Analysis of Ethanol and Isotopomers by 240 Quadrupole Ion Trap GC/MS

Application Note

Energy and Fuels - Biofuels

Authors

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Abstract

The use of ion trap technology to discriminate between singly labeled positional isotopomers of ethanol presented an unique opportunity to develop an analytical method which is analyte specific. Four individual analytes were identified by Electron Ionization and then confirmed by Methane Chemical Ionization. A mixture of the isotopically labeled ethanol standards was then analyzed using the benefits of Gas Chromatography coupled to Quadrupole Ion Trap Mass Spectrometry.

Introduction

Ethanol is a clean-burning, high-octane motor fuel that is produced from renewable sources. Ethanol is grain alcohol, produced from crops such as corn. Because it is domestically produced, ethanol helps reduce America's dependence upon foreign sources of energy. However, the future of ethanol fuel cannot rely on food. To solve this problem, researchers are investigating other possible source materials such as algae.

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Unblended 100% ethanol is not used as a motor fuel. A percentage of ethanol is combined with unleaded gasoline. Ethanol is a key additive in gasoline, serving as both a smog reducer as well as a fuel supplement.

Experimental

The process for ethanol production can be monitored by analyzing the headspace of the vessel. The identification of 100% ^{12}C-EtOH, 1-^{13}C-EtOH, 2-^{13}C-EtOH, and $^{13}C_2$-EtOH is a first step.

- Then identify different mixes of these by qualitive methodology. As each structure is slightly different, use ion ratios as well as Methanol Chemical Ionization.
- Distinguish between singly labeled and doubly labeled ethanol.
- Discriminate between singly labeled positional isotopomers.
- Know if ethanol is either singly labeled on either carbon, or doubly labeled, and the relative abundance of these species.

Headspace analysis was performed using an Agilent 240 Ion Trap GC/MS system using the Agilent 7890A GC System with the 240 Ion Trap GC/MS and an Agilent 7697 Headspace Sampler. The GC was equipped with a HP-1 MS UI Column. The 240 Ion Trap GC/MS was operated in both Electron Impact (EI) ionization mode and Chemical Ionization (CI) mode using Methane as a reagent.

Materials and Methods

Compounds were identified by full-scan spectra from reference standards, followed by CI to confirm compound identify for the analysis.

All standards were 2 mL volume at 0.1% (v/v) isotopically labeled ethanol (790 mg/L) in filtered artificial seawater. Appropriate volumes of 0.1% (v/v) stock solutions were mixed to generate isotopomer blends listed in Sample mixes.

Agilent 7890A GC conditions

Column	Agilent HP-1MS UI 30 m × 250 µm, 0.50 µm
Injection mode	Headspace analysis Split/Splitless Inlet, Split: 500:1 0.5 mL injection volume Purge flow 50 mL/min at 0.75 minutes
Inlet temperature	200 °C
Carrier gas	Helium, constant flow mode, 0.5 mL/min
Oven program	30 °C for 3 minutes Total run time 3 minutes

Agilent 240 Quadrupole Ion Trap MS conditions

Ionization	Internal ionization
Tune	Auto-tune
Acquisition	EI, second run by CI
CI reagent gas	Methane
Solvent delay	0.0 minutes
MS temperatures	Trap 200 °C, Manifold 60 °C, Transfer line 250 °C

Standards

1. 100% ^{12}C-Ethanol
2. 100% 1-^{13}C-Ethanol
3. 100% 2-^{13}C Ethanol
4. 100% $^{13}C_2$ Ethanol

Sample mixes

1. 70:30 ^{12}C:1-^{13}C
2. 70:30 ^{12}C:2-^{13}C
3. 70:30 ^{12}C:$^{13}C_2$
4. 70:15:15 ^{12}C:1-^{13}C:2-^{13}C
5. 70:15:15 ^{12}C:1-^{13}C:$^{13}C_2$
6. 70:15:15 ^{12}C:2-^{13}C:$^{13}C_2$
7. 70:10:10:10 ^{12}C:1-^{13}C:2-^{13}C:$^{13}C_2$

Results and Discussion

Methane CI gives an M+1 Spectra

Less clutter and confirmation of Ion Molecular Weight.

