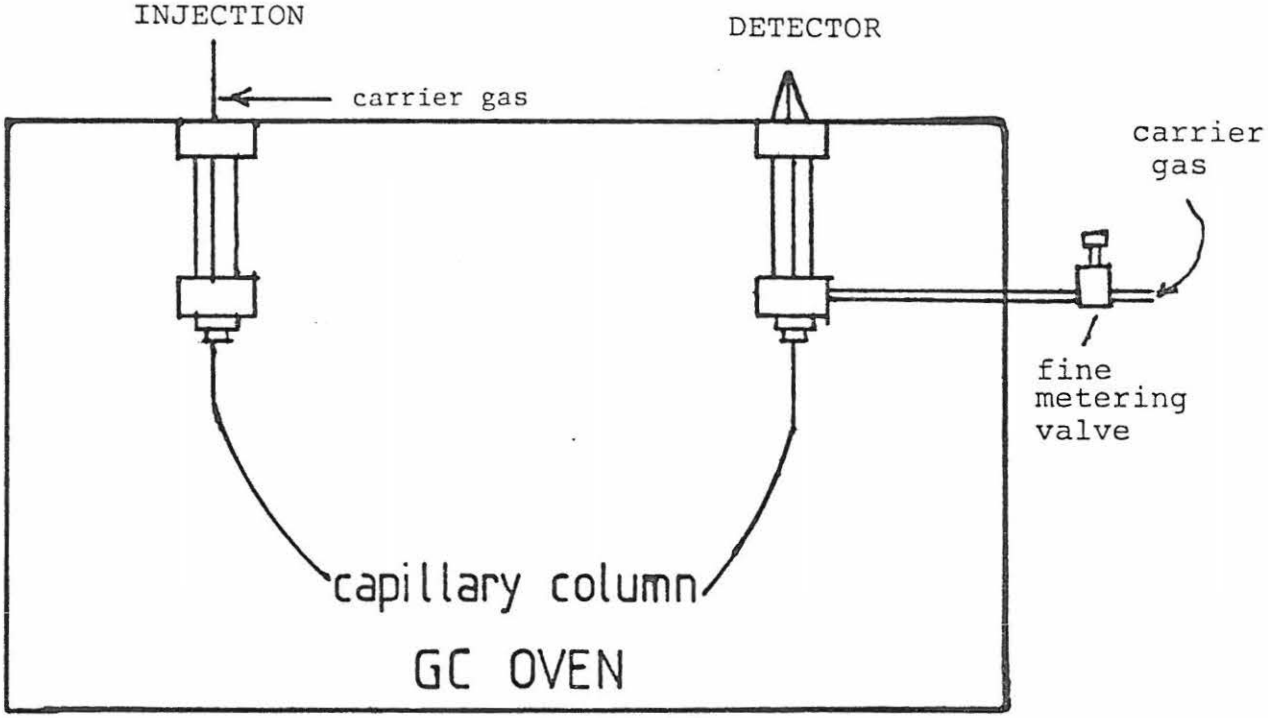
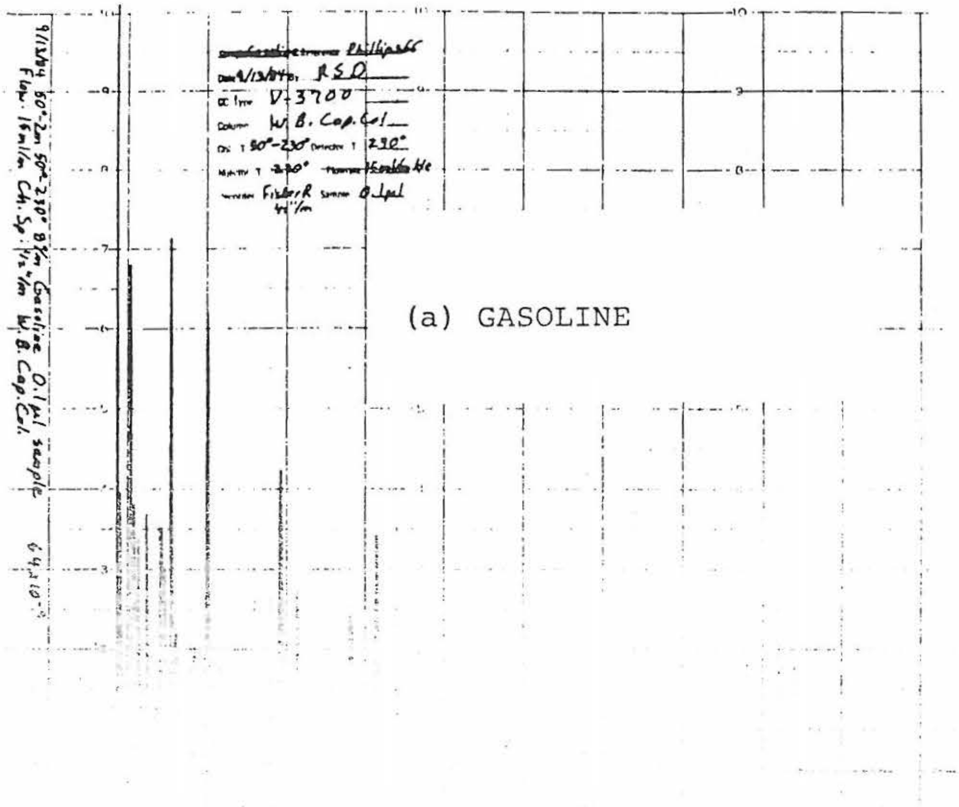
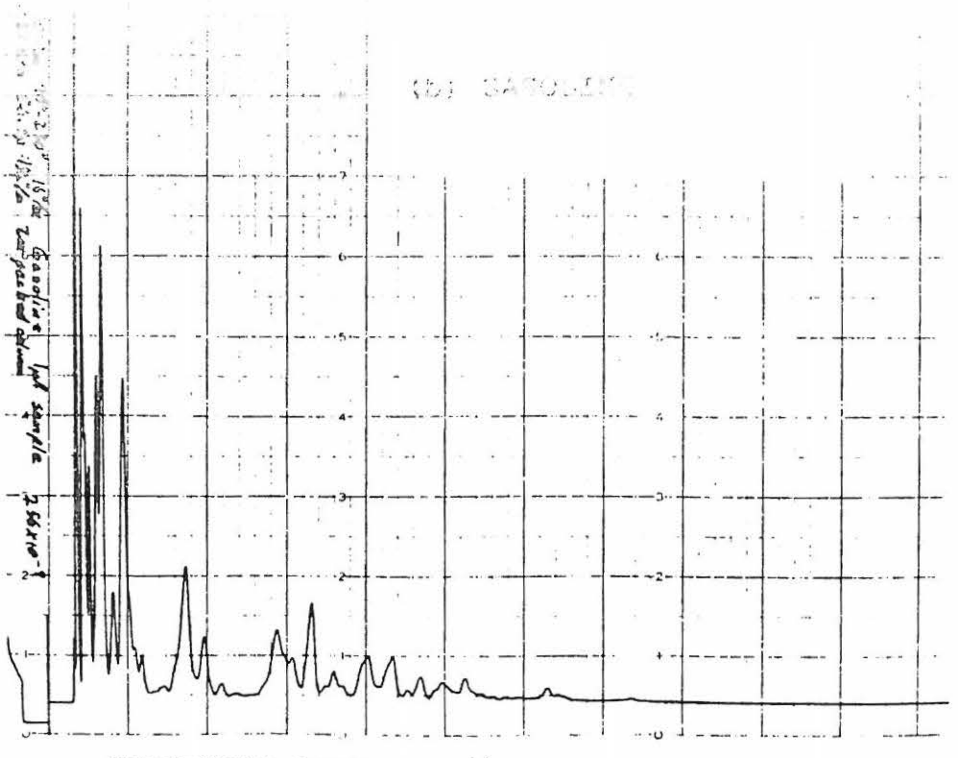


