

Interpretation of Ignitable Liquid Residues in Fire Debris Analysis:

Effects of Competitive Adsorption

Amanda Heeren, BS*, J. Graham Rankin, PhD

Forensic Science Program, Marshall University, Huntington, WV 25701



Abstract

The common practice utilized for analysis of ignitable liquids is the ASTM E1412 method, passive headspace concentration using activated charcoal strips and classifying with the E1618 method. One area for misinterpretation stems from problems associated with competitive adsorption. Whether due to the increased surface area after charring, or the similar components located on the activated charcoal strip and substrates, initial studies demonstrate that the total overall response of the chromatogram is indeed affected by the amount (percent weight loss) of charring on a substrate. Understanding the problems associated with this method will aid analysts in interpreting and classifying ignitable liquids.

Introduction

Fire debris analysis is defined as a science related to the examination of fire debris samples performed to detect and identify ignitable liquid residues (ILR)¹. Ignitable liquids are classified based on the physical and chemical properties of the liquid. Ignitable liquids are defined as petroleum based or related products that have certain flammable or combustible properties². The main goal in fire debris analysis is to identify and classify substances as ignitable liquids. Pattern recognition and interpretation of chromatograms are the most important aspects of fire debris analysis. The ASTM E1618³ method specifies the classes of ILR as well as how they are determined from GCMS analysis. Ignitable liquids, based on this standard are classified into eight classes with three subclasses of each (light, medium and heavy) plus a separate class for gasoline. Complications can arise in classifying particular ignitable liquids if the total overall response of the chromatogram is affected. One way that the chromatograms are affected is by competitive adsorption.

The E1412 method uses activated charcoal strips (ACS) for concentration and recovery of ILR vapors. Because charred wood and other fire debris are basically charcoal, it has been understood that there may be competitive adsorption between the charred substrate and the ACS for the ILR. Because different classes of hydrocarbons in the ILR may be selectively retained by the charred fire debris, the resulting chromatographic patterns used by analysts for classification may be misinterpreted⁴.

Materials and Methods

Procedure

- Samples were weighed pre and post charring
- Samples were approximately 2"x2"x 3/4"
- Charring was performed with propane torch (see Figure 1)
- Samples spiked with gasoline or kerosene
- Samples prepared to ASTM E1412-07 Method⁵
 - Samples were placed into 1 quart paint can
 - Cans placed in oven for 16 hours at 60°C
 - Carbon disulfide (approximately 150 µL) was used to extract the IL
- All sample sequences contained an E1618 Standard (Restek), kerosene and/or gasoline sample for comparison



Figure 1. Charring process for wood samples.

Gas Chromatography-Mass Spectrometry

Samples were analyzed on a Varian Gas Chromatograph with a Saturn 2200 which uses an ion trap Mass Spectrometer. The column was a 30m x 250 µm x 0.25 µm Restek Rxi[®]-5ms. Helium was used as the carrier gas. The injector temperature was at 250 °C with a 20:1 split ratio. The initial temperature was 60 °C (held for 2 minutes) and increasing at a rate of 10 °C/minute up to 320 °C (held for 19 minutes).

