

# Guidelines For Laboratories Performing Chemical and Instrumental Analyses of Fire Debris Samples

*Prepared by the Forensic Science & Engineering Committee of the International Association of Arson Investigators, March, 1988.*

## Introduction

In May of 1987, the Forensic Science & Engineering Committee of the IAAI was requested to develop a set of guidelines that encourages uniformity in the reporting of analytical results. What follows is the Committee's response to that request, and should be considered by members of the IAAI as a set of minimum standards to which laboratories analyzing fire evidence should adhere. These guidelines are intended to form the initial framework for a set of criteria which will, it is hoped, one day be used in the certification of laboratories for this type of analysis.

## Section I — Methodology

Before any attempt can be made to encourage uniformity in reporting, an attempt must be made to identify the acceptable methods of analysis.

In the analysis of samples of fire debris to check for the presence of flammable or combustible liquids, it is recognized that there are many different methods which, used properly, will result in an accurate determination. These guidelines are not intended to restrict the wide variety of sample preparation and analytical techniques, but rather, their purpose is to inform laboratories and their clients of the minimum requirements for a good analysis.

### A. Sample Preparation Techniques

Separation of volatile materials from debris samples can be achieved through any number of methods, and certain methods are more appropriate for certain samples than others. The relative merits of these techniques have been the subject of numerous studies, and there is not total agreement about which technique applies best to a given situation. Sample preparation is widely acknowledged to be a critical step in the analysis of fire debris. Different techniques result in different recovery rates, which affect the limits of detection of a procedure. Additionally, fractionation of accelerants can occur during sample preparation, resulting in the loss of heavier or lighter compounds of a mixture. The following is a description of some of the methods currently in use in forensic laboratories.

1. Steam distillation. This is a classical chemistry technique, and is one of the oldest techniques used by forensic laboratories. In this process, the sample material is placed in a flask with water, the water is brought to a boil, and the vapors produced are condensed in a volatile oil distillation trap. The vast majority of flammable or combustible liquids are petroleum based products which do not mix with water and are less dense than water. As a result, the petroleum based liquids, and other immiscible materials less dense than water, float on top of a column of water in the trap. After the sample has been boiled for a sufficient period of time, the separated materials can be removed from the trap for gas chromatographic analysis.

This technique is especially appropriate for samples which contain high concentrations of flammable or combustible liquids, although care must be taken to avoid fractionating mixtures of light and heavy distillates. This is best accomplished by continuing the distillation until all visible condensation of oily material ceases. The flammable or combustible liquid can be removed neat, and can be used as an exhibit at the time of trial.

Collecting the petroleum distillate as a neat liquid allows

various analytical tests to be performed if needed. Steam distillation is not a particularly sensitive technique. It is not appropriate for samples which have very low concentrations of petroleum distillates, or for samples which bear residues of water soluble flammable liquids such as acetone or alcohol.

2. Headspace Analysis. This method involves removing a portion of the vapor above the debris in a sample container, and analyzing that vapor directly by gas chromatography. The vapor may be withdrawn at room temperature, or the sample may be heated to increase the volatilization of the accelerants and, therefore, increase the concentration of flammable or combustible liquids in the headspace vapor.

Headspace analysis is a relatively sensitive, very rapid procedure, but the analyst must be very careful to reproduce the sampling conditions exactly if reproducible chromatograms are to be obtained. This method is considerably more sensitive to the lower boiling compounds than the higher boiling compounds. This technique is more sensitive, as a rule, than steam distillation, but not as sensitive as solvent extraction or adsorption/elution. The heated headspace analysis is considerably more sensitive than the unheated analysis. For samples having high concentrations of flammable or combustible liquid, headspace analysis can provide a very rapid identification.

3. Solvent Extraction. In this separation procedure, the sample is washed with a pure liquid in which petroleum distillates are soluble. Examples of commonly used solvents are pentane, diethyl ether, and carbon disulfide. The solvent, now containing any suspected flammable or combustible liquid, is evaporated to a small volume (0.5 to 1.0 ml), in order to concentrate the liquid. A small portion of the concentrated solvent is then analyzed by gas chromatography.

