Houston Forensic Science Center

Verification of the Solvent Extraction Method for Ignitable Liquids

Verification Report

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10/11/2016

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Verification Report for the Solvent Extraction of Ignitable Liquids

Purpose

Solvent extraction is a technique used to recover ignitable liquids present in fire debris evidence. The extraction process involves rinsing or soaking all or a portion of the fire debris evidence in a suitable solvent. The fire debris evidence is then removed and the solvent either analyzed directly or a portion of the solvent is removed by gentle evaporation. After evaporation the remaining material is analyzed.

Introduction

Ignitable liquids are commonly extracted from substrates using passive headspace concentration with activated charcoal. However, there are instances when extracting a suspected ignitable liquid from a substrate using a solvent may be useful. An example would be for the extraction of heavy (C12 and greater) ignitable liquids as defined within the ASTM 1618 classification schemes. The extraction procedure outlined in this verification study follows the procedure outlined in ASTM E1386 in which the substrate is extracted with a solvent and then either analyzed directly or after evaporating a portion of the solvent.

ASTM E1386 describes the extraction of ignitable liquids from substrates with the intended purpose of being able to identify the extracted ignitable liquids. This verification study also covers a situation where the substrate contains a mixture of a medium or light (less than C12) ignitable liquid mixed with a suspected heavy ignitable liquid. An example of such a mixture is gasoline/motor oil mixtures commonly used in two-stroke engines. For this procedure the light or medium ignitable liquid would first be extracted using the traditional procedure of passive headspace concentration with activated charcoal followed by solvent extraction. The solvent extraction procedure then would employ the evaporation of the light or medium ignitable liquid (and the solvent) from the sample in order to concentrate the heavy petroleum product.

The study also includes the verification of an instrumental (gas chromatography-mass spectrometry or GC-MS) method developed for the analysis of heavy fractions that may be encountered in the analysis of ignitable liquids.

This verification study examined three different types of extractions:

1. Extraction of an ignitable liquid poured onto an absorbent material.
2. Extraction of ignitable liquid from a substrate such as glass, plastic cap, or container.
3. Extraction of a gasoline/motor oil mixture poured onto an absorbent material where the gasoline is allowed to partially evaporate and an attempt is made to identify the heavy component.

Additional work completed as part of this study was the development and testing of a GC-MS program designed specifically for the analysis of heavy petroleum distillates.

Procedure

Development of a GC-MS method for the analysis of heavy petroleum distillates

Heavy petroleum distillates are defined in ASTM E1618 as having a carbon range of $C_9 - C_{20+}$, although typically the majority of the compounds present in heavy petroleum products will be greater than C_{12}. The standard fire debris GC-MS method used to analyze ignitable liquids is optimized for compounds of C_{20} and less, as these are the most commonly encountered ignitable liquids found in fire debris evidence. However, heavy petroleum products containing compounds greater than C_{20} may be encountered. A program designed specifically for heavy petroleum products would be useful for their identification.

Changes from the standard program to the program for heavy products are as follows:

	Standard GC-MS Method (FiredebrisV1.m)	**Heavy Petroleum GC-MS Method (heavyfiredebrisV1.m)**
Inlet Temp:	200°C	250°C
Start Mass:	29 amu	50 amu
End Mass:	400 amu	550 amu
Initial Temp:	35°C	100°C
Hold Time:	1 minute	2 min
Post Run Temp:	50°C	100°C
Rate 1:	6.5°C/min to 100°C	15°C/min to 300°C
Rate 2:	15°C/min to 300°C	None

Seven motor oil samples were analyzed on both the standard method and the heavy petroleum method.

Extraction 1 – Ignitable liquid poured onto an absorbent material

Three different ignitable liquids (gasoline, mineral spirits, and diesel) were poured separately onto three different pieces of absorbent material (Kimberly-Clark WypAll). The absorbent material was then extracted with pentane and the pentane analyzed by GC-MS. An unused portion of the absorbent material with no ignitable liquid added was also extracted with pentane as an extraction blank. The gasoline/pentane mixture was analyzed directly, while the mineral spirits/pentane and the diesel fuel/pentane were partially evaporated. All three ignitable liquids were analyzed using the standard fire debris GC-MS method. The diesel fuel was also analyzed using the heave petroleum GC-MS method.