One advantage of the ion trap is that hardware does not have to be changed to run this mode. Both sets of data are available by just changing the method and rerunning the samples.

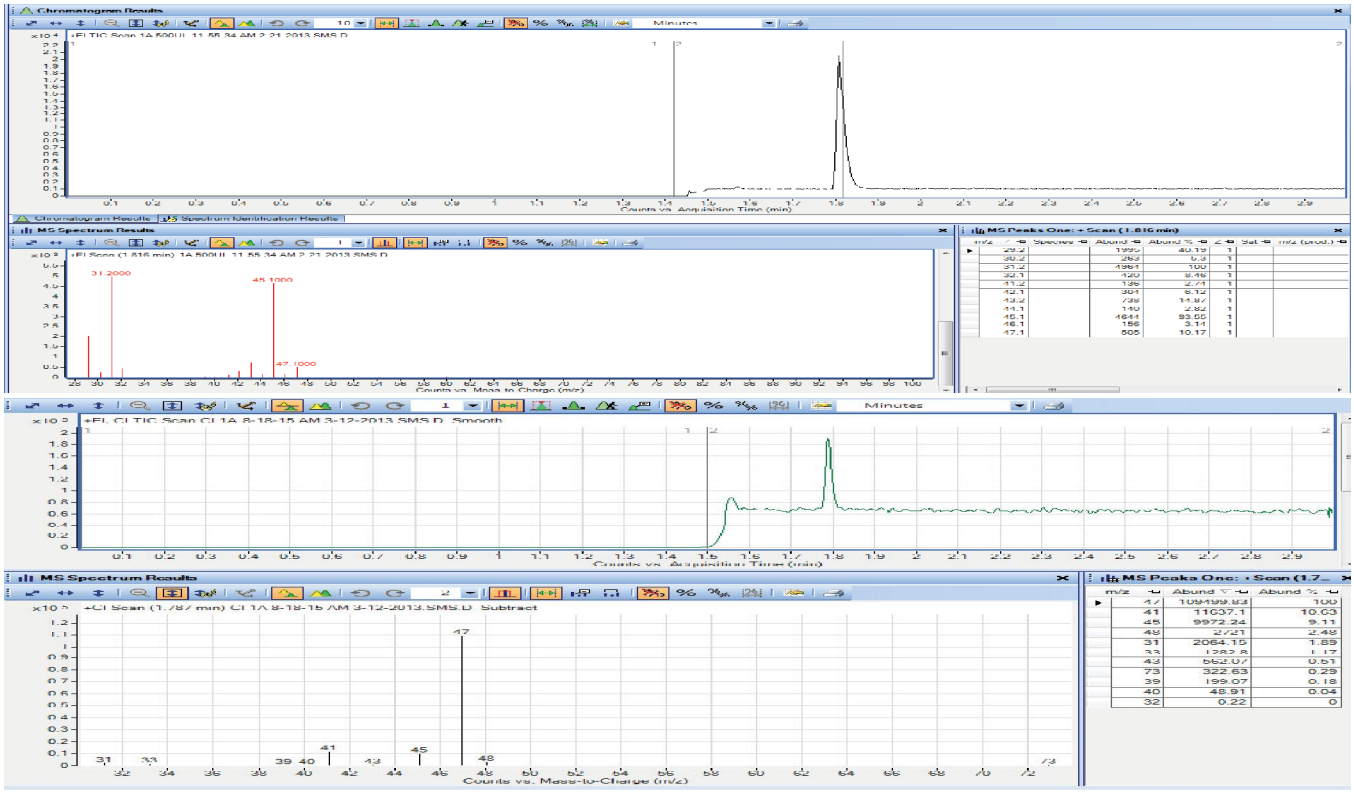

Figure 1. EI and CI chromatogram and spectra of Standard 1, 100% ^{12}C-Ethanol.