Figure 1 - Schematic of a chromatograph adapted for wide bore capillary column



(a) GASOLINE



(b) GASOLINE

Figure 2 - Gas chromatographic separation of gasoline components on (a) wide bore capillary and (b) packed OV-101 column.

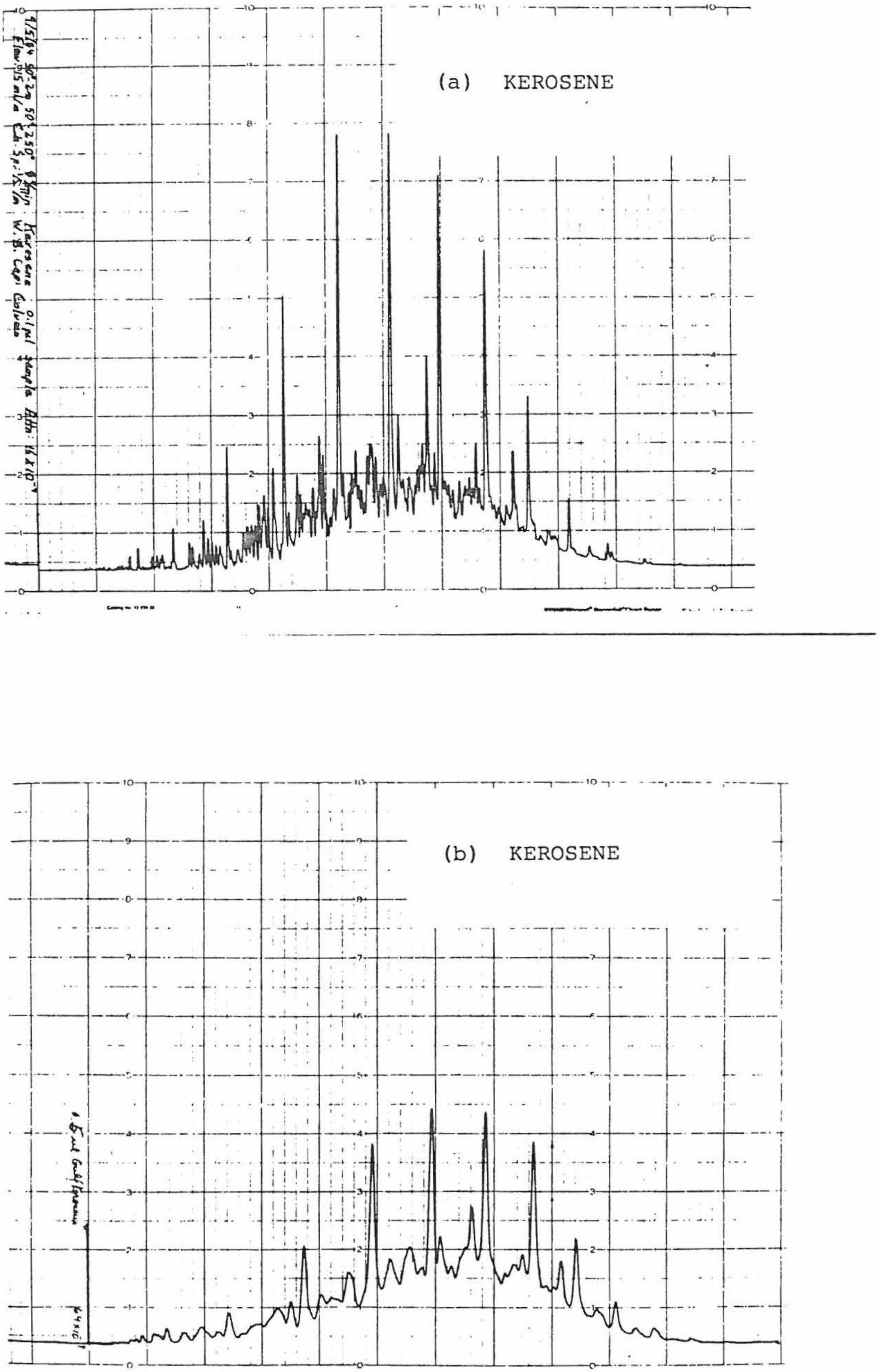
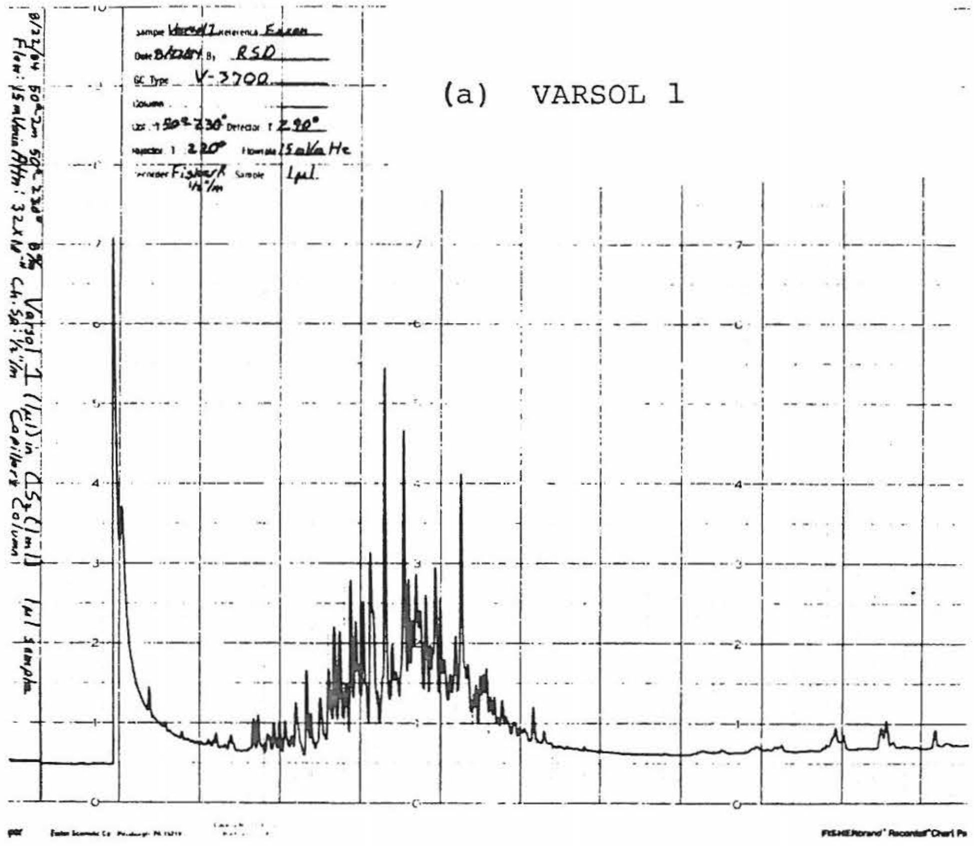


Figure 3 - Gas chromatographic separation of kerosene components on (a) wide bore capillary and (b) packed OV-101 column.