Extraction 2 – Extraction of an Ignitable Liquid from a Substrate by Rinsing

Two different types of substrates, plastic caps and glassware, were rinsed first with an ignitable liquid then with pentane. One plastic cap was rinsed with mineral spirits and the other with gasoline. One of the glass substrates was rinsed with mineral spirits and three others with charcoal lighter fluid. The pentane was allowed to evaporate to a final volume of approximately 1 mL then analyzed using the standard fire debris GC-MS method.

Extraction 3 – Extraction and Concentration of a Gasoline/Motor Oil Mixture

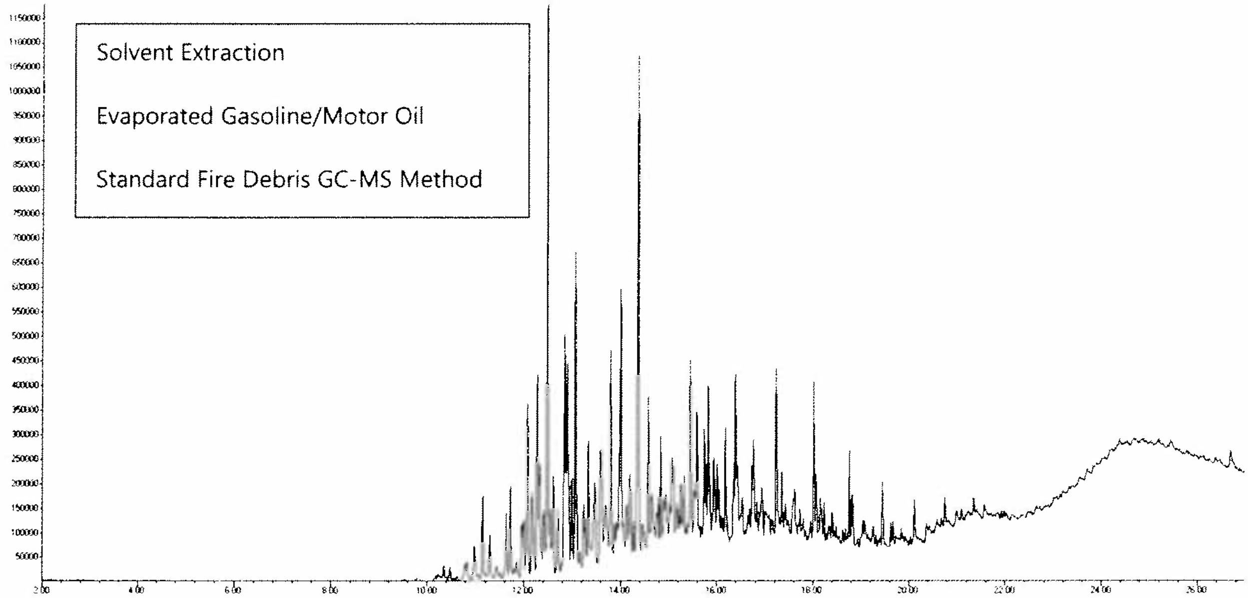
Approximately ½ mL of a gasoline/motor oil mixture was placed on a piece of absorbent material (Kimberly-Clark WypAll) then the absorbent material was extracted with pentane. The pentane was allowed to evaporate until only an oily residue remained. Pentane was added to the oily residue as a solvent for analysis by GC-MS. The sample was analyzed using both the standard GC-MS fire debris method and the heavy petroleum GC-MS method.

Findings

GC-MS method for heavy petroleum products:
The heavy petroleum method works well for ignitable liquids containing heavy molecular weight compounds like those typically found in motor oil. When analyzing fire debris evidence where the ignitable liquid is a residue, the heavy method should only be used after analysis using the standard method when heavy molecular weight compounds are detected in the sample run or in the following blank run (heavy compounds run on the standard method may sometimes appear in the following blank run).

Extractions:
The solvent extractions 1 – 3 worked well in all instances with the exception of one of the glassware solvent extractions where no charcoal lighter fluid was detected. Charcoal lighter fluid is a medium petroleum distillate and may have evaporated off of the glassware before it was rinsed with pentane. Glass is a non-porous material.