Results

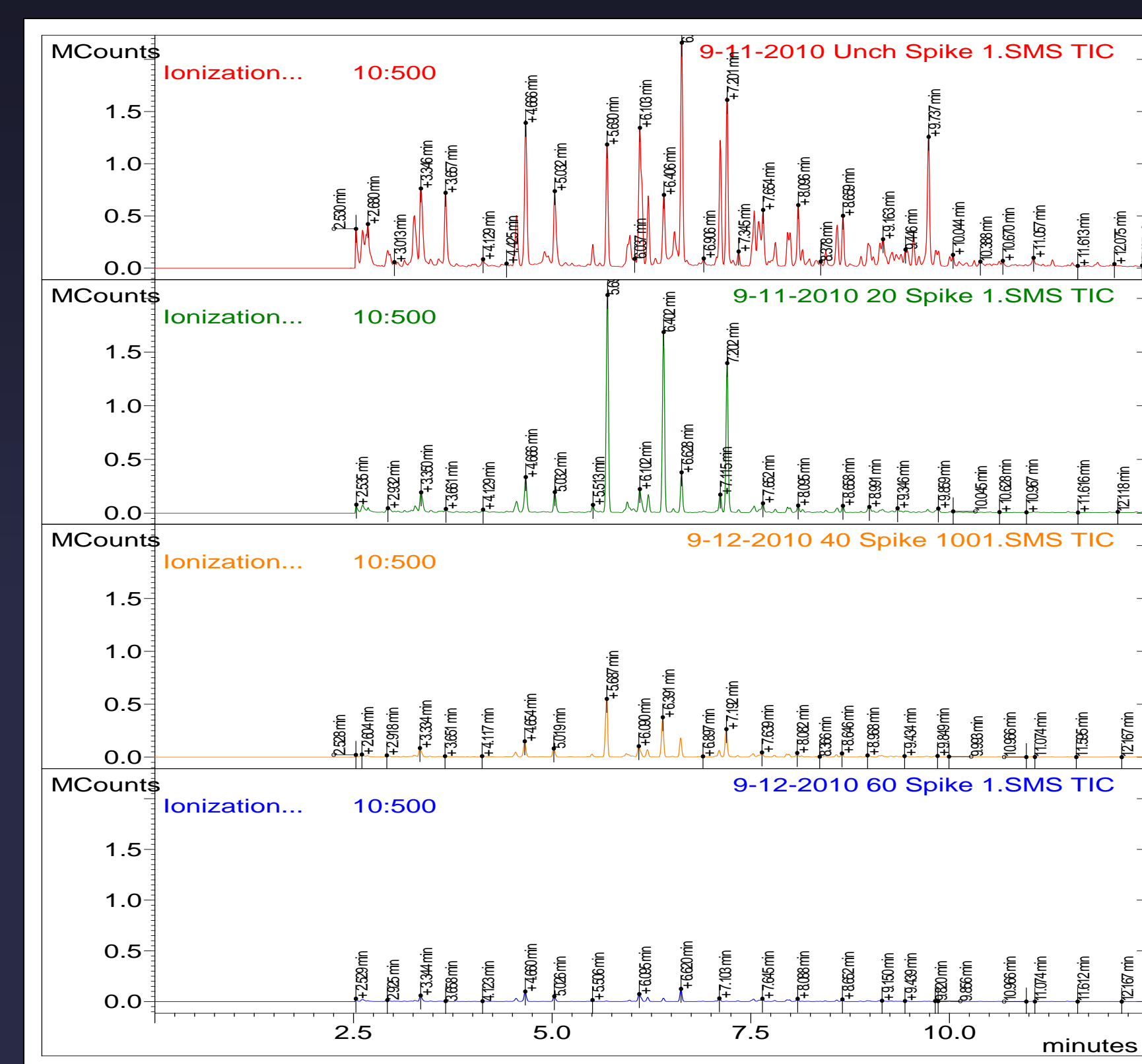


Figure 2. Total Ion Chromatogram (TIC) demonstrating a gasoline spike of yellow pine substrate at a 0% (red), 20% (green), 40% (orange) and 60% (blue) weight loss displayed on the same axes for comparisons of overall relative response.