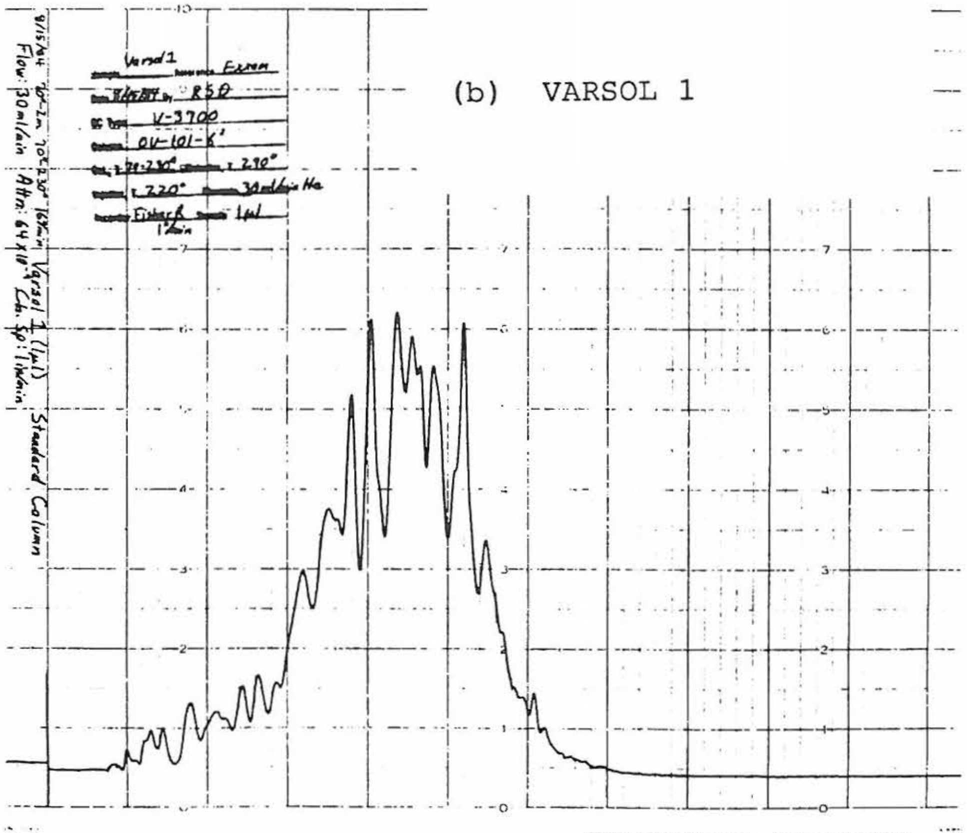
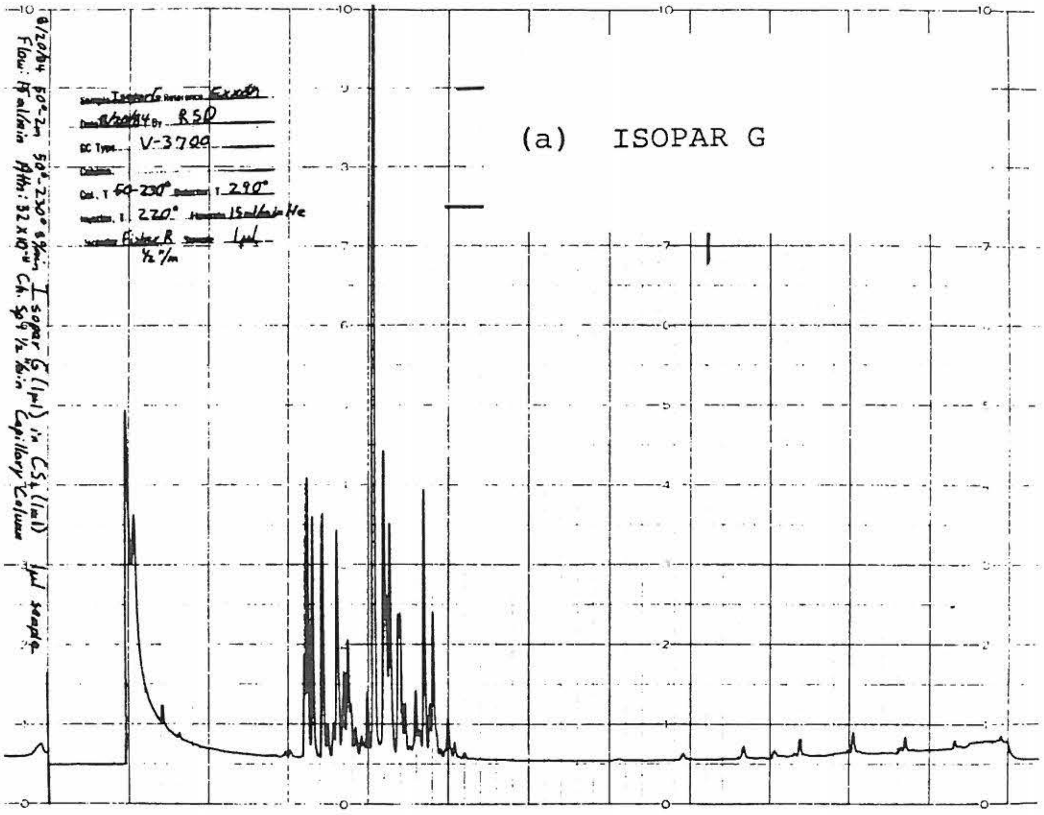


Figure 4 - Gas chromatographic separation of Varsol-1 components on (a) wide bore capillary and (b) packed OV-101 column.