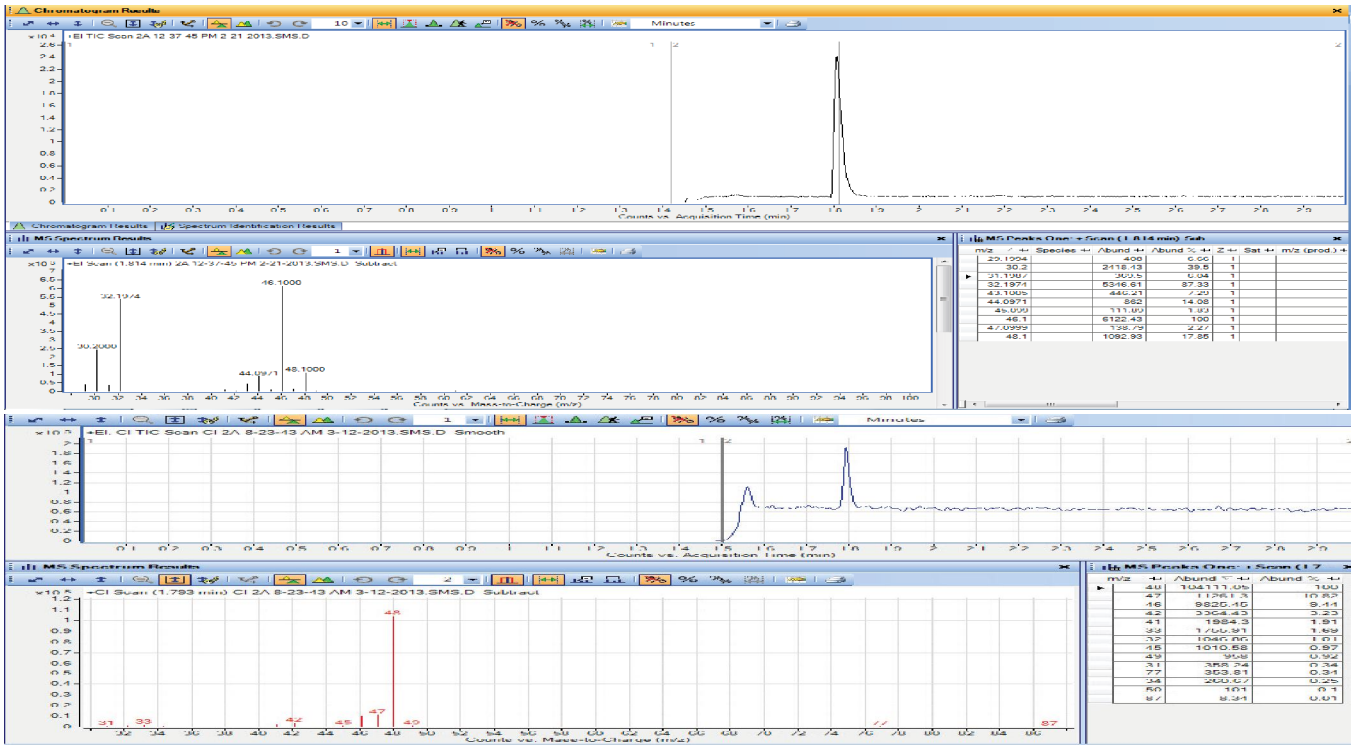

Figure 2. EI and CI chromatogram and spectra of Standard 2, 100% 1-^{13}C-Ethanol.

