Poster Reprint

ASMS 2018
TP-180

Low Energy EI and High Resolving Power Instrumentation for the Analysis of Arson Samples

Matthew Curtis
Agilent Technologies, Santa Clara, CA

Introduction

The FBI Uniform Crime Reporting Program reported 56,825 arson cases in 2010 in the United States with 46% of those involving structures such as residential, storage and public property. The average loss was almost $18,000, with industrial structures having the highest loss average of $134,000. The ability to quickly and confidently identify if an accelerant or ignitable liquid was used in the origin of a fire is vital to an investigator. With the number of easily accessible ignitable liquids increasing and their diversity decreasing, a sensitive and accurate analysis is required. Most of the current analyses of arson utilize the total ion chromatograms of ignitable liquids to match the sample to a known accelerant[1]. The complexity of the sample matrix and possible mixtures of the accelerants hinders the ability to quickly match the chromatogram from the database of images.

The data presented in this poster illustrates the analytical capability of an accurate mass high resolution GC/Q-TOF with low energy EI functionality (Figure 1) to help with unknown compound detection and increased identification confidence to provide detailed information on specific ignitable liquids.

Figure 1: Agilent 7250 GC/Q-TOF

Experimental

Sample Preparation:

Substrate samples that required only solvent extraction prior to injection were analyzed. These substrates were soaked in different accelerants and different concentrations. Two additional sample collection types were analyzed; a laboratory wipe of the accelerant and a wood chip with the accelerant. A Detailed Hydrocarbon Analysis (DHA) standard sample included paraffins, isoparaffins, aromatics, naphthalenes and olefins, was used for the analytes used for quantitation. Carbon disulfide was used for the extraction of the substrate to increase the recoveries of the naphthalene isomers.

Analytical conditions for the GC/Q-TOF platform are listed in Table 1

Low eV Optimization:

A survey of multiple eV settings was acquired, then reviewed to determine the amount of spectral tilt necessary for high confidence in the detection of molecular ions.

Software:

All data analysis was performed with the MassHunter Suite. This included MassHunter Qualitative Analysis B08, MassHunter Quantitative Analysis B08, MassHunter Unknowns Analysis, and Molecular Structure Correlator.

Table 1: Agilent 7250 GC/Q-TOF; 7890B GC Parameters[2]

GC and MS Conditions:		
Column	DB-1ms UI, 60 m, 0.25 mm ID, 0.25 µm film	
Injection volume and liner	1µL	Single-taper low-pressure drop
Split	20:1 split	
Inlet temperature	260 °C	
Oven temperature program	50 °C for 3.5 min	
	5 °C/min to 120 °C	
	12 °C/min to 300 °C; hold 5 min	
Carrier gas	Helium at 1.6 mL/min constant flow	
Transfer line temperature	300 °C	
Source temperature	280°C	
Quadrupole temperature	150°C	
Spectral range	30 to 300 m/z	
Spectral acquisition rate	12 Hz, both centroid and profile	
Electron Energy	70 eV and 13 eV	
Emission	5µA and 0.8µA, respectively	