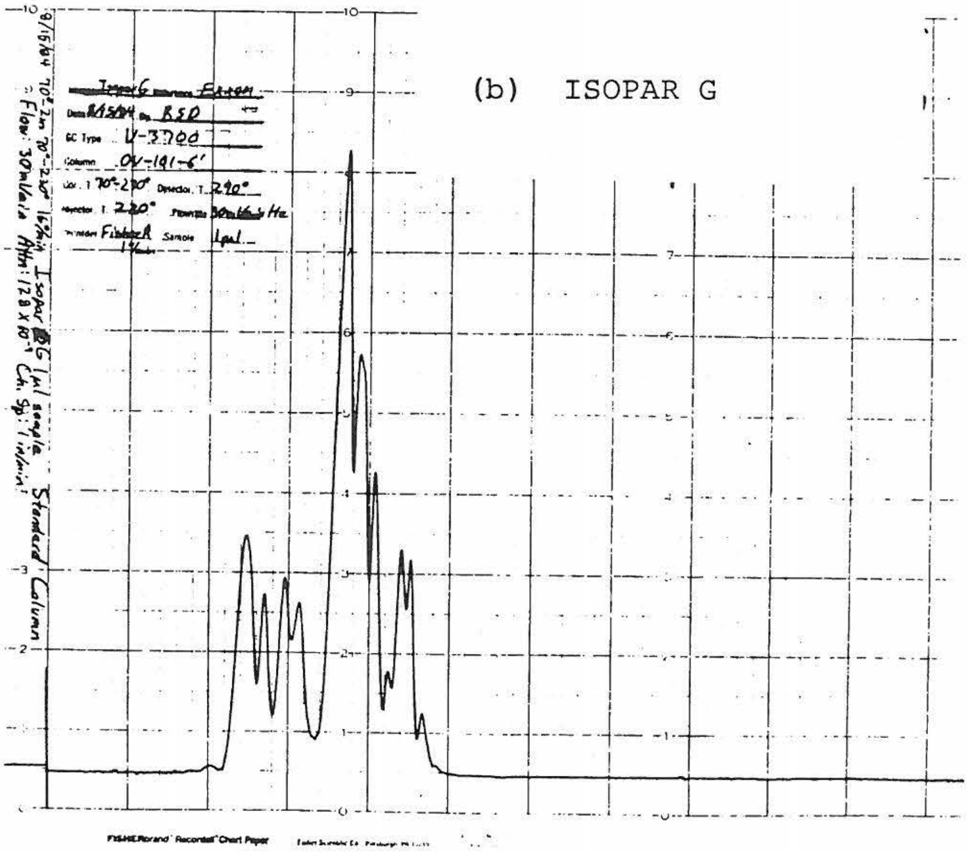


Figure 5 - Gas chromatographic separation of Isopar G (Exxon) components on (a) wide