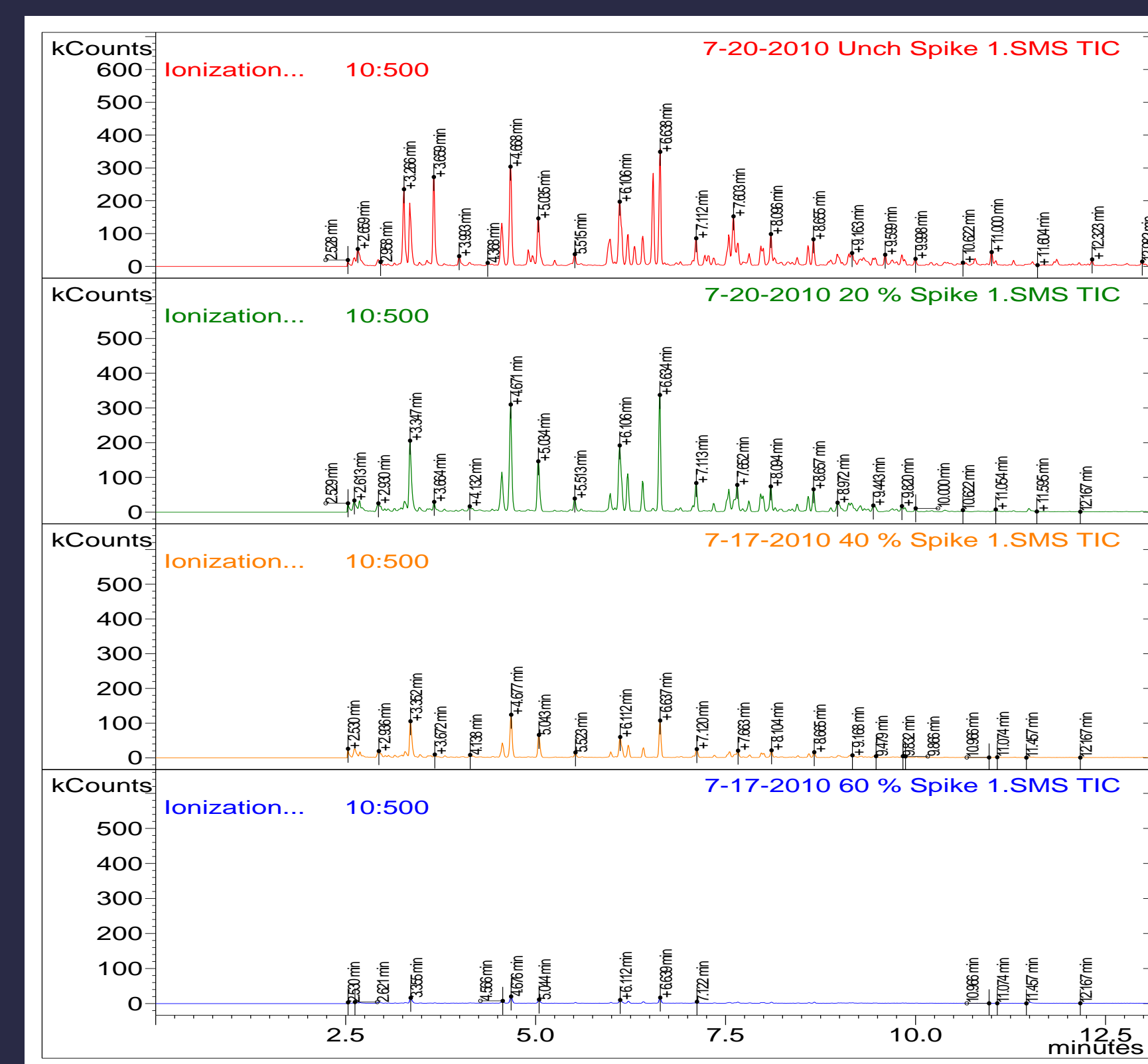


Figure 3. TIC demonstrating a gasoline spiked white pine substrate following overall weight loss order as Figure 2.

