The Differentiation of Kerosene Samples by Target Compound Ratio Analysis

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ABSTRACT

A statistical basis for declaring a similarity between any two kerosene samples is required by the courts and the recent National Academy of Sciences report. Gas Chromatography Mass Spectrometry (GCMS) was used to differentiate kerosene samples and fire debris residues using target compound ratio analysis. The relative amount of normal hydrocarbons to iso- and cycloparaffins shows both reproducibility and statistical difference between kerosene samples as neat liquids. Evaporated samples and burn tests show the robustness of these target compound ratios under a variety of conditions and substrates. Results suggest that target compound ratio analysis could be applied to other classes of ignitable liquids such as medium petroleum distillates (MPD).

INTRODUCTION

Target Compound Ratio Analysis

- Difficult to link ignitable liquid residues from fire debris to residues from a suspect's clothing
- No single method for the statistical comparison of ignitable liquids has proven to be the best in all cases involving fire debris analysis
- Kerosene: # 2 ignitable liquid used as an accelerant in arson crimes
- The subtle variations in peak area, between GCMS injections, cause variations in peak ratios; consequently, leading to a bigger variation between similarly classified samples
- The 36 target compounds selected have adequate concentrations and significant variations in the tested kerosene samples, which allow for reproducible ratios
- Evaporation studies show the effects of weathering on kerosene ratios
- Test burns demonstrate the effects of contamination on kerosene ratios

Previous Research

- Dolan and Ritacco have applied peak area ratio analysis to sequential peaks in order to establish a unique identifying profile for gasoline samples

Hypothesis

- Target compound ratio analysis can be used to statistically differentiate between kerosene samples

MATERIALS & METHODS

Samples

- Supplied by the Marathon Ashland Refinery, Catlettsburg, KY (Figure 1)

Instrumentation

- Agilent 6890N Network GC System/Agilent 5973 Network Mass Selective Detector with a Varian 60M DB-1 (60m x 250µm x 1µm) column
- Oven temperature program: 100°C for 1 minute; temperature ramp of 5°C/min to 150°C (no hold time); then 5°C/min to 275°C (5 min. hold time)

Part 1: Comparisons

- Target compound analysis identified key components in kerosene using ChemStation software as the output tool for the GCMS data (Table 1)
- The peaks of interest were selected based on retention time and target ions
- A spreadsheet template developed by Bondra, similar to that of Dolan and Ritacco for gasoline, calculated sequential ratios from the averages of the 3 GCMS injections using Excel©
- A relative standard deviation (RSD) under 5% was used as the criterion for acceptable repeatability among 3 individual injections of each sample

Part 2: Evaporations

- QA/QC kerosene composite sample (K034)
- ~200mL of QA/QC was evaporated on a hot plate; a steady N_2 flow was applied to the liquid to disrupt the surface tension for even evaporation
- Evaporation levels: 25%, 50%, 75%, & 90% (by vol.)

Part 3: Burn Tests

- Samples: kerosene samples K005 & K006
- Controls: ~ 20µL of neat K005 and K006 on Kimwipes®, unburned wood, carpet, & carpet pad
- ~1 mL kerosene was dispensed on ~2x2" (5x5 cm) squares of wood, carpet, or carpet pad, ignited with a butane lighter, and allowed to self-extinguish
- Kerosene residue was tested using the passive adsorption (ACS) ASTM Method E1412 with carbon disulfide as the extraction solvent

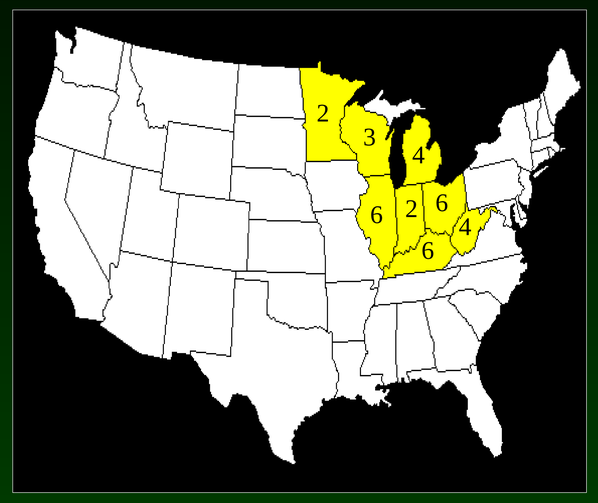

Figure 1: Geographical distribution of kerosene samples obtained from Marathon - Ashland

Table 1: Target compound list, estimated retention time, and corresponding ratios identified in each kerosene sample