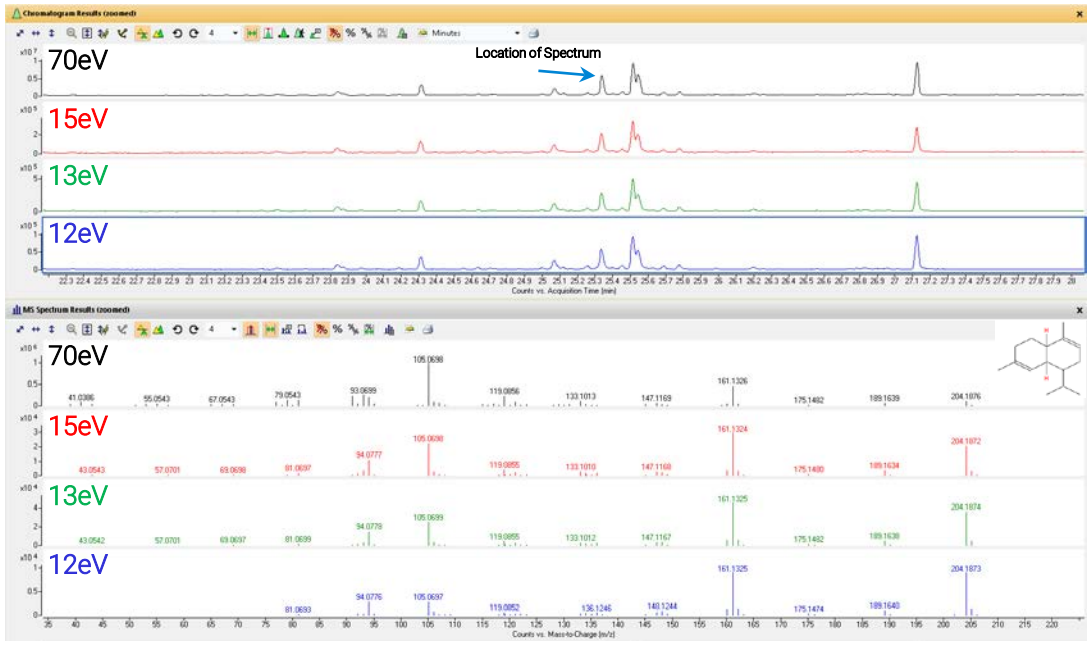

Figure 2: Illustrates the spectral tilt observed as the eV is decreased with the low energy ion source.

Figure 3: Comparing 70eV (above) and low eV (below) for a low level component with mass accuracy maintained.

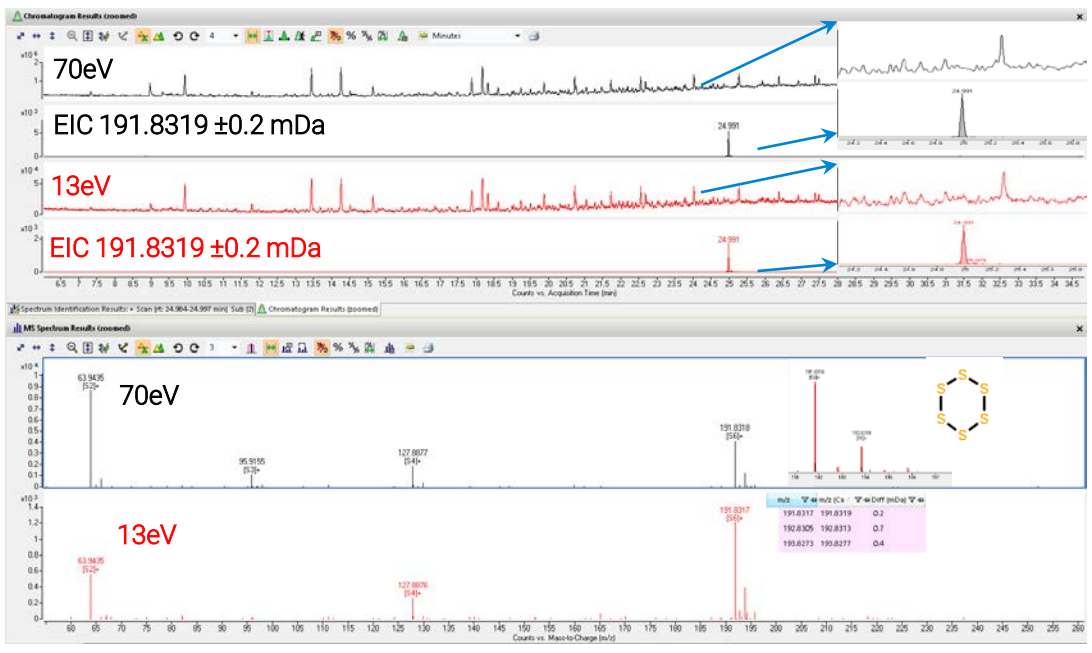

Figure 4: Exact mass ion extraction to locate suspected components. Low eV was sensitive enough to detect the component with an accurate mass.

Figure 5: Molecular Feature Extraction and NIST17 library searches provided quick identification of C3-naphthalenes.