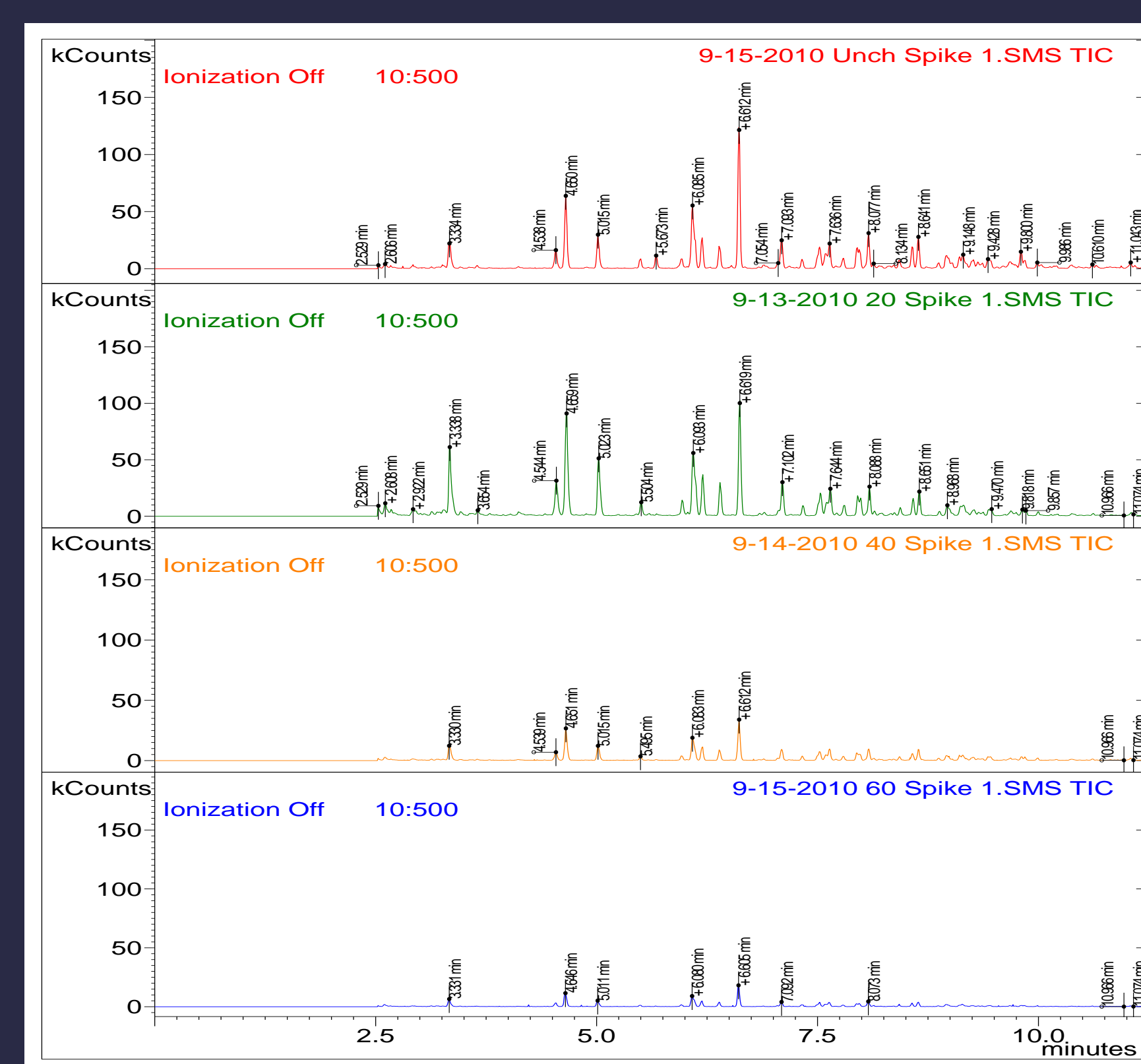


Figure 4. TIC demonstrating a gasoline spiked pressure treated pine substrate following same weight loss order as Figure 2.

Table 1. Actual percentage of weight loss (WL) for different wood substrates tested.

Substrate	White Pine WL	Pressure Treated Pine WL	Yellow Pine WL	Aspen WL
20 Blank	22	26	18	22
40 Blank	39	41	38	44
60 Blank	65	54	62	73
20 Spike	30	29	31	25
40 Spike	43	40	36	40
60 Spike	56	67	61	60