Peak #	Target Compound	Est. RT	Ratio	Peak Ratio
(1)	Toluene	7.98	1	2/1
(2)	p-Xylene	10.20	2	3/2
(3)	Nonane	10.75	3	4/3
(4)	1-ethyl-2-methyl-benzene	12.58	4	5/4
(5)	ethyl-methyl-benzene	12.68	5	6/5
(6)	a-trimethyl-benzene	12.76	6	7/6
(7)	ethyl-methyl-benzene	13.18	7	8/7
(8)	Decane	13.42	8	9/8
(9)	1,2,4-trimethyl-benzene	13.58	9	10/9
(10)	a-trimethyl-benzene	14.50	10	11/10
(11)	a-diethyl-benzene	15.26	11	12/11
(12)	3-methyl-decane	15.48	12	13/12
(13)	Undecane	16.26	13	14/13
(14)	a-methyl-trans-decalin	17.67	14	15/14
(15)	compound-a	18.00	15	16/15
(16)	2-methyl-undecane	18.11	16	17/16
(17)	compound-b	18.20	17	18/17
(18)	methyl-ethyl-benzene	18.36	18	19/18
(19)	1,2,3,4-tetrahydro-napthalene	18.82	19	20/19
(20)	Dodecane	19.12	20	21/20
(21)	compound-c	19.24	21	22/21
(22)	2,6-dimethyl-undecane	19.55	22	23/22
(23)	compound-d	20.36	23	24/23
(24)	compound-e	20.81	24	25/24
(25)	a-dihydro-dimethyl-1H-indene	21.21	25	26/25
(26)	1,2,3,4-tetrahydro-6-methyl-napthalene	21.75	26	27/26
(27)	Tridecane	21.90	27	28/27
(28)	a-tetrahydro-dimethyl-napthalene	23.12	28	29/28
(29)	Tetradecane	24.55	29	30/29
(30)	1,7-dimethyl-napthalene	26.09	30	31/30
(31)	2,6,10,14-tetramethyl-hexadecane	26.20	31	32/31
(32)	3-methyl-tetradecane	26.39	32	33/32
(33)	Pentadecane	27.07	33	34/33
(34)	Hexadecane	29.45	34	35/34
(35)	Heptadecane	31.71	35	36/35
(36)	Octadecane	33.85		

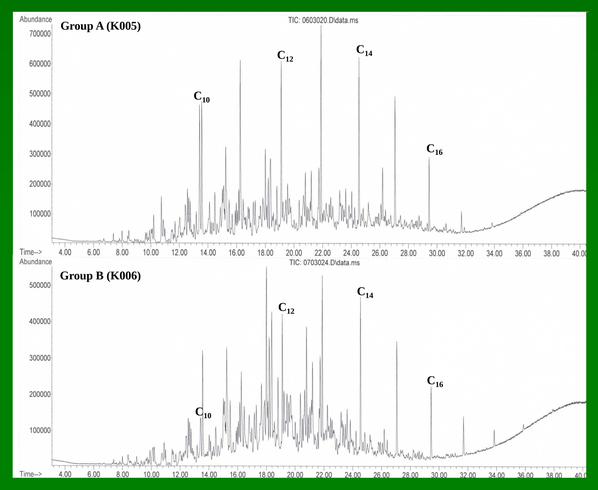

Figure 2: Total Ion Chromatograms (TIC) show differences in the abundance of normals relative to iso- and cycloalkanes between Group A and Group B kerosenes

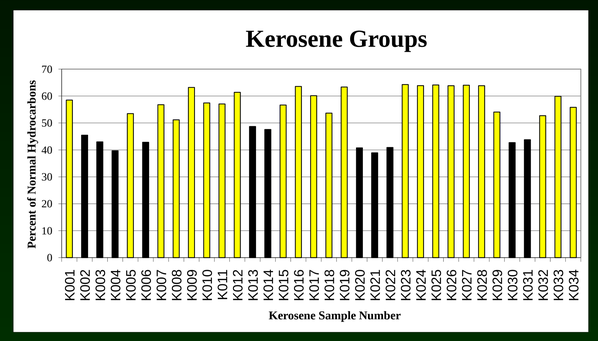

Figure 3: Abundance of normal hydrocarbons (% of total area) in each kerosene (Yellow = Group A/Black = Group B)