Extraction followed by evaporation of the gasoline/motor oil mixture allowed for the heavy fraction of the mixture (the motor oil component) to be concentrated relative to the gasoline fraction. The heavy component was readily detected in analyses using the standard fire debris GC-MS method and the heavy petroleum GC-MS method, but more heavy compounds (late eluters) were detected in the heavy petroleum method and provided a better over-all GC pattern of the heavy component of the mixture (See Figure 1). While most of the heavier gasoline components were present in the analysis, many of the target compounds used to identify gasoline were missing. This finding demonstrates the need to only perform this type of extraction after extracting the sample using the traditional passive headspace concentration with activated charcoal method. When the same gasoline/motor oil mixture was analyzed using the passive headspace method the gasoline component was readily detected but the oil component was not.



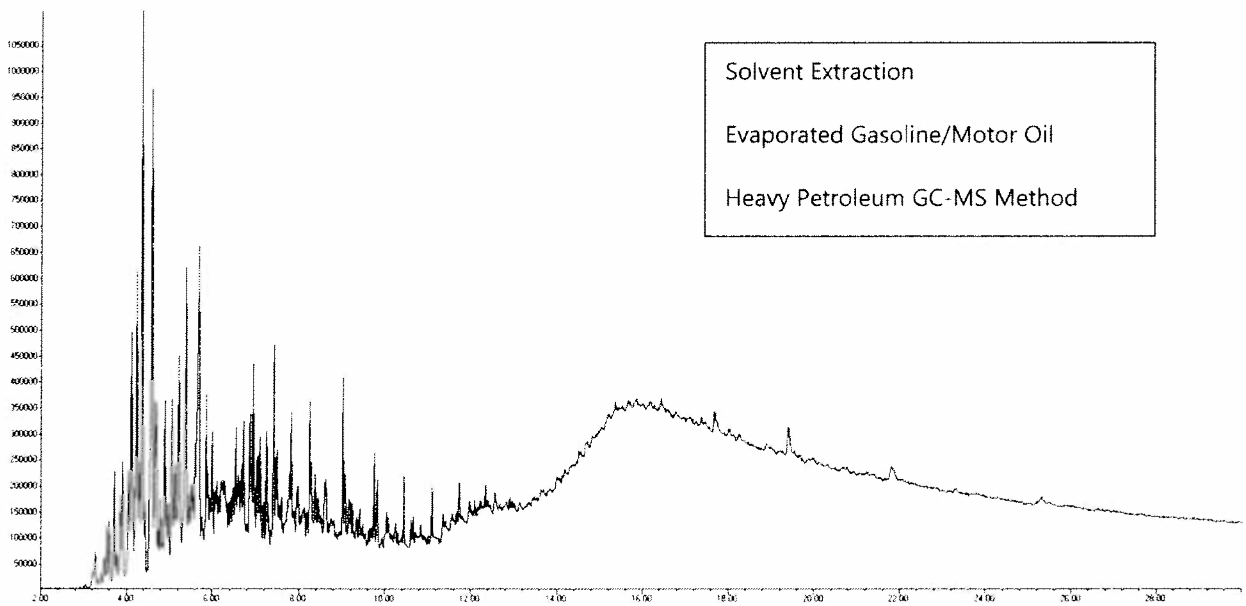


Figure 1. Total Ion Chromatograms showing the evaporated solvent extractions of a gasoline/motor oil mixture run on the standard fire debris GC-MS method (top) and the heavy petroleum GC-MS method (bottom).

Conclusions

Fit-for-Purpose Statement

This study has demonstrated that the heavy petroleum GC-MS method is fit for the purpose of analyzing samples known to or suspected of containing heavy petroleum ignitable liquids. However, this method should only be used after initial analysis by the standard fire debris method unless previous knowledge (such as label on a container) exists that the product contains a heavy ignitable liquid. The solvent extraction method was shown to be fit for the purpose of extracting medium to heavy ignitable liquids from absorbent materials and other substrates such as plastic and glassware. It also demonstrated that a heavy component of mixture (where the other component is a lighter ignitable liquid) can be concentrated by allowing the lighter component to evaporate following solvent extraction. This type of sample extract concentration should only be performed following the traditional extraction procedure (either passive headspace concentration with activated charcoal or solvent extraction without evaporation of the lighter component) and when a heavy component is suspected.

Data from this study demonstrates that the heavy petroleum GC-MS method and the solvent extraction method are fit for use in casework involving fire debris evidence.