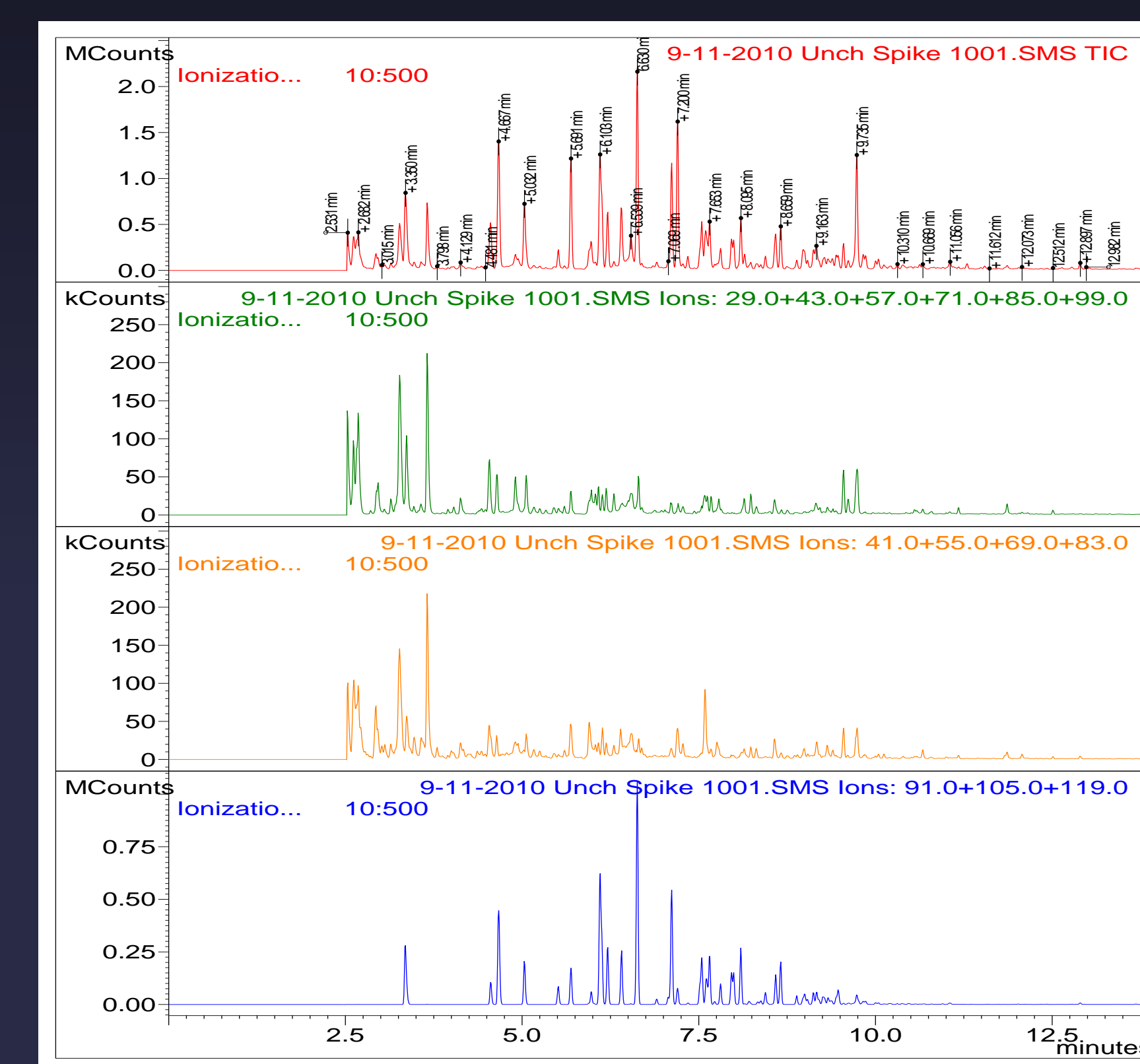


Figure 5. TIC demonstrating the 0% weight loss gasoline spiked yellow pine substrate (red) and the extracted ion chromatograms (EICs) for alkanes (green) using ions 29, 43, 57, 71, 85 and 99, cycloalkanes (orange) using ions 41, 55, 69 and 83, and finally aromatics (blue) using ions 91, 105 and 119.

