TR 9134

Forensic Analysis

Technical Report No. 9134

A New Forensic Tool for Arson Analysis, the Tandem PID/FID

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Introduction

In the examination of arson samples, the identification of residual fuels at the site is critical in compiling evidence for prosecution. Even after a structure is totally destroyed, a small amount of fuel may be collected from air on a carbon strip. An extract in pentane is then analyzed by capillary gas chromatography (GC) on a Flame Ionization Detector (FID) or a Mass Spectrometer (GC / MS) as specified in ASTM Method E 1387-95 by FID and E 1618-94 by GC / MS.[1] The data presented in this publication were collected using the GC FID method. Various fuels were diluted with pentane and analyzed by a split capillary injection. Several samples from a controlled burn were run. A Photoionization Detector (PID) was coupled in tandem with the FID for the study. Two fingerprint patterns of the total hydrocarbons and aromatics were produced from a single injection. The Tandem PID / FID provided confirmation of the suspected fuel through detailed characterization of the aromatics and other hydrocarbons.

Experimental

The Model 9001 GC was configured with a Tandem PID / FID and a split / splitless capillary injector with Electronic Pressure Control (EPC), *Figure 1*. The Tandem PID / FID is a high-temperature, dual detector for speciation of total petroleum hydrocarbons (TPHs). A 1 µL injection of the sample was made. The PID is available with a Krypton 10.2 eV or Xenon 9.6 eV lamp. The lower energy lamp totally removes all response for the alkanes. Only the aromatics which have Ionization Potentials less than 9.6 eV are detected, *Figure 2*. The response for aromatics with the 9.6 eV lamp is lower than with the 10.2 eV lamp. The instrument parameters are as listed below:

Instrument Parameters:

9001 GC
Column: Restek Rtx® 5 0.25mm x 30 meter, 1.0 µm
Column flow: 3 mL / min Helium EPC 28 psi constant pressure
Oven: 60°C, 1.0 min.; 30°C / min., 300°C, 20 min.
Split Injector: 250°C (Set at 20 / 1 split for all injections)
Split purge vent: 60 mL / min.
4 mm i.d. liner with silanized glass wool

Tandem PID / FID
PID: 300°C
Xenon lamp at 1.25 milliamp, 9.6 eV
FID: 300°C
Hydrogen : 20 mL / min.
Air: 200 mL / min
Make up: 12 mL / min Helium
CE AS 800 Liquid Autosampler
1 µL injection

1.) ASTM Method E 1387-95(GC), "Standard Test Method for Ignitable Liquid Residues in Extracts From Fire Debris Samples by Gas Chromatography" and E 1618-94 (GC / MS) " Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas ChromatographyMass Spectrometry"

