



Standard Guide for Identification of Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography-Mass Spectrometry¹

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1. Scope

1.1 This guide covers the identification of residues of ignitable liquids in extracts from fire debris samples. Extraction procedures are described in the referenced documents.

1.2 While this guide is suitable for all samples, it is especially appropriate for extracts that contain high background levels of co-extracted materials from the substrate or pyrolysis products. This guide is also suitable for the identification of single compounds, simple mixtures, or non-petroleum based ignitable liquids.

1.3 This guide is intended as an alternative to the method described in Test Method E 1387. It is not intended to be a replacement of that document or to supersede any of the information contained therein.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 ASTM Standards:

- E 752 Practice for Safety and Health Requirements Relating to Occupational Exposure to Carbon Disulfide²
- E 1385 Practice for Separation and Concentration of Flammable or Combustible Liquid Residues from Fire Debris Samples by Steam Distillation³
- E 1386 Practice for Separation and Concentration of Flammable or Combustible Liquid Residues from Fire Debris by Solvent Extraction³
- E 1387 Test Method for Flammable or Combustible Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography³
- E 1388 Practice for Sampling of Headspace Vapors from Fire Debris Samples³
- E 1412 Practice for Separation and Concentration of Flammable or Combustible Liquid Residues from Fire Debris

Samples by Passive Headspace Concentration³

E 1413 Practice for Separation and Concentration of Flammable or Combustible Liquid Residues from Fire Debris Samples by Dynamic Headspace Concentration³

E 1492 Guide for Receiving, Documenting, Storing, and Retrieving Evidence in a Forensic Laboratory³

3. Summary of Guide

3.1 The sample is analyzed with a gas chromatograph (GC) which is interfaced to a mass spectrometer (MS) and a data system (DS) capable of storing and manipulating chromatographic and mass spectral data.

3.2 Post-run data analysis generates mass chromatograms (selected ion profiles) characteristic of the chemical compound types commonly found in petroleum-based ignitable liquids and specialty products. Additionally, specific chemical components (target compounds) may be identified by their mass spectra and retention times. Semi-quantitative determination of specific chemical components (target compounds) which are identified by mass spectra and retention time may be used to develop target compound chromatograms (TCCs).

3.2.1 The total ion chromatogram (TIC), selected ion profiles (SIP) for the alkane, alkene, alcohol, aromatic, cycloalkane, ester, ketone and polynuclear aromatic compound types, or target compound chromatograms (TCC), or combination thereof, are evaluated by visual pattern matching against known standards.

3.2.2 Petroleum-based products may be grouped into one of five major petroleum classifications or one miscellaneous class, as described in this guide.

3.2.3 Non-petroleum distillate-based specialty products may be identified by specific compound identification or categorized in the Miscellaneous (Class 0) category, or both.

4. Significance and Use

4.1 The identification of an ignitable liquid residue in samples from a fire scene can support the field investigator's opinion regarding the origin, fuel load, and incendiary nature of the fire.

4.2 Materials normally found in a building, upon exposure to the heat of a fire, will form pyrolysis products. Selected ion profiling and target compound identification techniques described herein may facilitate the identification of an ignitable

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² Annual Book of ASTM Standards, Vol 11.03.

³ Annual Book of ASTM Standards, Vol 14.02.

liquid in the extract by reducing interference by components generated as products of pyrolysis and identification of pyrolysis products.

5. Apparatus

5.1 *Gas Chromatograph*—A chromatograph capable of using capillary columns and being interfaced to a mass spectrometer.

5.1.1 *Sample Inlet System*—A sample inlet system that can be operated in either split or splitless mode with capillary columns; the inlet system may use on-column technology.

5.1.2 *Column*—A capillary, bonded phase, methylsilicone or phenyl methylsilicone column or equivalent. Any column length or temperature program conditions may be used provided that each component of the test mixture is adequately separated.

5.1.3 *Oven*—A column oven capable of reproducible temperature program operation in the range from 50 to 300°C.

5.2 *Mass Spectrometer*—Capable of scanning between 20 to 600 m/e with unit resolution or better, with continuous data output.

5.2.1 *Sensitivity*—The system must be capable of detecting each component of the test mixture and providing sufficient ion intensity data to identify each component, either by computer library search or by comparison with standard spectra.

5.3 *Data Station*—A computerized data station, capable of storing chromatographic and mass spectral data from sample runs.