Solvent extraction is an extremely sensitive sample preparation technique. It results in a liquid sample which is easily manipulated and can be repeatedly tested. This method is especially suitable for rinsing out containers suspected to have held flammable or combustible liquids, but it is suitable for analysis of any type of debris sample. Occasionally, however, the solvent will dissolve sample components which are not petroleum distillates. This may hinder the interpretation of the chromatogram. Solvent extraction is very useful when the avoidance of thermal fractionation of the sample is critical. Care must be taken to ensure the purity of the solvent, by running blanks on evaporated solvent samples. Each batch of solvent must be tested, as the purity of the solvent may vary widely from one batch to the next.

4. Adsorption/Elution. This method of sample preparation is known by a variety of names including Charcoal Tube, Vapor Concentration, Headspace Concentration, Swept Headspace, Dynamic Headspace and Purge and Trap. (It should not be confused with Headspace Analysis, described previously.) The volatile materials in a sample are separated in two steps. First, the volatile materials are adsorbed onto an active surface. Then, the adsorbed materials are removed from that surface and analyzed.

An adsorbent, a material with a large surface area, is used to trap sample vapors in a gas stream. The two most frequently used adsorbents are activated coconut charcoal and Tenax. There are a number of ways to bring vapors from the

sample into contact with the adsorbent, and a variety of ways to desorb, or elute, the adsorbed vapors from the adsorbent. While it is possible for a platinum wire, bead or polymer film coated with charcoal to passively adsorb flammable or combustible liquid vapors from the headspace of a sample, the most sensitive adsorption methods employ the active movement of headspace vapors through a tube containing the adsorbent.

Some methods apply a vacuum to the sample, and place the adsorbing tube between the sample and the vacuum pump. This requires that air being drawn through the sample container (to replace the air being drawn out) be pre-filtered to prevent contamination of the sample with ambient air. A second method involves the pressurization of the sample with air or nitrogen, pushing the gas through the sample and out to the adsorbing tube. In both the vacuum and positive pressure methods, the sample is heated (by oven or microwave) while the adsorbing is going on. Each laboratory needs to optimize the various parameters used in the adsorbing process such as sample temperature, gas pressures and flow rates, and adsorption time.

Desorption can be accomplished in one of two ways. The adsorbent can be either chemically or thermally desorbed. In the thermal desorption methods, the adsorbent is placed in the injection port of a gas chromatograph and rapidly heated to flash off the trapped flammable or combustible liquid vapors. The vapors are then swept directly into the gas chromatograph for analysis. If the desorption parameters of time, temperature and flow rate are optimized, this method effectively removes the adsorbed material, but thermal desorption has the disadvantage of allowing only one look at the sample.

The chemical desorption, or elution, is done by trickling a solvent through the adsorbing tube. The solvent is usually carbon disulfide. The carbon disulfide, while a dangerous solvent, provides a solution which can be repeatedly analyzed.

The adsorption/elution method, originally used for measuring trace amounts of air pollutants, was first applied to fire debris samples in the early 1980s by the Bureau of ATF Laboratory. It is widely recognized as one of the most sensitive methods available, and is practiced in many forensic laboratories.

## B. Analysis of Volatile Materials

Once the volatile materials have been separated from a sample, they can be analyzed by a number of different methods, but they *must* be analyzed by gas chromatography. The accepted method for identification of flammable or combustible liquids is pattern recognition using a gas chromatograph with a flame ionization detector (FID). Photoionization and mass spectral detectors are also sufficiently sensitive to be used in pattern recognition. Other analytical methods which can be applied to the separated residues include liquid chromatography, thin layer chromatography, mass spectrometry, infrared and ultraviolet spectrophotometric analysis, and atomic absorption analysis. All of these methods can yield additional useful information about a sample, but cannot identify complex mixtures of hydrocarbons. Unless a petroleum distillate has been identified by the pattern recognition techniques described below, it has not been sufficiently identified.

These guidelines will not describe the specific parameters to be used in gas chromatography. The selection of instruments, columns, and other chromatographic parameters is left to the judgment of the individual chemist. At the least, however, the chromatographic procedures should be such as to allow the use of the accelerant classification system listed below. This necessarily requires the use of a column which can reasonably resolve the n-alkane series from C<sub>5</sub> to C<sub>25</sub>. Methylsilicone columns have been found to be adequate for this task.

## Criteria for the Identification of Flammable or Combustible Liquids

It has long been recognized that petroleum distillates can be identified by the pattern produced by a gas chromatograph equipped with a flame ionization detector. The following petroleum distillate classification and identification system was produced by the Bureau of ATF Laboratories and the Center for Fire Research of the National Bureau of Standards during an interlaboratory evaluation which was carried out in 1981. This system was first published in the *Arson Analysis Newsletter*, Vol. 6, No. 3, in May of 1982. The system has been adopted by many forensic laboratories, and the purpose of its inclusion in these guidelines is to increase the adoption of this system.