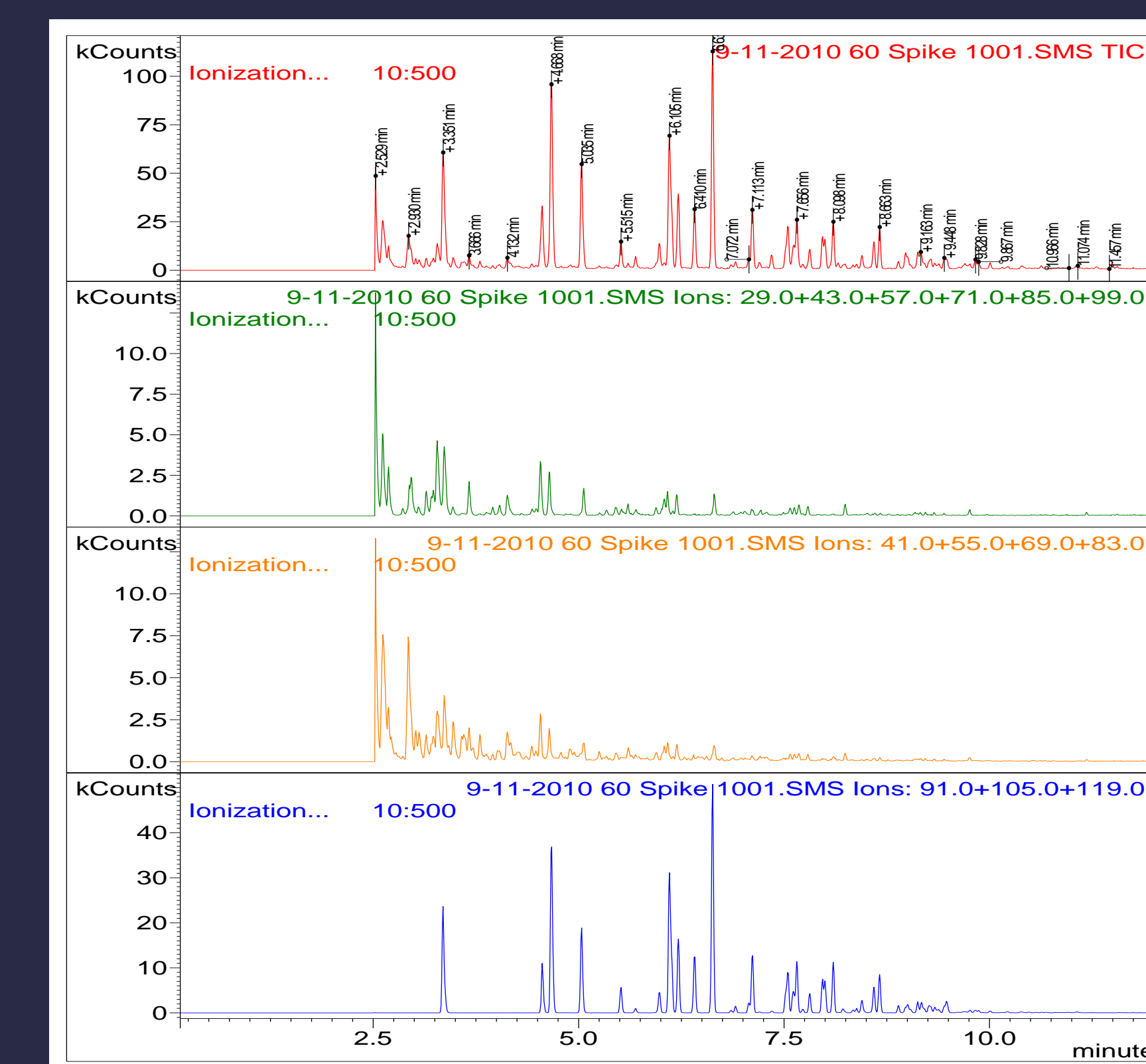


Figure 6. TIC demonstrating the 60% weight loss gasoline spiked yellow pine substrate and the corresponding EICs in same order as Figure 5.