5.3.1 *Data Handling*—The data system must be capable of performing, either through its operating system or by user programming, various data handling functions, including input and storage of sample data files, generation of selected ion profiles, searching data files for selected compounds, and qualitative and semi-quantitative compound analysis.

5.3.2 *Mass Spectral Libraries*—The system must be capable of retrieving a specified mass spectral scan from a data file and comparing it against a library of mass spectra available to the data system. This capability is considered an aid to the analyst, who will use it in conjunction with chromatographic data and known standards to identify unknown components.

5.4 *Syringes*—A microsyringe capable of introducing a sample size in the range from 0.1 to 10.0 μL .

6. Chemicals, Reagents, and Standards

6.1 The test mixture shall consist of equal parts by volume of the even-numbered normal alkanes (ranging from *n*-hexane through *n*-eicosane), methylbenzene (toluene), 1,4-dimethylbenzene (*p*-xylene), 1-methyl-2-ethyl benzene (*o*-ethyltoluene), 1-methyl-3-ethyl benzene (*m*-ethyltoluene), and 1,2,4-trimethylbenzene. Additional compounds may be included at the discretion of the analyst. The final test solution is prepared by diluting the above mixture to a concentration of 0.05 % volume/volume (0.5 microlitre per millilitre) in the chosen solvent (see 6.3).

6.2 Standards (commercially available products) must be available for gasoline, kerosene, diesel fuel, mid-range petroleum distillates (mineral spirits, paint thinners, charcoal starters, and the like), light petroleum distillates (camp fuels, VM&P naphthas, cigarette lighter fluid, and the like), isopar-

affinic solvents, and specialty products (lacquer thinner, carburetor cleaner, spot removers, and the like), as described in Table 1.

6.3 *Solvent/Diluent*—Carbon disulfide, pentane, or other solvent that will not interfere with the analysis. It is generally desirable to use a solvent whose volatility greatly exceeds that of the solute to facilitate sample concentration by evaporation, if necessary.

6.4 *Carrier Gas*—Helium or hydrogen of purity 99.995 % or higher.

7. Tuning of Mass Spectrometer

7.1 Tune the mass spectrometer using perfluorotributylamine (PFTBA), or another appropriate calibration standard, according to the instrument manufacturer's specifications, prior to use. This should be done at least on a daily basis.

7.2 Maintain tuning documentation as a portion of the quality control documentation.

8. Sample Handling

8.1 Only samples of appropriate dilution should be analyzed on a GCMS system. Generally, standards of flammable/combustible liquids are diluted 1:1000. Depending on column capacity and injection technique, petroleum distillates can be made somewhat more concentrated to ensure detection of minor target compounds.

8.1.1 If carbon disulfide is used, read and follow the safety precautions described in Practice E 752.

8.2 Methods for isolating ignitable liquid residues from fire debris for analysis by this guide are described in Practices E 1385, E 1386, E 1412, and E 1413.

8.3 System blanks will be periodically analyzed and the documentation maintained. System blanks are obtained by using the same methods employed to extract and concentrate the sample.

8.4 *Cleaning of Equipment:*

8.4.1 Change septa and clean injector liner on a periodic basis to avoid sample contamination by "carry-over."

8.4.2 Clean syringes thoroughly between injections. For autosamplers, perform and document periodic syringe carry-over studies.

8.4.3 System blanks should be run to ensure no carry-over between samples.

8.5 Run and maintain reference files of known standards which have been analyzed in the same manner as the questioned samples.

9. Procedure—Data Handling

9.1 The hydrocarbon compounds of ignitable liquids derived from crude oil consist of five major hydrocarbon types: alkane (both normal and branched), alkene, cycloparaffin, aromatic, and polynuclear aromatic. Other types exist, but are considered insignificant for the purposes of this guide