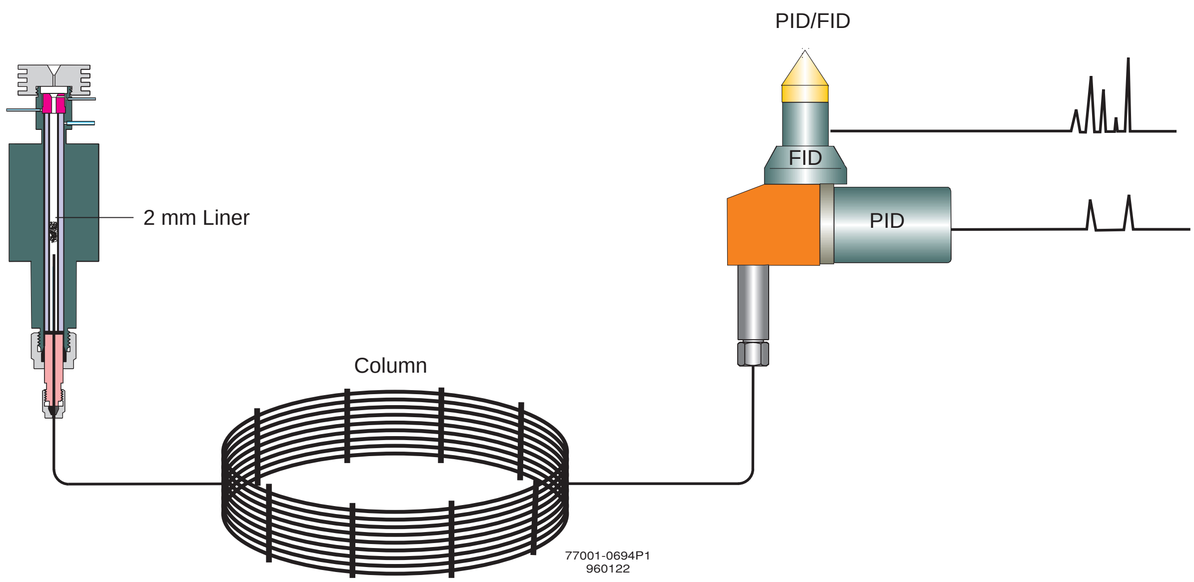

Figure 1. Split Capillary Analysis with Tandem PID/FID

Results

Since the chromatogram of the fuel is interpreted by pattern recognition, a resolution check mix listed in Table 1 from Restek was run to establish the carbon number of the pattern and the presence of certain aromatics *Figure 2*. No response for the alkanes was observed on the PID, due to its specificity for aromatics. The detector selected must show adequate sensitivity for a 0.05% dilution of a liquid fuel when injecting 1 µL at a split of 20 / 1 as specified in the method. Two gasoline samples were diluted to 0.05% and injected to prove sensitivity *Figures 3a* and *3b*. One sample came from Texas and the other from California. Some distinct pattern differences were noted on the PID at 7 minutes in the run.

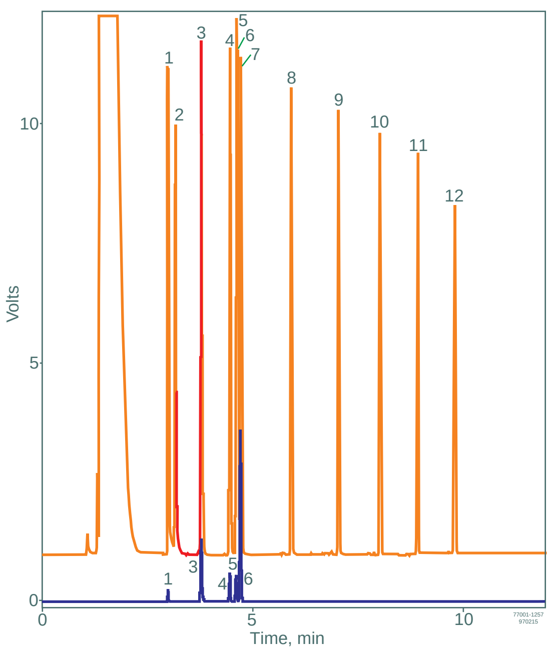

Figure 2. Resolution Mix at 2000 ppm each (20/1 Split)

Table 1. (For Figure 2)

Peak #	Component	Peak #	Component
1.	Toluene	7.	Decane ($C_{10}H_{22}$)
2.	Octane (C_8H_{18})	8.	Dodecane ($C_{12}H_{26}$)
3.	p-Xylene	9.	Tetradecane ($C_{14}H_{30}$)
4.	3-Ethyltoluene	10.	Hexadecane($C_{16}H_{34}$)
5.	2-Ethyltoluene	11.	Octadecane ($C_{18}H_{38}$)
6.	1,2,4-Trimethylbenzene	12.	Eicosane ($C_{20}H_{42}$)

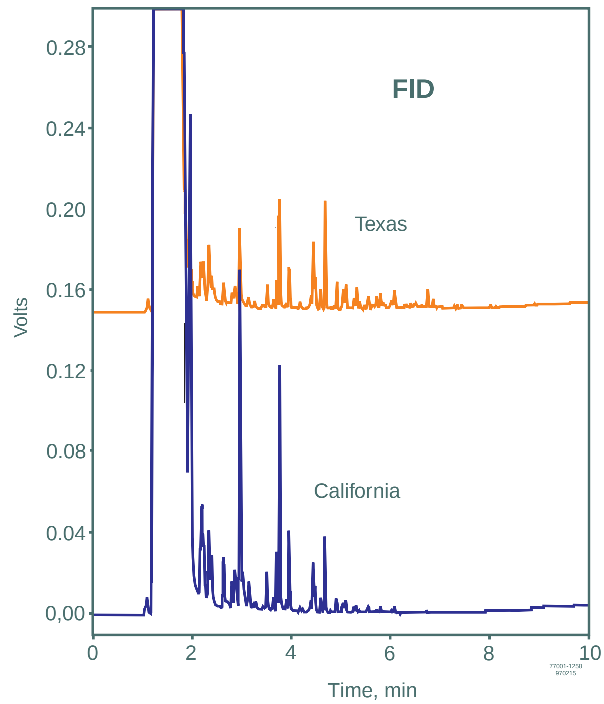

Figure 3a. Comparison of Gasolines at 0.05% on the FID (20/1 Split)