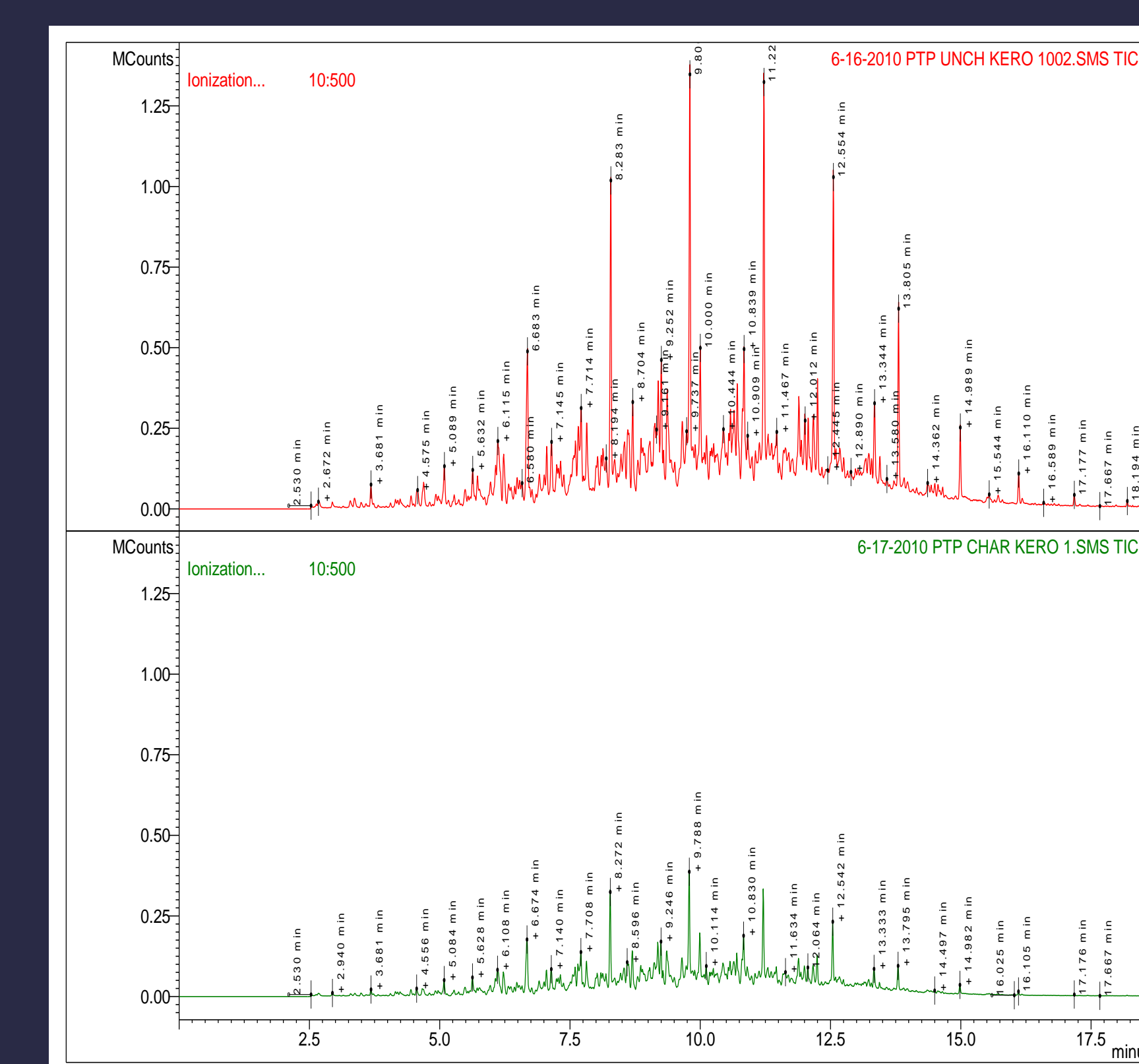


Figure 7. Chromatogram demonstrating a kerosene spiked pressure treated pine substrate at a 0% (red) and a 20% (green) weight loss both displayed on the same axes for comparisons of overall relative response.

Table 2. Displays the substrates that have been tested at different weight loss (WL) levels spiked with kerosene (K) and/or gasoline (G).

Wood Substrate	20% WL	40% WL	60% WL
Aspen	G, K	G	G
Plywood	G,K		
Poplar	G, K		
Pressure Treated Pine	G, K	G	G
Red Oak	G, K	G	G
Select White Pine	G, K		
Western Red Cedar	G, K	G	G
White Pine	G, K	G	G
Yellow Pine	G, K	G	G