The interpretation of gas chromatographic patterns is a skill which requires extensive training, and the more subtle interpretations require years of practice. The criteria for identification listed below codifies certain pattern recognition methods which most analysts have been using for years. Generally, when an analyst reaches a conclusion that there is "sufficient similarity" between the pattern produced by the sample and the pattern produced by a known petroleum distillate, that judgment of sufficiency is based on criteria very similar to the ones listed below. The listing of these minimum identification criteria will, it is hoped, allow for better communication between laboratories and better understanding of what is meant by an identification of a flammable or combustible liquid in a laboratory report.

### Petroleum Distillate Classification System

Five classes of complex liquid products are recognized as "usually identifiable by GC-FID patterning alone" when recovered from fire debris.

It is a further attribute of the following system that products listed as examples of the same class are (as debris extracts) indistinguishable from each other by GC-FID alone. This is not to say that examples of the same class cannot be distinguished from each other. The burden of proof of distinction, however,

CLASS NO. (CLASS NAME)	"PEAK SPREAD" BASED ON N-ALKANE CARBON NO'S.	EXAMPLES
Light Petroleum Distillates (LPD)	C <sub>4</sub> - C <sub>8</sub>	Petroleum ethers Pocket lighter fuels Rubber cement solvents Skelly solvents Lacquer thinners
2 Gasoline	C <sub>4</sub> - C <sub>12</sub>	All brands & grades of automotive gasoline, including gasohol. Some lantern fuels.
3 Medium Petroleum Distillates (MPD)	C <sub>8</sub> - C <sub>12</sub>	Charcoal starters. Paint thinners (oil based), Mineral spirits. "Dry-cleaning" solvents Torch fuels.
4 Kerosene	C <sub>9</sub> - C <sub>16</sub>	No. 1 Fuel Oil, Jet-A (aviation) fuel. Insect sprays, Charcoal starters.
5 Heavy Petroleum Distillates (HPD)	C <sub>10</sub> - C <sub>23</sub>	No. 2 fuel oil, Diesel fuel

lies with the analyst. When such a distinction is made, the analyst should be prepared to show sufficient data to support the distinction. The same type of burden would apply to an examiner making an identification of a mixture of two or more products.

#### **MIMUM REQUIREMENTS FOR CLASS IDENTIFICATION.**

The following criteria have proven to be useful in a majority of cases worked by several forensic laboratory systems.

##### **Class 1**

At least four major peaks in the C<sub>4</sub> to C<sub>6</sub> range. No major peak above C<sub>8</sub>, (unless the Class 1 liquid is part of a mixture of flammable and/or combustible liquids.)

##### **Class 2**

The *m*-ethyltoluene/pseudocumene 5-peak group must be present; this group occupies the range between C<sub>9</sub> and C<sub>10</sub> and is still present in gasolines which have lost as much as 90 percent of their initial ("fresh") weight by evaporation or combustion.

Higher peak groupings characteristic of gasoline, with cutoff between C<sub>12</sub> and C<sub>13</sub>, must also be present.

##### **Class C**

Pattern starts between C<sub>8</sub> and C<sub>10</sub>, ends near C<sub>12</sub>, and contains at least three major peaks between C<sub>8</sub> and C<sub>12</sub>.

Weak resolution causes an imaginary line connecting peak "valleys" to describe a bell-shaped curve.

##### **Class 4**

Pattern starts above C<sub>8</sub>. At least five consecutive n-alkane peaks between C<sub>12</sub> and C<sub>17</sub> must be present.

##### **Class 5**

Pattern starts above C<sub>9</sub>. At least five consecutive n-alkane peaks between C<sub>17</sub> and C<sub>22</sub> must be present.

It is recognized that a distinction between Class 4 and Class 5 may be difficult or impossible to determine when a sample has been badly burned or weathered. A category which includes both classes may be referred to as "fuel oil" as long as five consecutive n-alkane peaks can be identified.