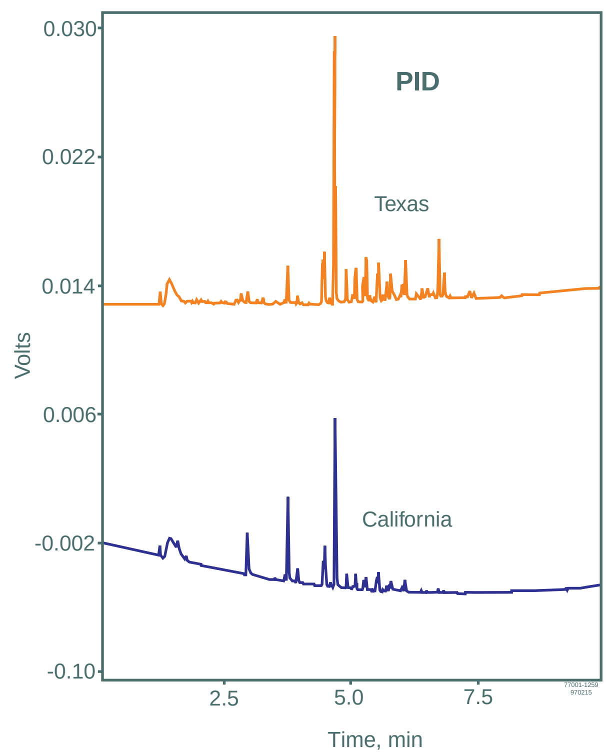

Figure 3b. Comparison of Gasolines at 0.05% on the PID (20/1 Split)

The samples from the controlled burn site were collected on strips of charcoal ribbon and extracted with 100 μL of pentane to determine the fuel used for the burn. A representative chromatogram of California reformulated fuel gasoline diluted in pentane was injected first at 0% and 94% evaporation and compared to the Resolution Check Mix. *Figures 4a* and *4b*.

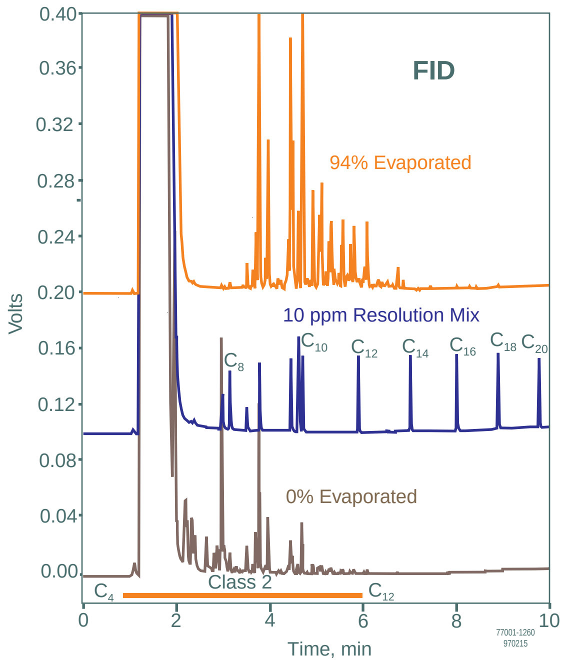

Figure 4a. California gasoline on the FID at 0.05% (20/1 Split)

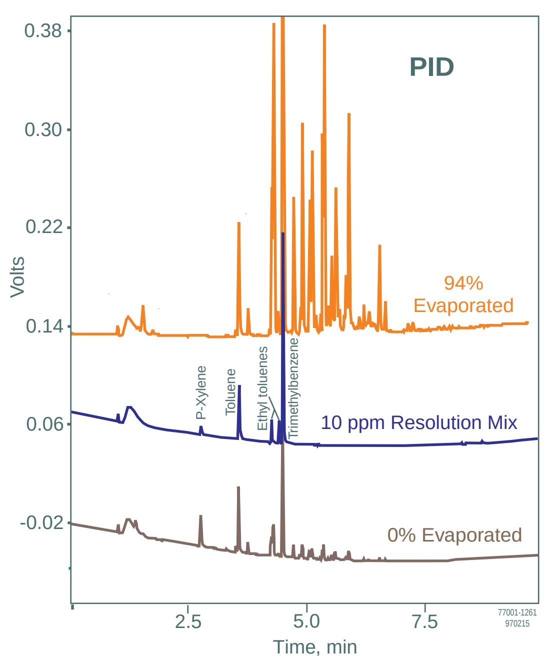

Figure 4b. California gasoline on the PID at 0.05% (20/1 Split)

Method E 1387-95 lists the protocol for interpretation of a chromatogram by pattern recognition and comparison. Ignitable liquids fall in one of five categories as listed in *Table 2*. Gasoline is designated as a Class 2 fuel. A wide variety of other fuels were analyzed for determination of their classes *Figures 5, 6 and 7*. Several samples from the burn site were then compared to the known fuels. A match to the California gasoline at 94% evaporation was determined in *Figures 8* and *9*.