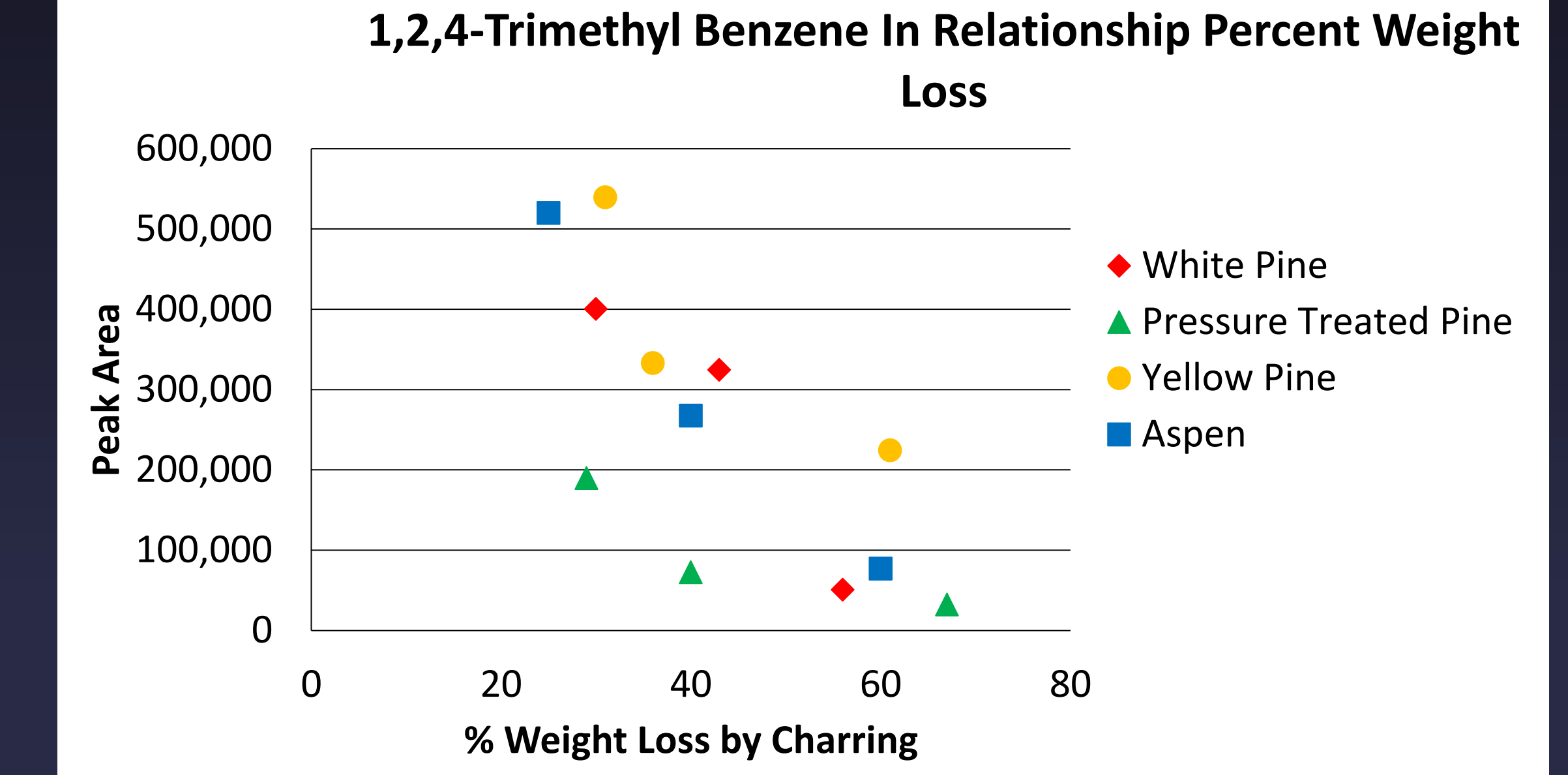


Figure 8. Plot of 1,2,4-Trimethyl Benzene in relationship to percent weight loss of wood substrate (see Table 1).

Discussion

A decrease in overall relative response of the chromatogram is noticed in most samples with increasing weight loss. White pine, yellow pine and pressure treated pine are compared to demonstrate the different reactions to the weight loss of the wood substrate and the amount of IL lost or retained by the substrate. Comparing the pine substrate chromatograms, all three different substrates displayed the most significant decrease in overall response with 60% weight loss. Differences can be seen by observing the relative abundance of different ions present in the EIC. A comparison of the EIC 0% weight loss to the 60% weight loss substrate of yellow pine demonstrates that the more weight loss, the more loss of abundance of alkanes and cycloalkanes. This concept was seen in most samples analyzed.

In the kerosene spiked substrates, a decrease of overall response was seen in most samples. The overall response was more significance when compared to the same substrate and weight loss spiked with gasoline. The decreased could be explained by the chemical make-up of the particular ignitable liquid. Due to the nature of these compounds, it might be more difficult for the wood or the char to retain particular compounds in the kerosene samples.

Two explanations potentially can explain the decrease in overall relative response. One explanation of decreased response could be due to the increased charred surface area retaining the compounds. The other is due to the fact that both charcoal and IL are competing for space on the activated charcoal, and the competition between the two increases with more weight loss.

Conclusion

Overall, competitive adsorption, in initial studies, suggests potential problems that could cause misinterpretation of results. In future studies, more ignitable liquids, perhaps in the low and medium petroleum range will be used to see the reaction of different ignitable liquid categories. Different substrates will be tested to observe the overall chromatogram response as well.

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