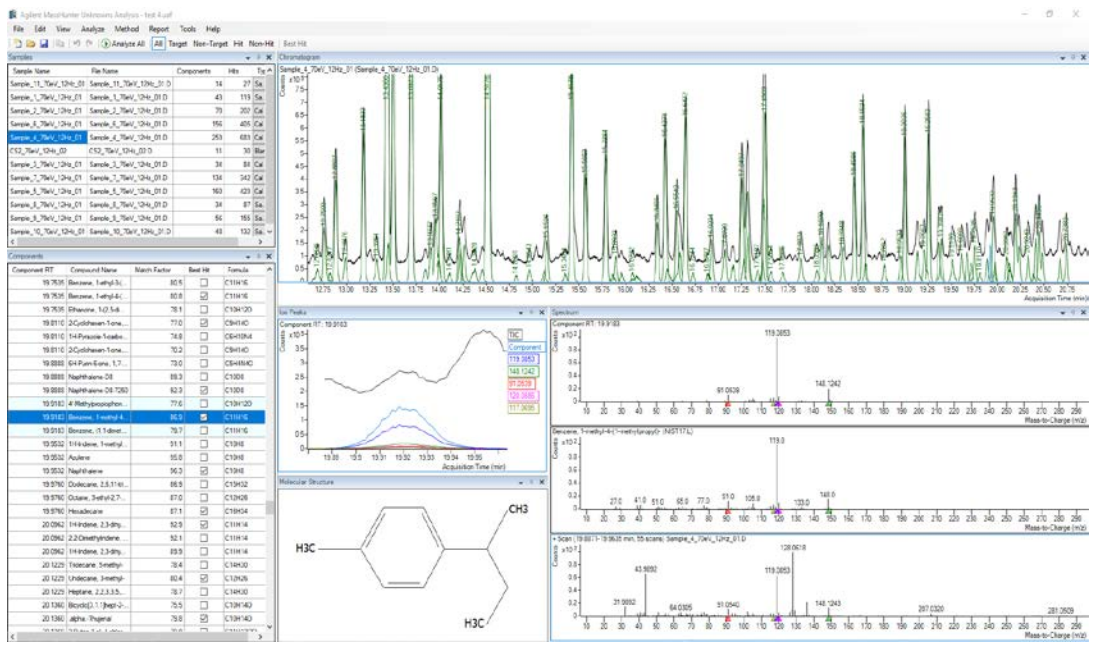

Figure 6: Unknowns Analysis utilized Agilent SureMass, a signal processing algorithm, to identify individual components and clean the spectra from co-eluting peaks and background.