bore capillary and (b) packed OV-101 column.

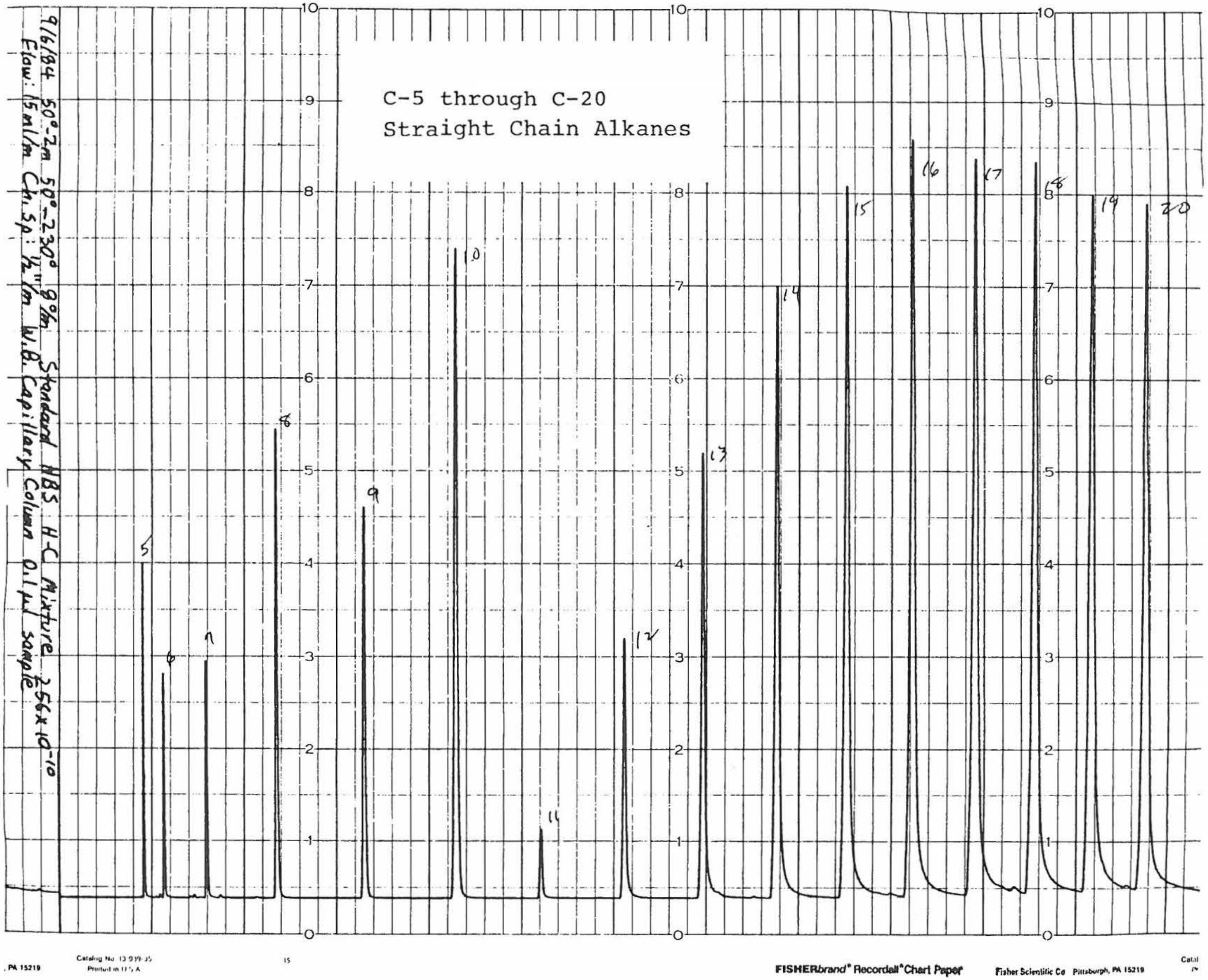
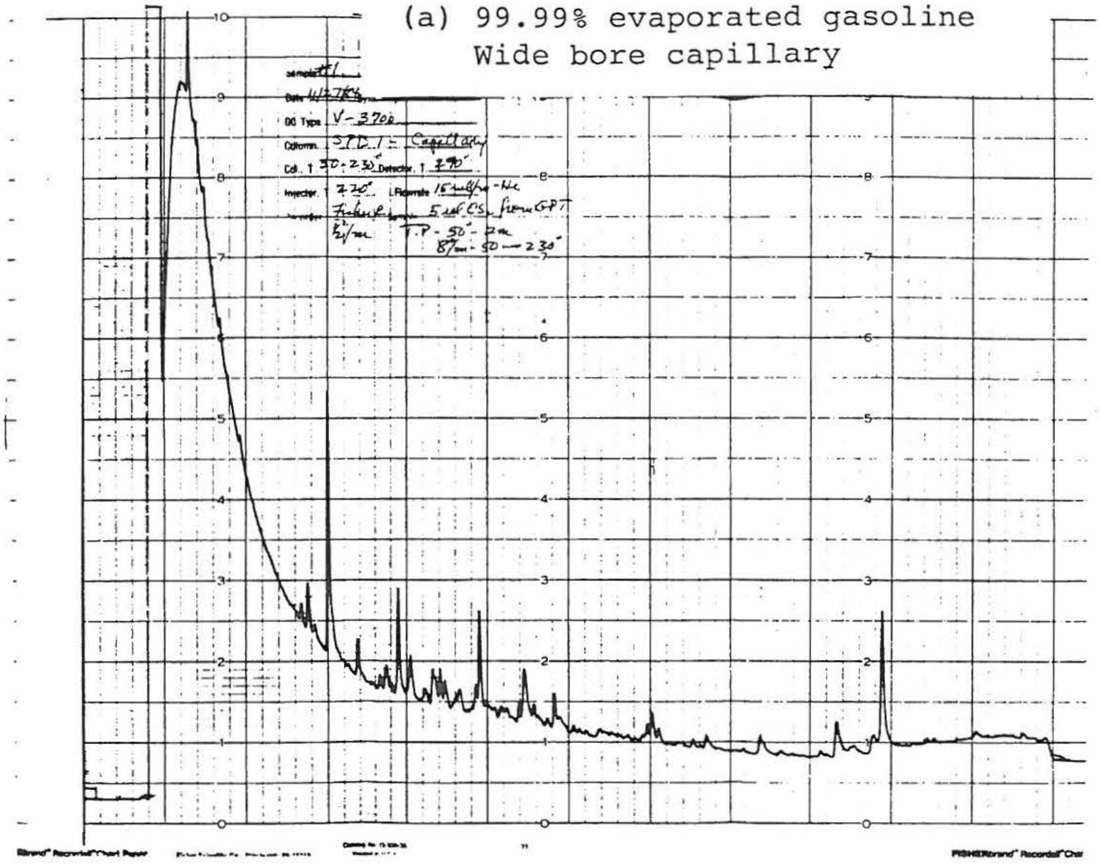