9.1.1 Hydrocarbon compounds of each type produce characteristic major ion fragments. These ions are listed in Table 2.

9.1.2 Additional data analysis may be carried out using either mass chromatography or target compound analysis, or both.

9.2 *Mass Chromatography Analysis:*

TABLE 1 Ignitable Liquid Classification System

Class Number (Class Name)	"Peak Spread" Based on <i>n</i> -Alkane Carbon Numbers (Unvaporated Liquid)	Examples
1. Light Petroleum Distillates (LPD)	C ₄ -C ₁₁	Petroleum ethers, pocket lighter fuels, some rubber cement solvents, Skelly solvents, V M and P naphtha, some camping fuels
2. Gasoline	C ₄ -C ₁₂	All brands and grades of automotive gasoline, including gasohol.
3. Medium Petroleum Distillates (MPD)	C ₈ -C ₁₂	Mineral spirits, some paint thinners, some charcoal starters, "dry-cleaning" solvents, some torch fuels, some solvents for insecticides and polishes, some lamp oils
4. Kerosene	C ₈ -C ₁₇	No. 1 Fuel Oil, Jet-A (aviation) fuel, insect sprays, some charcoal starters, some torch fuels, some paint thinners, some solvents for insecticides and polishes, some lamp oils
5. Heavy Petroleum Distillate (HPD)	C ₉ -C ₂₃	No. 2 Fuel Oil, diesel fuel
0. Miscellaneous	variable	Single compounds, turpentine, specialty mixtures which cannot be further classified into one of the categories below.
0.1 Oxygenated solvents	variable	Alcohols, esters, ketones
0.2 Isoparaffins	variable	Isoparaffin products, some charcoal starters, some copier fluids, some aviation gasolines, some lamp oils, some solvents for insecticides and polishes, some camping fuels
0.3 Normal alkanes	variable	Specialty products formulated from normal alkanes, insecticides and polishes
0.4 Aromatic solvents	variable	Light, medium and heavy "aromatic naphtha" used as solvents for paints and plastics
0.5 Naphthenic/paraffinic solvents	variable	Specialty solvent/fuel products made from Class 3 or Class 4 distillates treated to remove normal alkanes and aromatics, with higher cycloalkane content than isoparaffin products

TABLE 2 Major Ions Present in Mass Spectra of Common Flammable and Combustible Liquids^A

Compound Type	m/e
Alkane	43, 57, 71, 85
Cycloalkane and alkene	55, 69
<i>n</i> -Alkylcyclohexanes	82, 83
Aromatic—alkylbenzenes	91, 105, 119; 92, 106, 120
indanes	117, 118; 131, 132
Alkyl-naphthalenes	128, 142, 156, 170
Alkylstyrenes	104, 117, 118, 132, 146
Alkylanthracenes	178, 192, 206
Alkylbiphenyls/acenaphthenes	154, 168, 182, 196
Monoterpenes	93, 136
Ketones	43, 58, 72, 86
Alcohols	31, 45

^A R. Martin Smith, *Analytical Chemistry*, Vol 54, No. 13, November 1982, pp 1399A-1409A.

9.2.1 The data station is used to extract and draw mass chromatograms (selected ion profiles) for major ions characteristic of each compound type. Individual mass chromatograms for two or more characteristic ions may be summed to enhance signal-to-noise and decrease interference by extraneous compounds that contain only one of the ions.

9.2.2 Mass chromatograms for an unknown sample are compared against the corresponding mass chromatograms from standard samples. This is generally done by visual pattern recognition; computerized pattern recognition techniques are also acceptable, provided that results are checked visually.

9.2.3 Major peaks in the mass chromatograms should be identified by searching their mass spectra against a suitable library. The final identification must be made by the analyst on the basis of the mass spectra and relative retention times of the components in question by comparison to standards.

9.3 Target Compound Analysis:

9.3.1 Target compound analysis uses key specific compounds to characterize an ignitable liquid. These target compounds are listed in Table 3, Table 4, and Table 5.

9.3.2 Semi-quantitative ratios for the target compounds must be derived and compared against standards to ensure not only their presence but also that their chromatographic patterns match. Computerized pattern matching techniques are acceptable, providing results are verified by the analyst.

9.3.2.1 Target compound pattern recognition may be improved by the production of target compound chromatograms, which are graphical representations of semi-quantitative peak areas for the target compounds. Target compound data may be plotted as a bar graph, with the *x*-axis representing retention time and the *y*-axis representing peak area. Each target compound is depicted by a single bar on the graph.

9.3.2.2 Target compound chromatograms for unknown

TABLE 3 Gasoline Target Compounds

1.	1,3,5-Trimethylbenzene
2.	1,2,4-Trimethylbenzene
3.	1,2,3-Trimethylbenzene
4.	Indane
5.	1,2,4,5-Tetramethylbenzene
6.	1,2,3,5-Tetramethylbenzene
7.	5-Methylindane
8.	4-Methylindane
9.	Dodecane
10.	4,7-Dimethylindane
11.	2-Methylnaphthalene
12.	1-Methylnaphthalene
13.	Ethyl-naphthalenes (mixed)
14.	1,3-Dimethylnaphthalene
15.	2,3-Dimethylnaphthalene