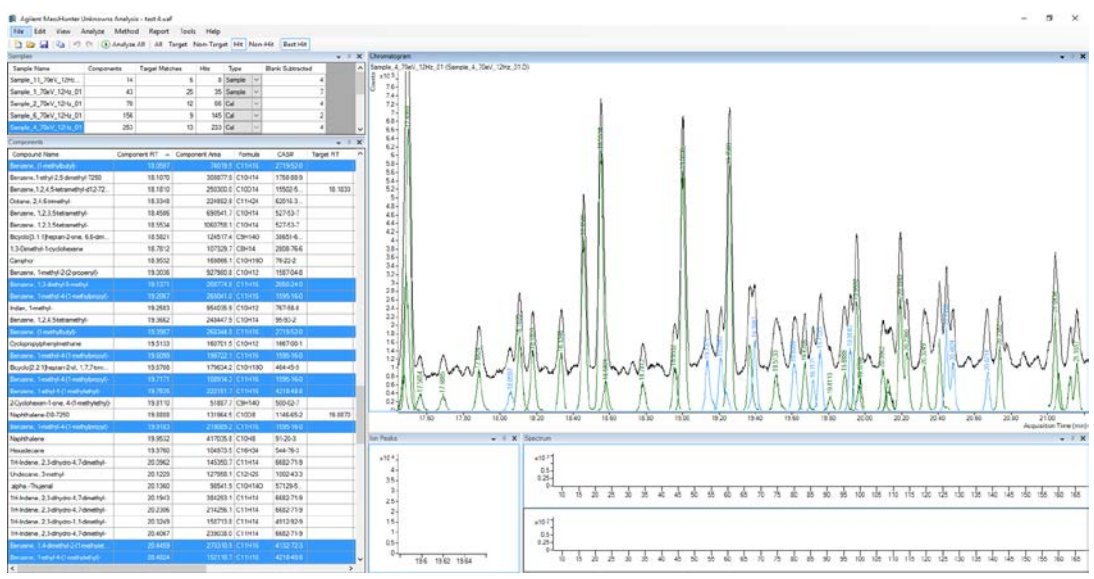

Figure 7: SureMass signal processing and NIST17 library search to identify the C5-benzenes from a gasoline soaked wood chip.