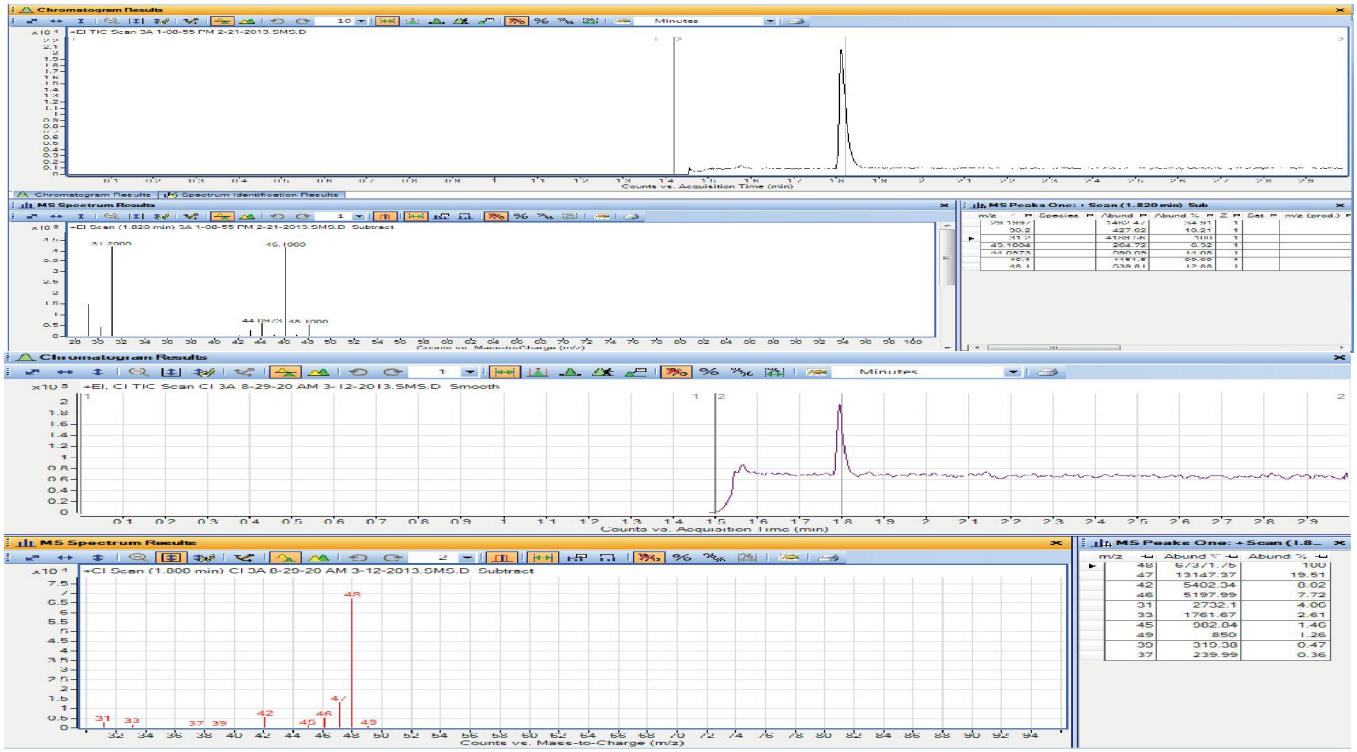

Figure 3. EI and CI chromatogram and spectra of Standard 3, 100% 2-^{13}C-Ethanol.

