Target Compound Ratio Analysis of Medium Petroleum Distillates

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Abstract

Medium petroleum distillates (MPD) that are commonly used during arsons to facilitate the growth of the fire and include paint thinners, dry cleaning solvents, and charcoal lighters. Gas Chromatography/Mass Spectrometry (GC/MS) data from MPD samples was analyzed using target compound ratios from key compounds found in medium petroleum distillates. Several compounds have been identified from mass spectra and retention times in medium petroleum distillates. These have been identified as possible key-component candidates. From those compounds, three ratios were calculated and compared for reproducibility within ignitable liquid and significant differences between liquids. Safer "green" paint thinners were also analyzed to determine chromatograms. This was an initial study to aid in future research including development of a database for statistical analysis of MPDs.

Introduction

Arson is one of the most dangerous and costly property crimes that occurs throughout the world. The presence of accelerant use at the crime scene indicates that a fire was intentionally set to cause damage to a property. The development of a method for target ratio analysis of MPDs will to aid in the creation of a database to assist in the identification of accelerants by fire debris analysts. In many reference collections medium petroleum distillates are represented by many different chromatograms due to the lack of homogeneity between products (5). Due to the lack of homogeneity, the research performed may not yield many useful ratios due to the variation of key components of the MPDs. Target-compound analysis can reduce background noise and interference allowing for greater sensitivity for detection of ignitable liquid residues. As a result they can be applied to create a database that can be used for statistical comparisons between samples (3).

Materials & Methods

All samples were run in triplicate on the Agilent GC 6890N & Agilent MS 5973N using these parameters:

- 60M DB-1 with an internal diameter of 250µm and a 1µm film thickness
- Helium was used as the carrier gas with a flow rate of 1.0 mL/min
- Split ratio of 50.0:1 and a split flow of 49.7:1mL/min
- 0.5µL syringe was with an injection volume of 0.2µL
- Injector temperature was 250°C
- Oven temperature program:
  - Initial temperature of 125°C
  - Hold for 1 minute
  - Temperature was increased to 250°C at a rate of 5.0°C/minute
  - Final hold for 5 minutes
  - Total run time 31 minutes.
- Pentane blanks between each sample
- E1618 standard test mixture
- 23 MPD samples

Key components were identified from this data, ratios were tested between these components including sequentially eluting components, and evaluated to be useful if the relative standard deviation was approximately 10% or below for each of the samples

Evaporation test

- A sample of Klean Strip® Paint Thinner was evaporated to 25, 50, 75 and 90% and then analyzed on the GC/MS

Burn tests

- E1412 extraction method using activated charcoal strips
- 5 cm by 5 cm sections of yellow pine, red oak, carpet, and carpet padding were charred to 50% of their original weight and spiked with either Klean Strip® mineral spirits sample, or Klean Strip® paint thinner sample or left blank

Klean Strip® Green products were tested for flammability by saturating yellow pine, carpet, and carpet padding with 1mL of the product and then using a propane torch to attempt to ignite the fluid

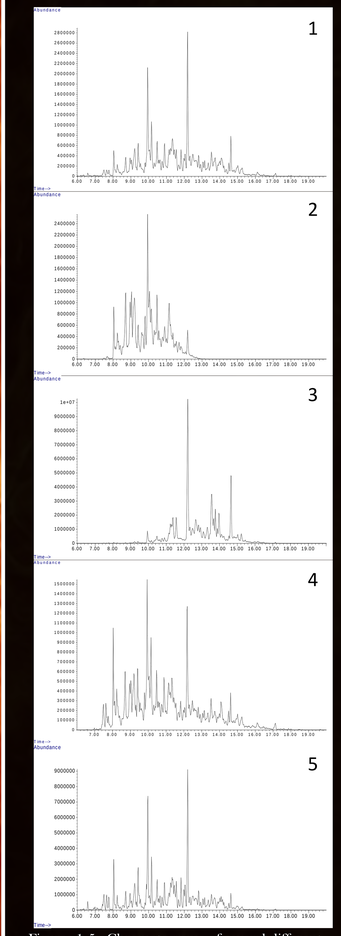
Results

- 21 key components were characterized from chromatograms
- Three ratios were identified as useful for statistical evaluations
- Approximately 30 ratios were tested

Evaporation tests demonstrated that the ratios calculated varied greatly between the neat sample and the evaporations.

Burn tests demonstrated that the ratios were robust enough to be calculated and compared to the neat samples. Substrate interference did not occur with the ratios used.

The Klean Strip® Safer Green Paint Thinner and Klean Strip® Green Odorless Mineral Spirits showed similar chromatograms for both analytes. Neither of the products were flammable.