Results and Discussion

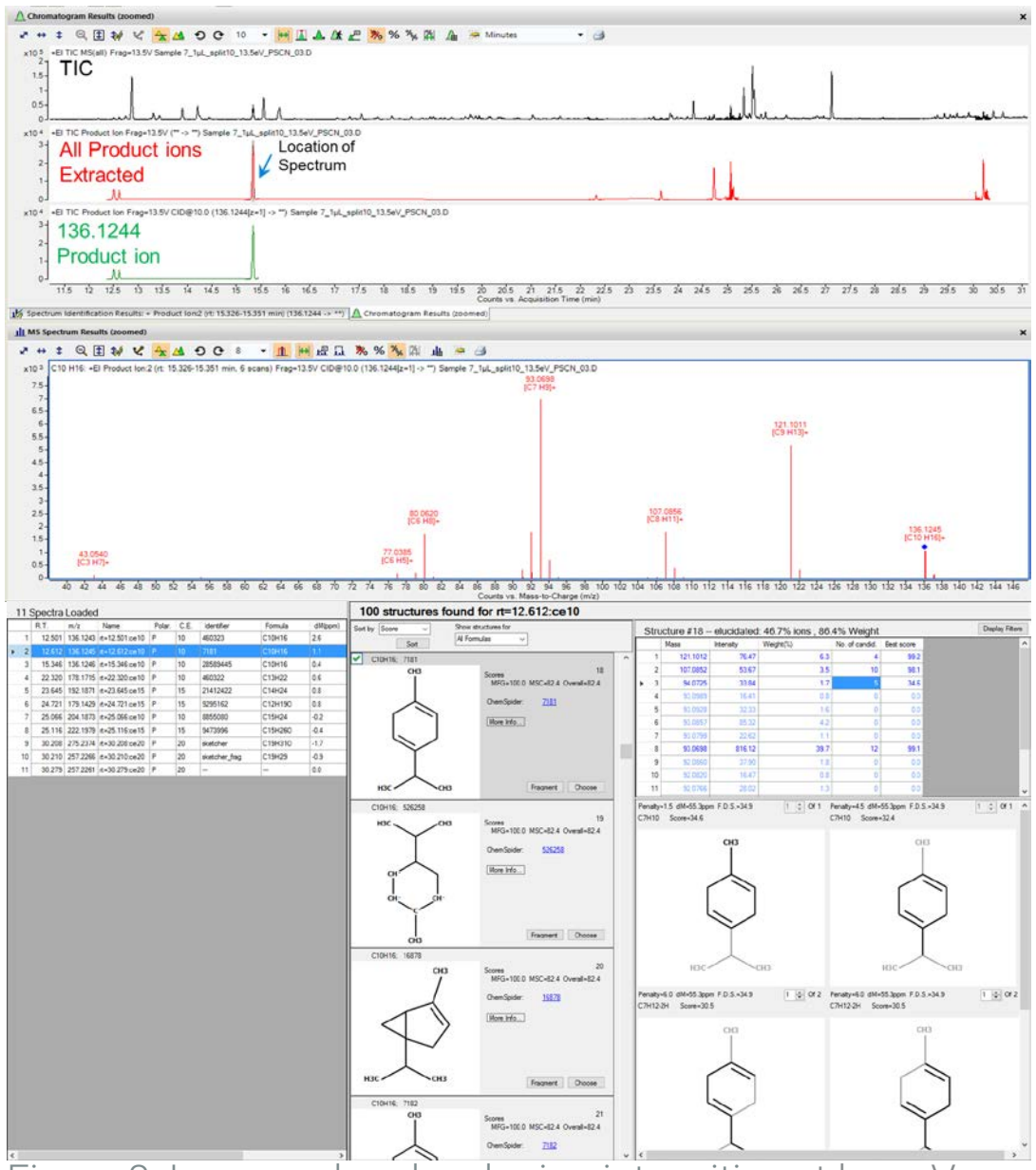

Figure 8: Increased molecular ion intensities at low eV improved MS/MS spectra to help with the identification of the structure using Molecular Structure Correlator.

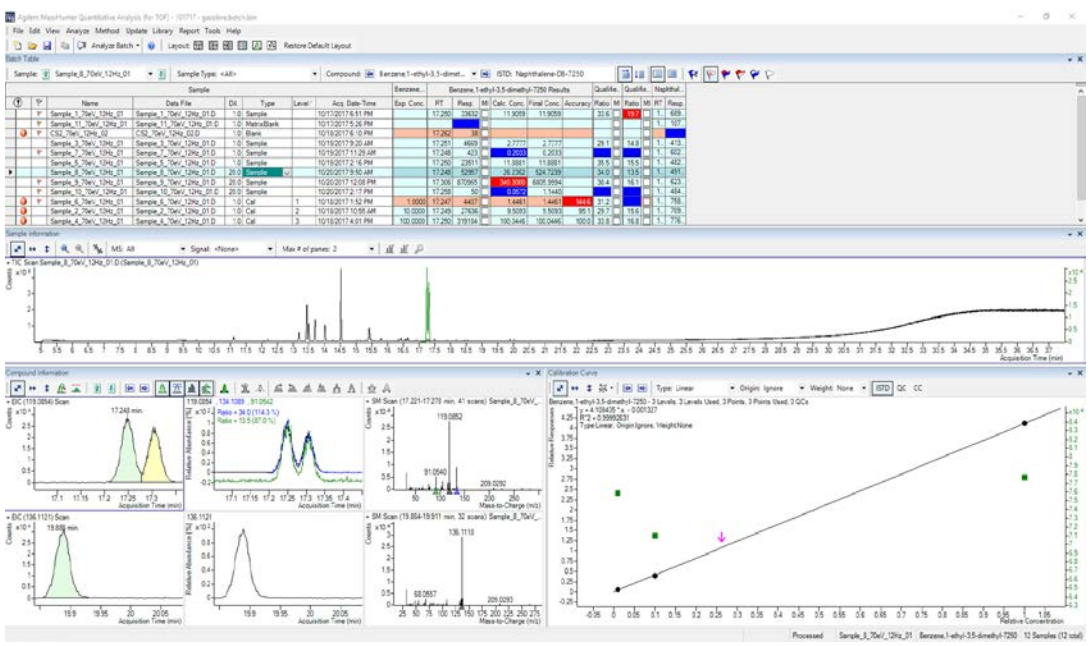

Figure 9: A quantitation curve was created from the DHA components and applied to an Exxon aromatic 100 sample, naphthalene-d8 was used as the ISTD.