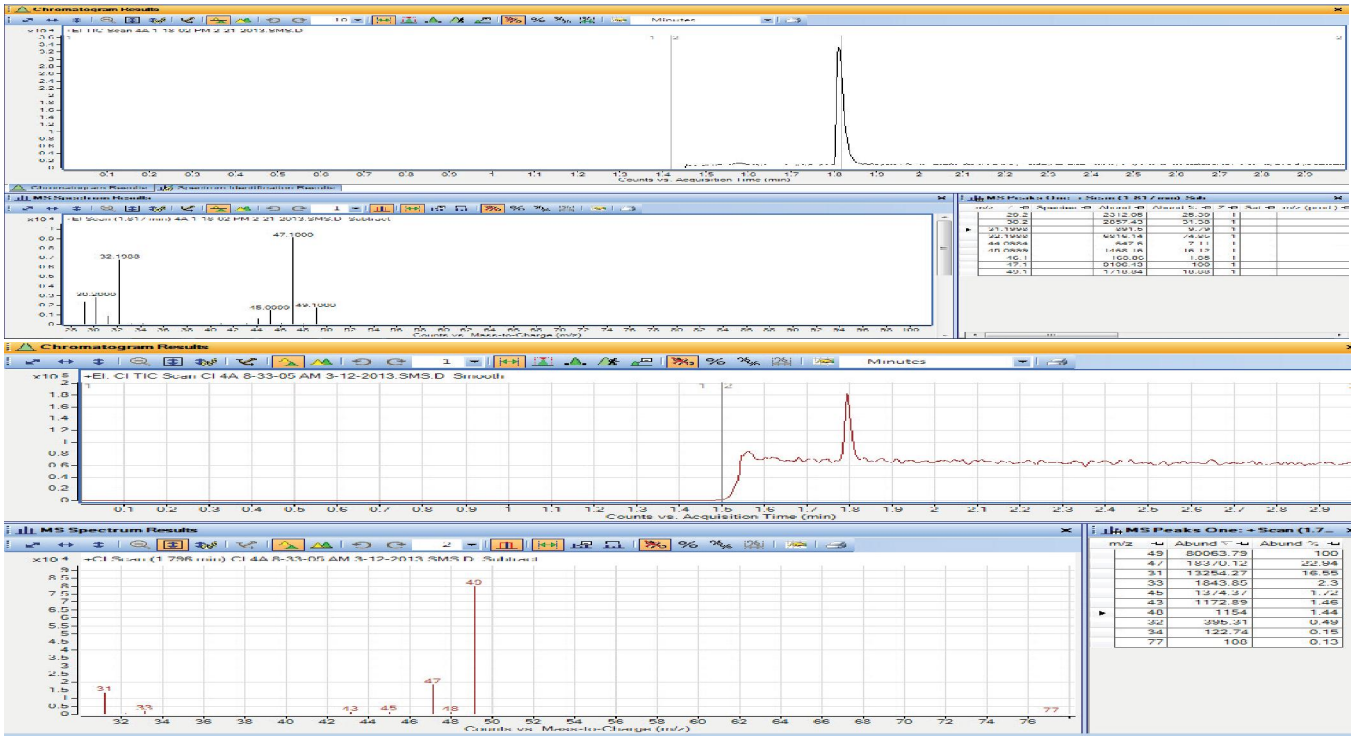

Figure 4. EI and CI chromatogram and spectra of Standard 4, 100% $^{13}C_2$-Ethanol.