Figure 6 - Gas chromatographic separation of a synthetic mixture of C-5 through C-20 straight chain alkanes on wide bore capillary column.


(a) 99.99% evaporated gasoline
Wide bore capillary

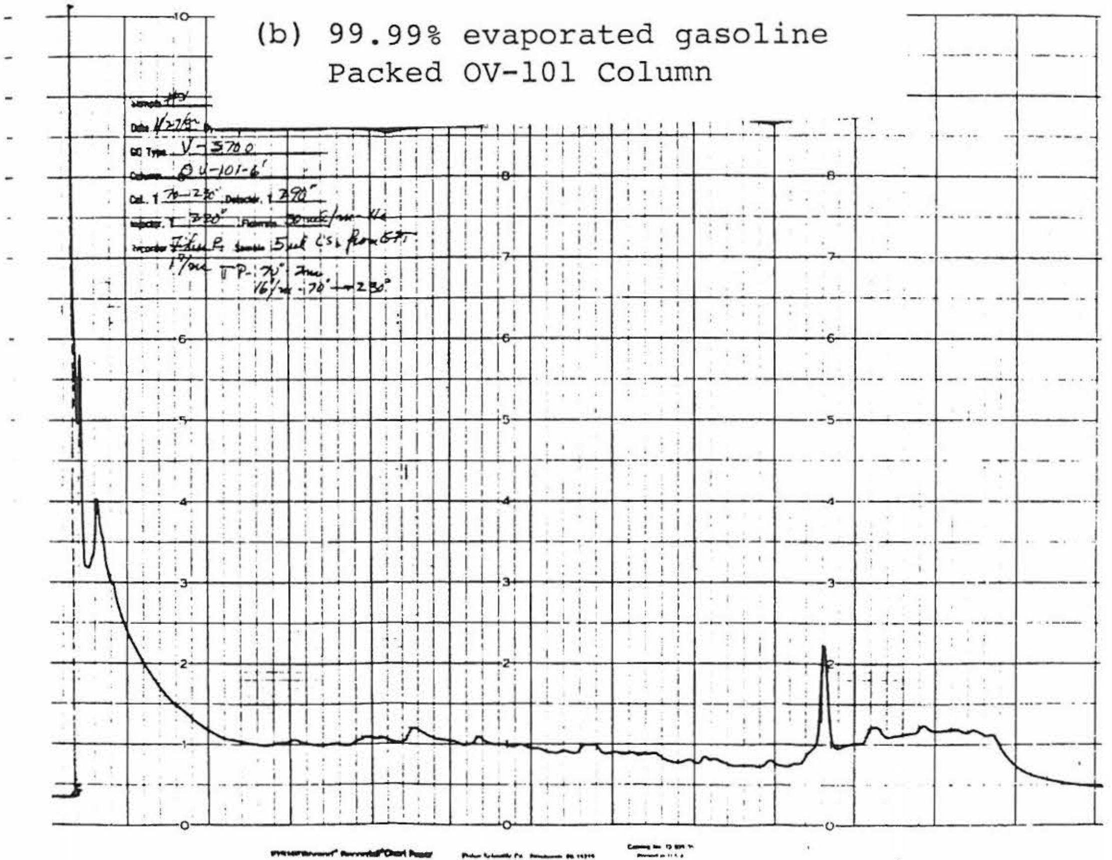

(b) 99.99% evaporated gasoline
Packed OV-101 Column

Figure 7 - Gas chromatographic separation of a severely evaporated gasoline (99.99%) on (a) wide bore capillary and (b) packed OV-101 column.