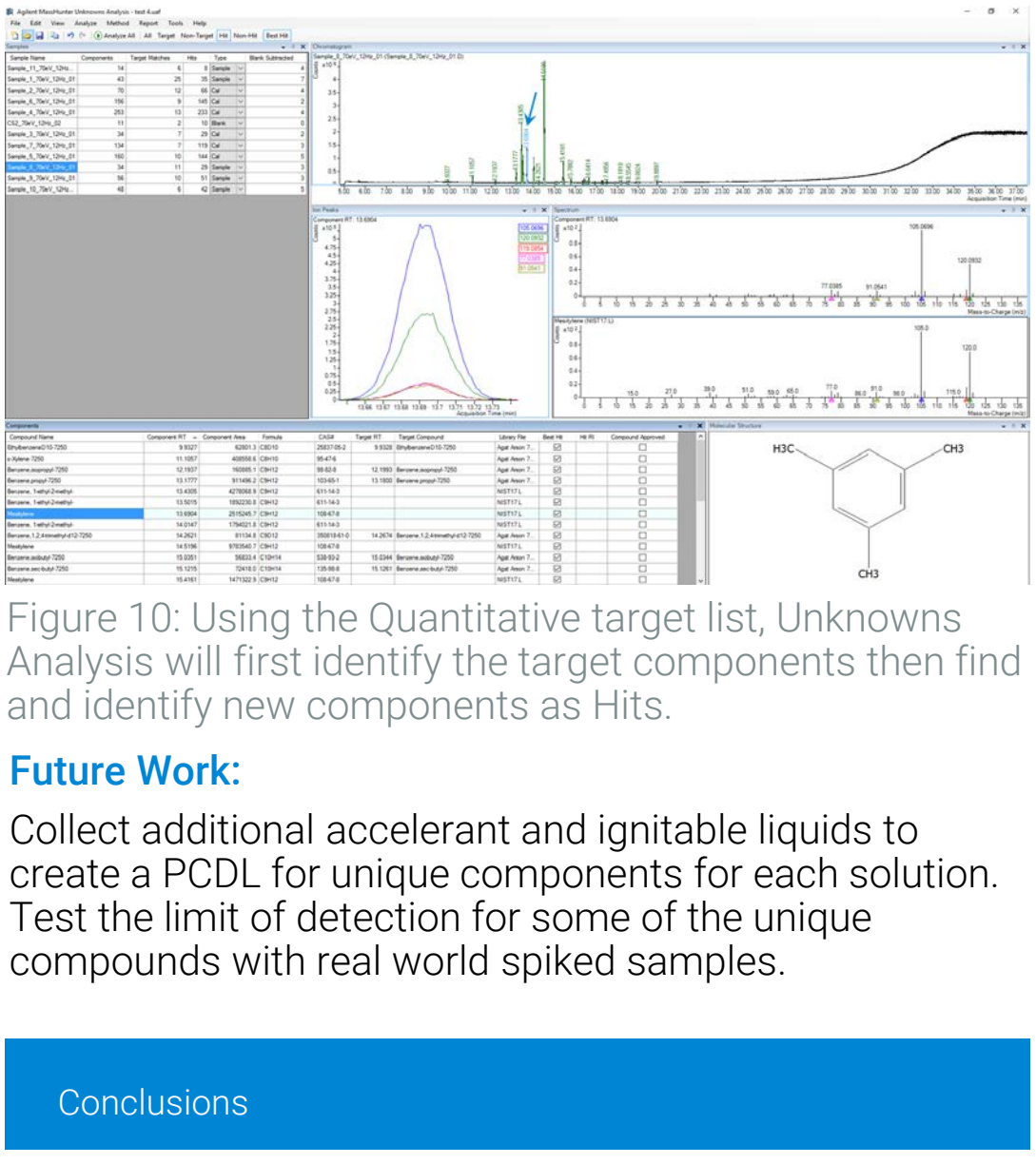

Figure 10: Using the Quantitative target list, Unknowns Analysis will first identify the target components then find and identify new components as Hits.

Future Work:

Collect additional accelerant and ignitable liquids to create a PCDL for unique components for each solution. Test the limit of detection for some of the unique compounds with real world spiked samples.

Conclusions

High resolving power, accurate mass and low eV provided additional information to a difficult analysis

- Software allowed quick analysis of the data to provide elemental compositions for low level compounds.
- MS/MS and structure correlation increased the confidence in the identification of components
- Low eV provided additional information and confirmation for fragile molecules.
- High resolving power quantitation provided excellent results for complex samples.

References

[1]Newman R, Gilbert MW, Lothridge K. 1997. GC-MS Guide to Ignitable Liquids. CRC Press.

[2]ASTM E1618-14, Standard Test Method for Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography-Mass Spectrometry, ASTM International, West Conshohocken, PA, 2014, www.astm.org

For Research Use Only. Not for use in diagnostic procedures.

Agilent

Trusted Answers