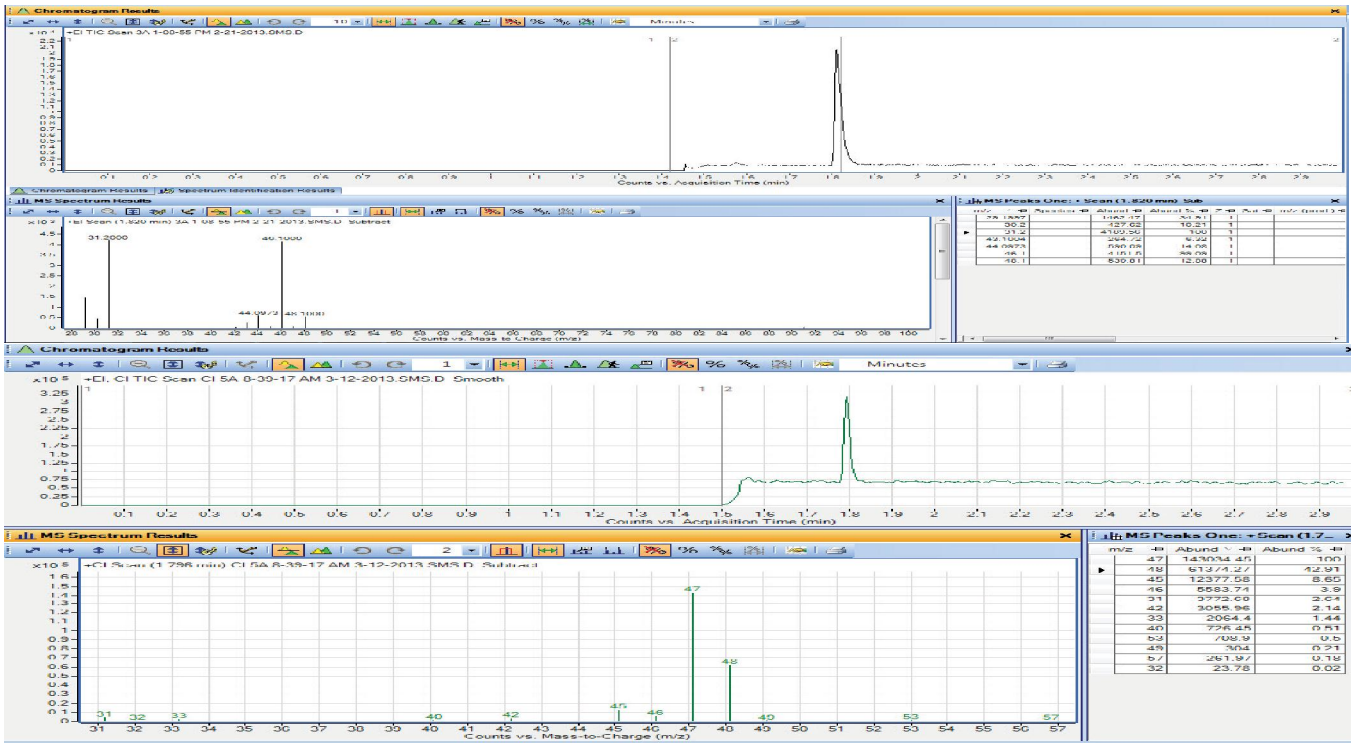

Figure 5. EI and CI chromatogram and spectra of Sample 1, 70:30 ^{12}C:1-^{13}C.