No classification system is likely to describe all possible accelerants. There are numerous commercial and industrial products which are flammable or combustible but do not fall into any of the above classes. Many of these are synthetic mixtures, consisting of only a few compounds rather than distillation fractions. Certain brands of paint removers, glue solvents, lacquer or paint thinner fall into this category. Single compound flammable or combustible liquids, such as acetone, toluene or xylene, obviously cannot be identified by a pattern. Many brands of lamp oil, duplicating fluid, and one brand of charcoal lighter (Gulf Lite) consist of a distilled mixture of isoparaffinic hydrocarbons which can be identified by their chromatographic pattern.

For those flammable or combustible liquids which do not produce a complex pattern of peaks, additional analytical steps must be taken to arrive at a credible identification. The use of multiple columns is indicated in such a situation. Other techniques which may be useful include GC/MS and IR.

This system is not intended as a substitute for good chromatographic procedure. Any identification made using this system of pattern recognition will necessarily be the result of finding "sufficient similarity" between the sample chromatogram and a known or standard chromatogram.

#### **Section II — Reporting of Results**

A report on the analysis of samples of fire debris should be structured like any scientific report. A properly constructed scientific report contains an introduction, a description of the test methods and results, and a conclusion. The report should

be written in language which is understandable both to the laboratory's client and to other scientists. Because the laboratory report deals strictly with physical evidence, there is no reason for the scientist to report anything less than what he knows or is prepared to testify to. The report should be written in clear understandable language which is not only technically accurate, but leaves a correct impression about the analysis of the sample. A report which is structured so that it can mislead or confuse the reader is a bad report.

The introduction of the report should clearly identify the subject matter at hand. The evidence should be described clearly in the introduction. The report should state what was delivered, what it was contained in, who sent or delivered it, how it was delivered, when it was delivered, and where it was identified as coming from. Finally, the introduction should state what type of analysis was requested.

The description of the evidence in the introduction would seem to be merely a clerical matter, but it is important that the analyst be sure the evidence is being described accurately, not just as it was identified on the evidence transmittal form. Fire debris samples, especially, tend to look pretty much alike from the outside. It is possible for samples coming from different locations within a fire scene or even from different fire scenes to be confused with each other.

While it is not possible for the analyst to distinguish by visual inspection the difference between carpeting from the living room and carpeting from the hallway, it is possible to determine by visual inspection the difference between bedding from the master bedroom and carpeting from the hallway or concrete from the basement. The information which a scientist puts in the introduction of a report should be verified by the scientist to the extent possible. A scientist's firsthand observations and information supplied by a client when a sample is delivered should be easily distinguishable.

The test methods and results section should identify how a sample was analyzed, in particular, stating which sample preparation method was used and which analytical method was used. The words "gas chromatographic analysis" should necessarily appear in this section. It should be remembered that the report will be read by others besides investigators and court officers. Other scientists may be called upon to review the test methods, and an accurate description of those methods will aid the reviewing scientist in understanding the report.

The conclusion section should give the scientist's opinion as to whether a flammable or combustible liquid was identified in the sample. If a negative result was obtained, a disclaimer to the effect that negative results do not preclude the possibility that accelerants were used at the fire scene may help to avoid misunderstanding by people reading the report. Some scientists prefer to let the results speak for themselves, and this is fine as long as the results are comprehensible to a layman. The conclusion section should be that part of the report where a nonscientist can turn and get the bottom line.

While the above describes what should be present in a report, there are several phrases which should *not* appear in a report. Gas chromatographic analysis gives the examiner an indication of the boiling range or molecular weight of the components of a sample. It should be noted, however, that components with the same boiling range are not necessarily the same or even similar in terms of their origin. A report which states that a sample was found to contain hydrocarbons in the boiling range of gasoline may or may not be describing a sample which did, in fact, contain gasoline. A report which states that gas chromatographic analysis resulted in the identification of a product "similar" to kerosene may or may not be describing kerosene.

If an analyst makes an identification using the word "gasoline" or "kerosene" or "middle range petroleum distillate", that identification should be based on the criteria listed above, and the scientist's client should be secure in the knowledge that the analysis of the samples was carried out using recognized methods, and that the identification was made according to recognized criteria.

#### **Conclusion**

These guidelines are intended to be used by analysts in the business of checking fire debris samples for the presence of flammable or combustible liquid residues. They are also intended to be used by the clients of those analysts in evaluating the quality of the service provided. It is the sincere hope of the Forensic Science and Engineering Committee of the IAAI that these guidelines be generally adopted by laboratories performing chemical analysis of fire debris samples. The Committee earnestly solicits the thoughts of the IAAI membership regarding these guidelines.

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