# FLASH POINT DETERMINATIONS IN FORENSIC PRACTICE

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## Introduction

The flammability potential of a liquid is commonly assessed by reference to its flash point, and many jurisdictions or agencies have chosen to incorporate flash point criteria into statutes concerned with flammable liquids. Originally flash point criteria were found to be useful for those codes dealing with the protection of the public by specifying the manner of transportation and storage of flammable liquids. Increasingly, however, flash point criteria have been incorporated into arson-related criminal statutes. For example, the California Penal Code Section dealing with Molotov Cocktails states in part "...For the purposes of this subdivision, a "firebomb" is a breakable container containing a flammable liquid with a flashpoint of 150 degrees Fahrenheit or less..."[1].

The intent of the California legislature in adopting this code section is obvious. Instead of listing each and every liquid which might be used to make a Molotov Cocktail, and thereby risking a situation where an effective firebomb was made with an obscure liquid not covered by the code, the legislature embraced the concept of flash point. If a liquid does not meet the statutory criterion, it will not pose a hazard with respect to flammability.

This is a reasonable, rational approach to the problem, but the California statutue is defective. It is defective in that it is not sufficiently explicit in specifying how flash point is to be determined, and in fact fails to define what flash point is. Unlike those optical and physical properties which are truly fundamental properties of materials, (*e.g.*, molecular or atomic absorption, atomic emission), and despite the fact that flash point is directly related to the boiling point and inversely related to the vapor pressure, flash point is nevertheless arbitrarily defined.

There is a general consensus as to the definition, but "general consensus" is rarely adequate for the intense scrutiny common to many forensic situations. The ASTM has defined flash point as "the lowest temperature, corrected to a pressure of 101.3 kPa (1013 mbar) at which the application of an ignition source causes the vapors above the sample to ignite, *under the specified conditions of test.* (Italics added) [2]. What are these "specified conditions of test," and why does the ASTM leave the conditions to the discretion of the analyst? The present work is an attempt to tidy up this messy subject. (As an aside for those who wish to be reminded of the presently preferred metric unit describing pressure, it is the kiloPascal (kPa). 101.3 kPa is the standard barometric pressure, equivalent to 1013 mbar or 760 mm of Hg).

## Parameters of Flash Point Testing

The flash point value that is experimentally derived is subject to a number of factors. These include the type and configuration of the testing apparatus, temperature control, ambient pressure, the nature of the ignition source, sample preparation and homogeneity, and the nature of the calibration liquids used. It is a major premise of the present work that it is essential for the forensic scientist working on arson-related cases to have a thorough knowledge of the effects of these factors.

## Type of Testing Apparatus

Two types of flash point testing devices are in vogue, the open cup and the closed cup. In the open cup technique, the sample is heated in an open container to a selected temperature. At that temperature a test flame is introduced over the sample and it is noted whether ignition in the form of a flash takes place. If not, the temperature is raised and the process is repeated. In the closed cup technique, the sample is not vented. Lower boiling components, although volatilized, are not lost to the atmosphere. If the increase in temperature is achieved slowly, the closed cup technique permits an equilibrium to be achieved between the liquid and the vapor states.

The reader might note that the California statute referred to as an example does not specify *which* type of device is to be used in the determination of flash point. It may be *inferred* that the intended method is the closed cup method, but "inferred" is scarcely the criterion to be applied to good forensic practice. (A failure to specify the method is not universally the case; as discussed below, the U.S. Department of Transporttation emphatically specifies that the closed cup method must be used). Both the open and the closed cup methods have advantages and disadvantages. The advantages of the closed cup system are that (1) they are more applicable with liquids of relatively low flash point, and (2) they provide a more realistic measure of the flammability of a liquid which is confined in a closed space, *e.g.*, a sealed container. The latter feature is less frequently encountered in arson cases than situations where the accelerant is widely distributed and exposed to the atmosphere. The advantage of the open tester is the converse of the second factor immediately above; the open test provides a more realistic measure of the flammability of a liquid which has been applied as an arson accelerant. A disadvantage of the open cup system is that with a mixture, *e.g.*, gasoline, lower boiling components may be volatilized prior to the application of the flame and thereby give an erroneously high flash point reading.

The American Society for Testing Materials currently describes five different flash point testing devices, and has published methods for the calibration and operation of each of these [3]. The five devices are (1) the Tag open cup (ASTM Method D1310); (2) the Tag closed cup (ASTM Method D56); (3) the Pensky-Martens closed cup (ASTM Method D93), (4) the Cleveland open cup (ASTM Method D92); and (5)the Setaflash closed cup (ASTM Method D3278). The Annual Book of ASTM Standards [3] provides schematic diagrams of the various devices.

The two open cup devices have been eclipsed by the Tag closed cup and the Setaflash testers as a result of action taken by the U.S. Department of Transportation. The Department of Transportation has ruled [4] that the closed cup method is the sole criterion for classifying a liquid as being flammable. The Tag closed cup device with the ASTM Method D56 was designated an acceptable method, with the Setaflash closed cup device with the ASTM Method D3278 designated as an acceptable alternative [5]. The precision of the Tag closed cup and the Setaflash method in routine use is between 1 and 2° F. [6]. (Despite the fact that the ASTM defines the pressure at which flash point is to be determined in metric units, flash point is still invariably given in degrees Fahrenheit). The ultimate precision is on the order of 0.5° F, coincidental with the precision of reading the thermometer. Indifference to proper technique or inexperience on the part of the analyst, however, could easily result in an error of 5° or more.