*Table 2. Classification of Fuels**

Class #	Name	N-Alkane Carbon #	Examples
1	Light Petroleum Distillates (LPD)	C4-C11	Pocket lighter fuels
2	Gasoline	C4-C12	Automotive gasolines
3	Medium Petroleum Distillates (MPD)	C8-C12	Lamp oils, charcoal starters, paint thinners
4	Kerosene	C9-C17	Jet-A aviation fuel, #1 fuel oil
5	Heavy Petroleum Distillates (HPD)	C9-C23	#2 fuel oil, diesel
0	Miscellaneous	Variable	Single compounds, turpentines
0.1	Oxygenated Solvents	Variable	Alcohols, esters, ketones
0.2	Isoparaffins	Variable	Copier fluids, camping fuels
0.3	Normal Alkanes	Variable	Lamp oils
0.4	Aromatic Solvents	Variable	Light, medium, heavy aromatic naphtha in solvents for paint and plastics
0.5	Naphthenic/paraffins Solvents	Variable	Fuel products made from Class 3 or 4 distillates-treated to remove normal alkanes and aromatics
*	ASTM Method E 1387-95 (GC), "Standard Test Method for Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography		

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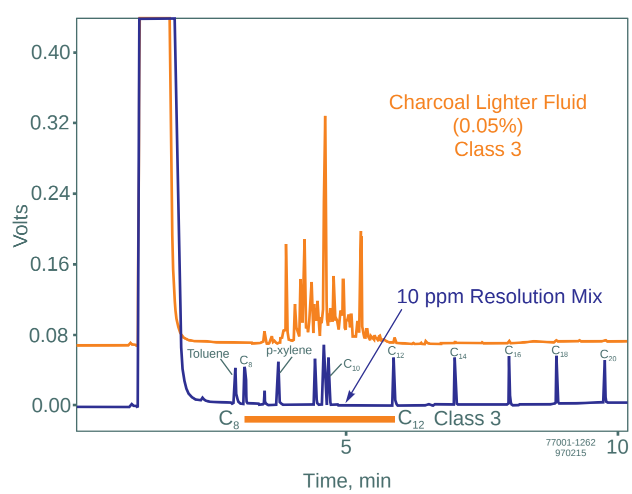

Figure 5. Charcoal Lighter Fluid, a Class 3 Fuel on the FID (20/1 Split)

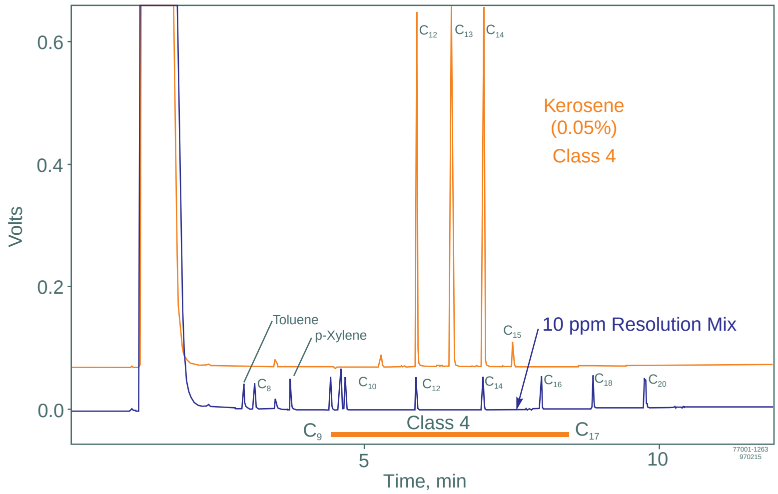

Figure 6. Kerosene, a Class 4 Fuel on the FID (20/1 Split)