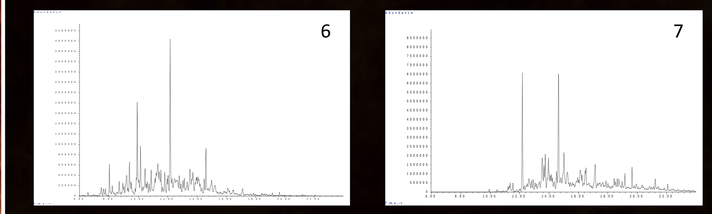
Figures 1-5. Chromatograms of several different medium petroleum distillates.

Table 1. A table of the key compounds characterized from the chromatograms of several medium petroleum distillates.

Peak #	Compound	Estimated RT
1	Toluene	6.36
2	Compound-a	7.49
3	P-xylene	7.77
4	Nonane	8.04
5	Compound-b	8.26
6	2,6-dimethyl-octane	8.72
7	Propyl-cyclohexane	9.04
8	4-methyl-nonane	9.22
9	1-ethyl-2-methyl-benzene	9.42
10	Decane	9.95
11	1,2,4-trimethyl-benzene	10.17
12	Compound-c	10.48
13	a-trimethyl-benzene	10.90
14	Compound-d	11.16
15	Compound-e	11.34
16	3-methyl-decane	11.56
17	O-propyl-toluene	11.83
18	Undecane	12.20
19	Compound-f	12.32
20	Compound-g	13.54
21	Dodecane	14.62

Table 2. A table of the ratios that were found to be most useful in determining individuality between samples.

Peak Ratio	Ratio	Components
1	11/4	1,2,4-trimethyl-benzene/nonane
2	18/10	Undecane/decane
3	15/13	Compound e/a-trimethyl-benzene



Figures 6-7. Evaporation chromatograms; (6) is the neat Klean Strip® paint thinner and (7) is 90% evaporated Klean Strip® paint thinner.

Conclusions

Peak ratios can be unique identifiers among medium petroleum distillates in addition to the various chromatogram patterns. Around 30 different ratios were tested in the development of the method and only the three ratios in Table 2 were found to work when analyzing most medium petroleum distillates. None of the ratios were found to work for all of the samples that were tested.

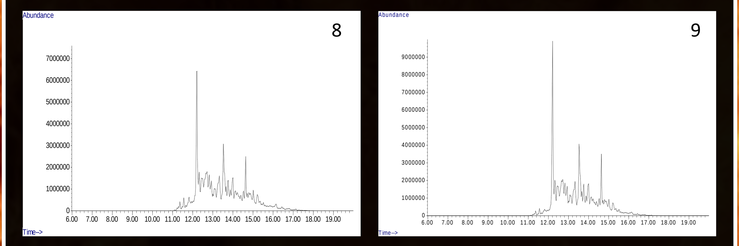
There was a marked difference in the ratios after the evaporation of the sample. The burn tests proved that the ratios were robust enough to still be observed in burned substrates, however this could be because the substrates were spiked after charring rather than using the MPD as the initial fuel for the fire.

The Klean Strip Safer products had chromatograms that were very similar to each other, which was unexpected due to the product's claim to be different from each other. Neither of the products ignited in laboratory conditions.

Further research needs to be conducted with a larger sample set to find a statistical method that would allow for any degree of similarity between any two ignitable liquid residues in fire debris analysis.

Table 3. A table of the ratios and standard deviations calculated from the selected target compound ratio method from burn samples spiked with Klean Strip® Paint Thinner.

Burn Study Sample	Ratio 1 Avg	Ratio 1 SD	Ratio 2 Avg	Ratio 2 SD	Ratio 3 Avg	Ratio 3 SD
Method Blank	ND	ND	ND	ND	ND	ND
Kimwipe	0.531	0.018	0.559	0.012	0.962	0.025
Uncharred Carpet	0.686	0.049	0.516	0.038	0.907	0.043
Uncharred Carpet Pad	0.598	0.041	0.530	0.027	0.904	0.039
Charred Yellow Pine	0.551	0.042	0.488	0.020	0.533	0.045
Charred Carpet	0.576	0.029	0.570	0.023	0.999	0.037
Charred Carpet Pad	0.615	0.007	0.454	0.017	0.704	0.077
Uncharred Yellow Pine	0.672	0.018	0.518	0.007	0.896	0.061
Uncharred Red Oak	0.481	0.022	0.554	0.031	0.957	0.009
Charred Red Oak	0.460	0.003	0.488	0.039	0.577	0.147



Figures 8-9. Klean Strip® Safer Green products; (8) is the safer paint thinner and (9) is mineral spirits.

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