The Pensky-Martens closed cup device is principally used for viscous, high molecular weight, high flash point liquids, *e.g*, lubricating oils and other liquids which are unlikely to be encountered as arson accelerants. This method, however, is the method of choice for liquids with a viscosity greater than 5.5 cSt at 104° F.

## Temperature Control

If the rate of heating is too fast, a lag will result between the temperature of the liquid and the thermometer from which the temperature is read at the time of ignition. For most testing devices, a rate of 2° per minute should not be exceeded when approaching the expected flash point. Good operating practice also demands that the testing device be situated out of drafts that might create a differential between the sample cup and the reading thermometer.

## Sample Size and Preparation

The volume of the air space above the liquid may influence the flash point, and so the recommended volume of liquid must be used for precise determination. While this may pose no particular problems for those concerned with the storage or transportation of large volumes of flammable liquids, it may pose a severe problem in connection with suspected arson cases. The Setaflash unit requires only 2 ml of sample, but the Tag closed cup method requires *50 ml*. In many actual case situations it may be impractical or even impossible to obtain even 2 ml.

Flash point determinations on complex mixtures give a composite or aggregate value. Consequently, if a sample has "weathered" through exposure to the atmosphere, the lighter fractions will be lost and the flash point value of the liquid will be elevated.

## Pressure

Flash point is a measure of the propensity of molecules to go from the liquid state to the gaseous state, and is therefore influenced by ambient pressure. In reporting flash point, the observed value should be corrected to standard barometric pressure of 760 mm of Hg (101.3 kPa). The correction is achieved by adding 0.06°F to the observed value for each mm of Hg below 760, or subtracting the same amount to the observed value for each mm above 760 mm.

## Ignition Source

The ignition flame must be adjusted properly. If the flame is too large, the flash point values will be depressed.

## Calibration Liquids

The ASTM has specified *p*-xylene as the liquid for calibrating the Tag closed cup and the Setaflash closed cup testers. Lance *et al.* [6], however, have advocated mixtures of cumene and pseudo-cumene. Mixtures of this sort do not show a significant change in flash point upon partial evaporation, and altering the proportion of the liquids can deliver a calibration liquid of any desired flash point between the flash point of cumene (88° F) and that of pseudo-cumene (117° F).

## Summary

As developed above, flash point determinations must be sufficiently parameterized if they are to be meaningful. The values observed may be dependent upon the apparatus used and numerous other considerations. Certain of these considerations have, arguably, a minor effect upon flash point, *e.g.*, a 10 mm difference in atmospheric pressure will result in only a 0.6° F difference in flash point. However, good professional practice suggests that *all* of the attendant considerations be countenanced. This is particularly true if inter-laboratory data are to be compared.

## References

[1]. Section 453, California Penal Code.

[2]. ASTM Ad Hoc Committee on Flash Point Methodology and Government Response, 1976.

[3]. American Society for Testing Materials, 1976 Annual Book of ASTM Standards, Parts 15 and 19.

[4]. U.S. Department of Transportation Hazardous Materials Regulations, Federal Register, Vol. 41, Section 173.115(d), p. 42472, Sept. 27, 1976.

[5]. Ibid., p. 42473

[6]. Lance, R.C., Barnard, A.J., Jr., and Hooyman, J.E. *J. Hazardous Materials* 3(1979) 107-119.

# AA Notes

The following information was submitted by Jew-ming Chao, Ph.D., Laboratory Director, Burlington County Public Safety, Woodlane Road, Mt. Holly, New Jersey, concerning the programs that were presented during the 37th Annual Meeting of the American Academy of Forensic Sciences, February 11-16, 1985 at the Riveria Hotel in Las Vegas, Nevada:

*Verifying Flame Retardant on Christmas Trees Involved in a Fatal Fire, William R. Dietz, B.S., and George F. Peterson, M.A., Bureau of Alcohol, Tobacco & Firearms, San Francisco, CA 94130.

*The Comparison of Automotive Gasolines using Capillary Gas Chromatography, Dale C. Mann, Criminalist, Washington State Patrol Crime Laboratory, Public Safety Building, Seattle, WA 98104.

*Limitations of Automotive Gasoline Comparisons in Casework, Dale C. Mann, Criminalist, Washington State Patrol Crime Laboratory, Public Safety Bldg., Seattle, WA 98104.

*Gunshot Residue Examination using the ND:YAG Laser, Amy P. Haralson, B.A., and Walton H. Haralson, Texas Forensic Services, Inc., 400 Medical Center Blvd., Suite 109, Webster, TX 77598.

*Identification of Inorganic Explosives by Microscopical Fusion Methods, John H. Kilbourn, B.S., Alabama Dept. of Forensic Sciences, Huntsville, AL.

*Fuel Source Differentiation Between Accelerant Residues from a Fire Scene and those from a Suspect's Clothing and Car in a Suspected Homicide Case, Thomas Morgan, B.S.; Vincent F. Cordova, B.A.; and Fredric Rieders, Ph.D.; National Medical Services, Willow Grove, PA 19090.

*Auto Ignition Locks-Fraud, Theft or Arson?, Michael K. Higgins, President, K-Chem Laboratories, 46 Clayton St., Boston, MA 02122.