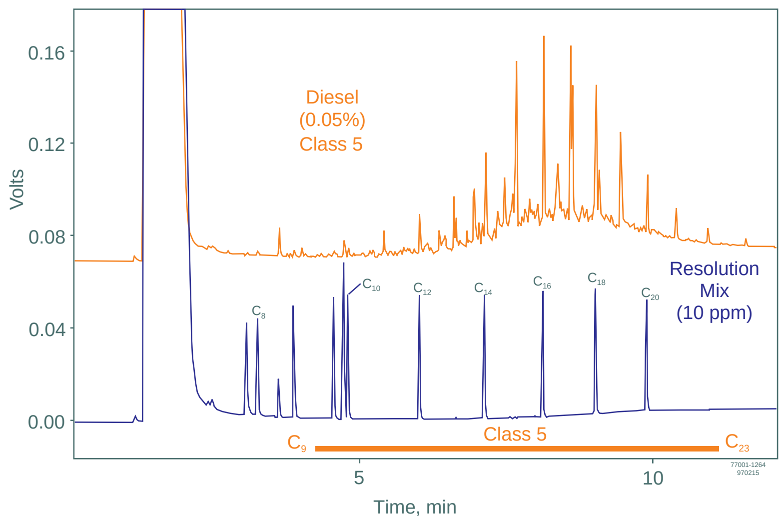

Figure 7. Diesel, a Class 5 Fuel on the FID (20/1 Split)

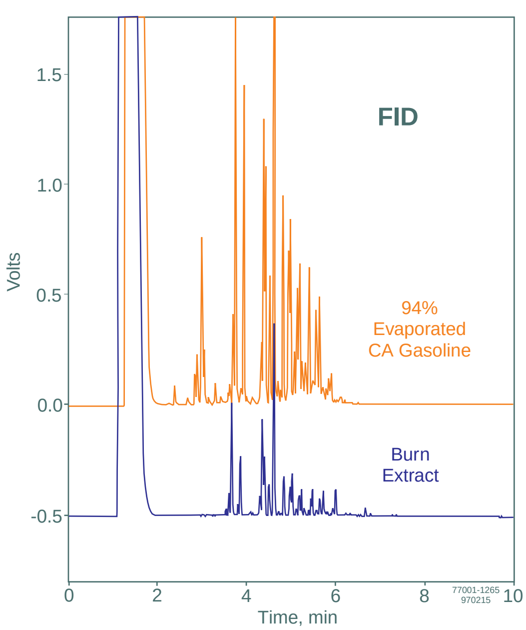

Figure 8. Match of California Gasoline with Burn Sample #6A (20/1 Split)

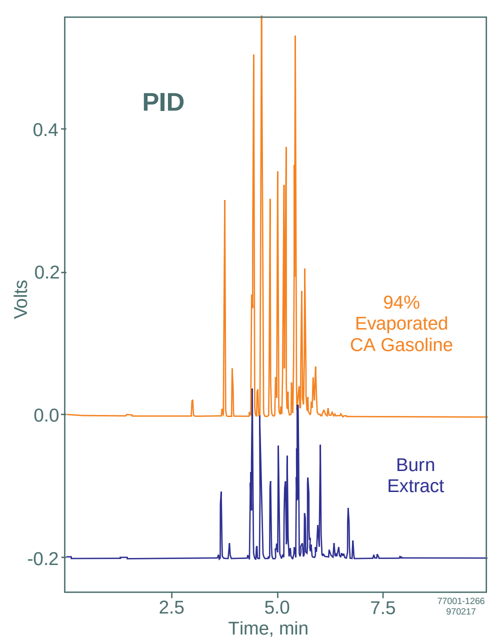

Figure 9. Match of California Gasoline with Burn Sample #6A (20/1 Split)

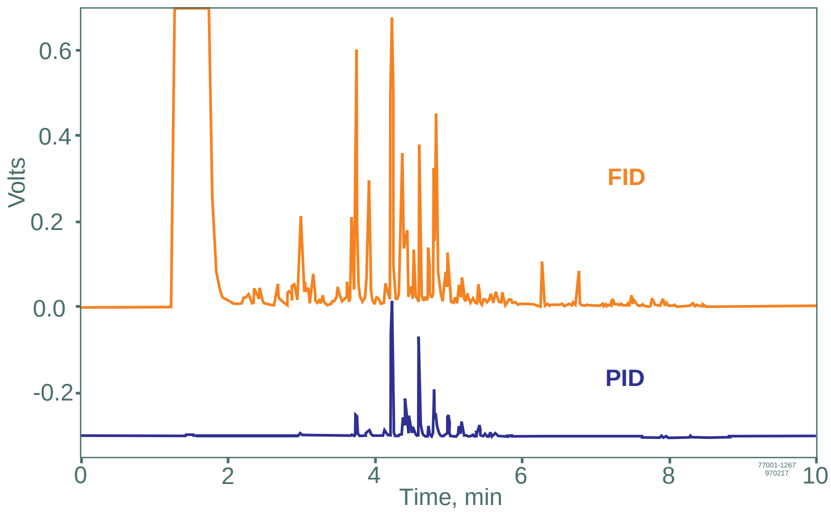

Figure 10. Pyrolysis of Burn Extract #6G (20/1 Split)