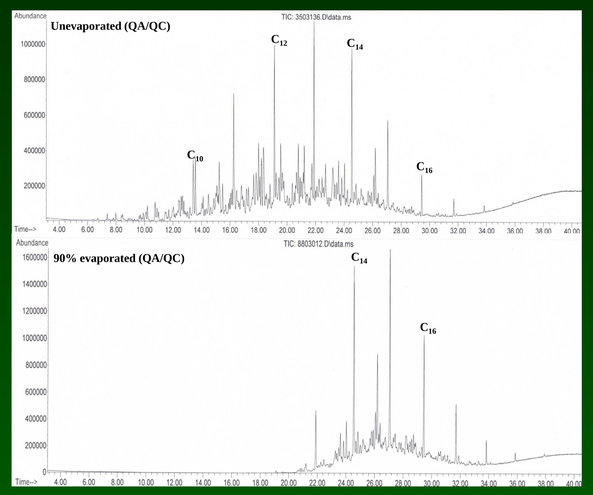

Figure 4: TIC of QA/QC kerosene unevaporated vs. 90% evaporated showing loss of light molecular weight compounds

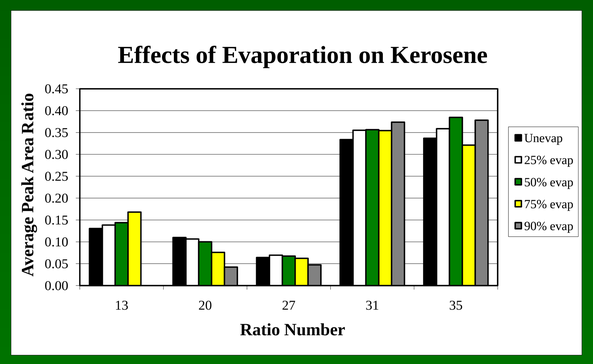

Figure 5: Effects of evaporation on peak area ratios (QA/QC kerosene composite sample). Compounds in Ratio 13 not detected at 90% evap. Ratio 20 is affected at 75% and 90% evap.

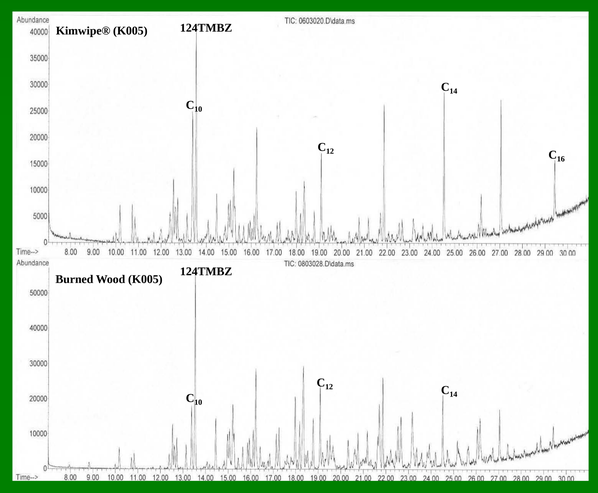

Figure 6: TIC from simulated fire debris – Spiked Kimwipe® vs. Burned Wood for kerosene sample K005 using E1412 Method (see Methods for details)

RESULTS

Part 1: Comparisons

- 36 target compounds & 35 sequential ratios were identified in each kerosene sample
- 2 distinct kerosene groups, distinguished by percent of normal hydrocarbons (Figure 2 & 3) Group A: 59% ± 4% & Group B: 43% ± 3%
- Odd/even predominance of normal hydrocarbons is not statistically different
- Pristane/phytane levels too low to be statistically reliable

Part 2: Evaporations

- Kerosene mix (K034) evaporated to 25%, 50%, 75%, and 90%
- Association between the evaporated samples and the neat kerosene mix
- With increasing evaporation, the ratios involving normals varied; however, may not be statistically significant (Figure 4 & 5)

Part 3: Burn Tests

- Target compound area ratios of neat samples on Kimwipes® (using the ASTM E1412 method) were similar to the neat injection samples, confirming no adsorption/desorption issues with the activated charcoal strip
- Pyrolysis products were seen in all of the burned substrates (burned wood-least) (Figure 6)
- Target compound ratios were similar between unburned and burned

CONCLUSIONS

In conclusion, kerosene samples like gasoline samples, can be analyzed using GCMS with target compound ratio analysis to differentiate neat samples. The number of kerosene samples collected so far is limited. All sequential ratios are retained even if they appear to not be statistically significant. Kerosene, unlike gasoline, is a simple distillation product from crude oil and may be strongly related to the petroleum from which it was distilled. The relative concentrations of components in kerosene will often change daily due to sources of crude oil. This variation may provide sufficient variability for comparison between kerosenes. In order to establish a greater degree of discrimination, more samples need to be collected from a variety of locations.

Initial kerosene results suggest that it may be possible to provide target compound ratio analysis for other classes of ignitable liquids. Comparisons of MPDs could be very useful in fire debris analysis. A database of kerosene, gasoline, and MPDs is being developed from a large number of samples from a variety of sources. This database will be necessary to establish the statistical criteria for declaring two samples similar with a probability of error.

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