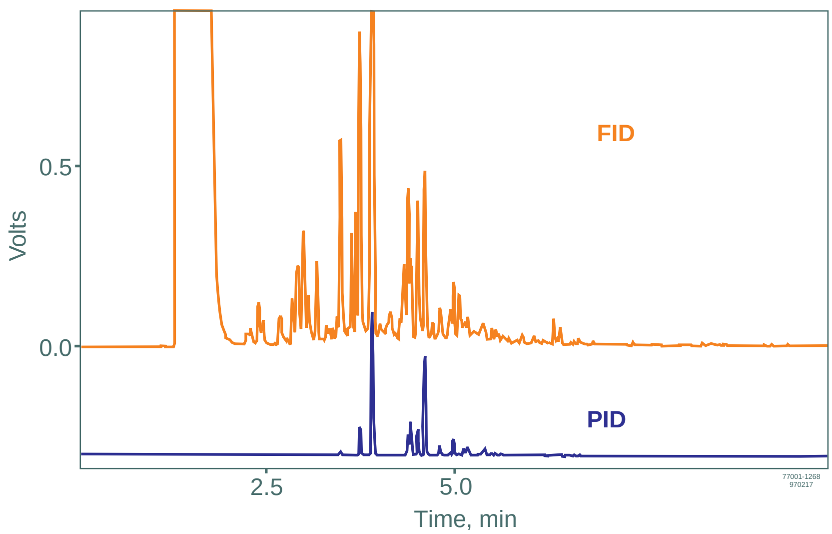

Figure 11. Pyrolysis of Burn Extract #7B (20/1 Split)

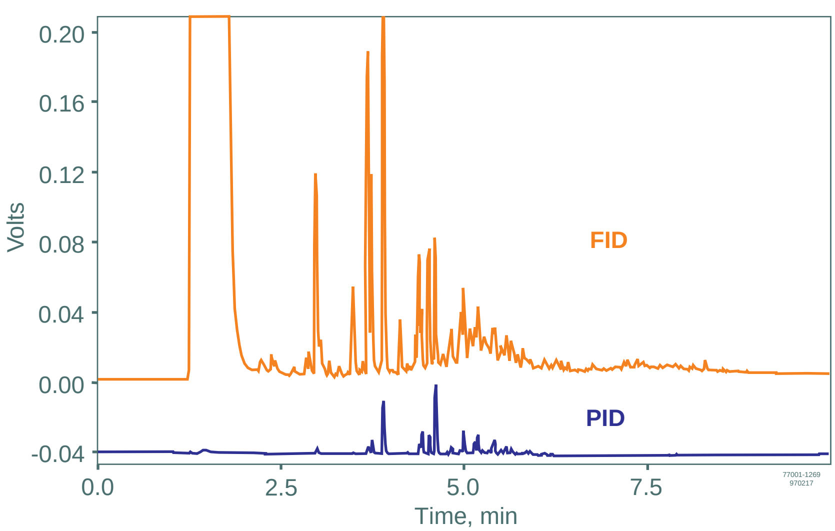

Figure 12. Pyrolysis of Burn Extract #6H (20/1 Split)

Careful examination of three burn samples in the same case study showed different aromatic patterns on the PID in *Figures 10, 11* and *12* from the sample shown in *Figures 8* and *9*. In an arson case, some samples undergo pyrolysis, resulting in very distinctive aromatic patterns.

Conclusion

The Tandem PID / FID met the criteria for ASTM Method E 1387-95. Both detectors demonstrated sensitivity in the low ppm range. Correlation between extracts analyzed at a controlled burn matched the fuel used for ignition. The detectors provided the selectivity for more accurate pattern recognition than that obtainable with only the FID. Since the detectors are coupled together in tandem, only a single injection is required. The data compiled from the simultaneous analysis with the FID and PID simplifies the examination of residues of ignitable liquids in the analysis of fire debris samples.

Acknowledgement:

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