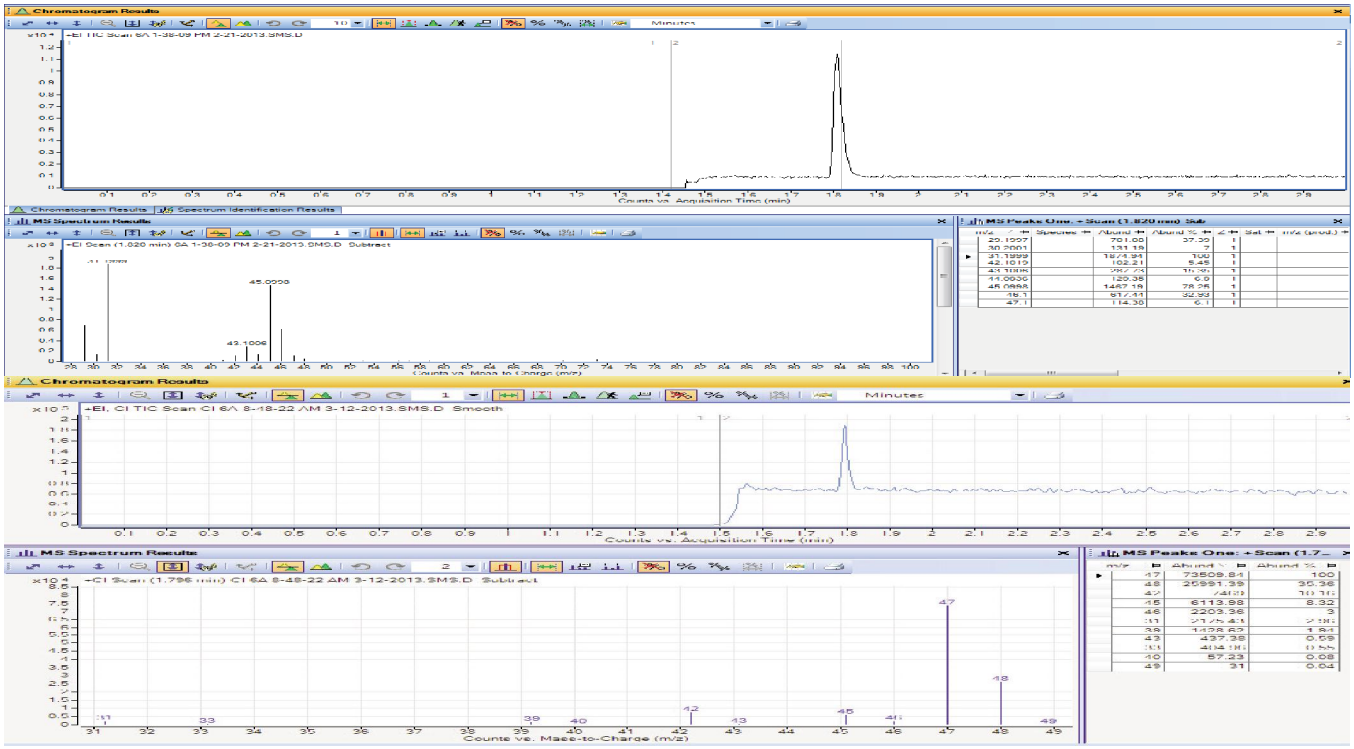

Figure 6. EI and CI chromatogram and spectra of Sample 2, 70:30 ^{12}C:2-^{13}C.

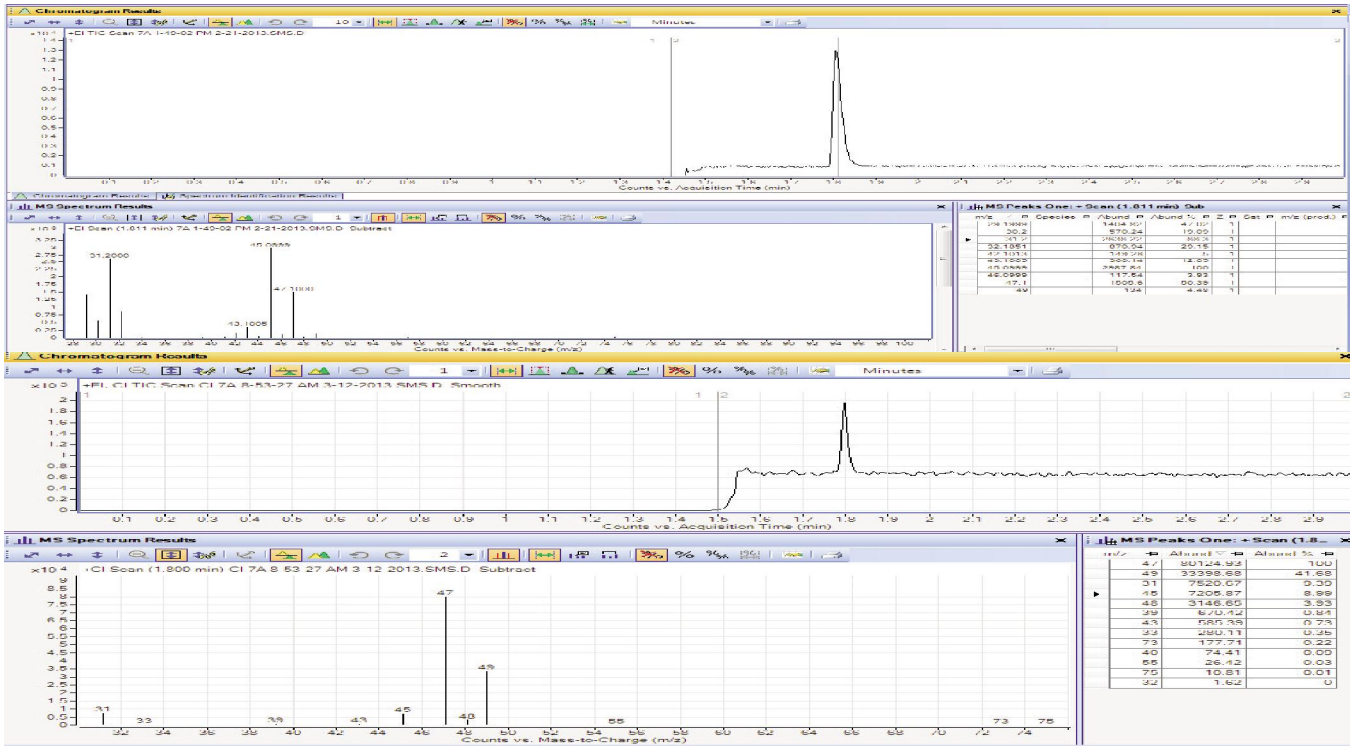

Figure 7. EI and CI chromatogram and spectra of Sample 3, 70:30 ^{12}C:$^{13}C_2$.

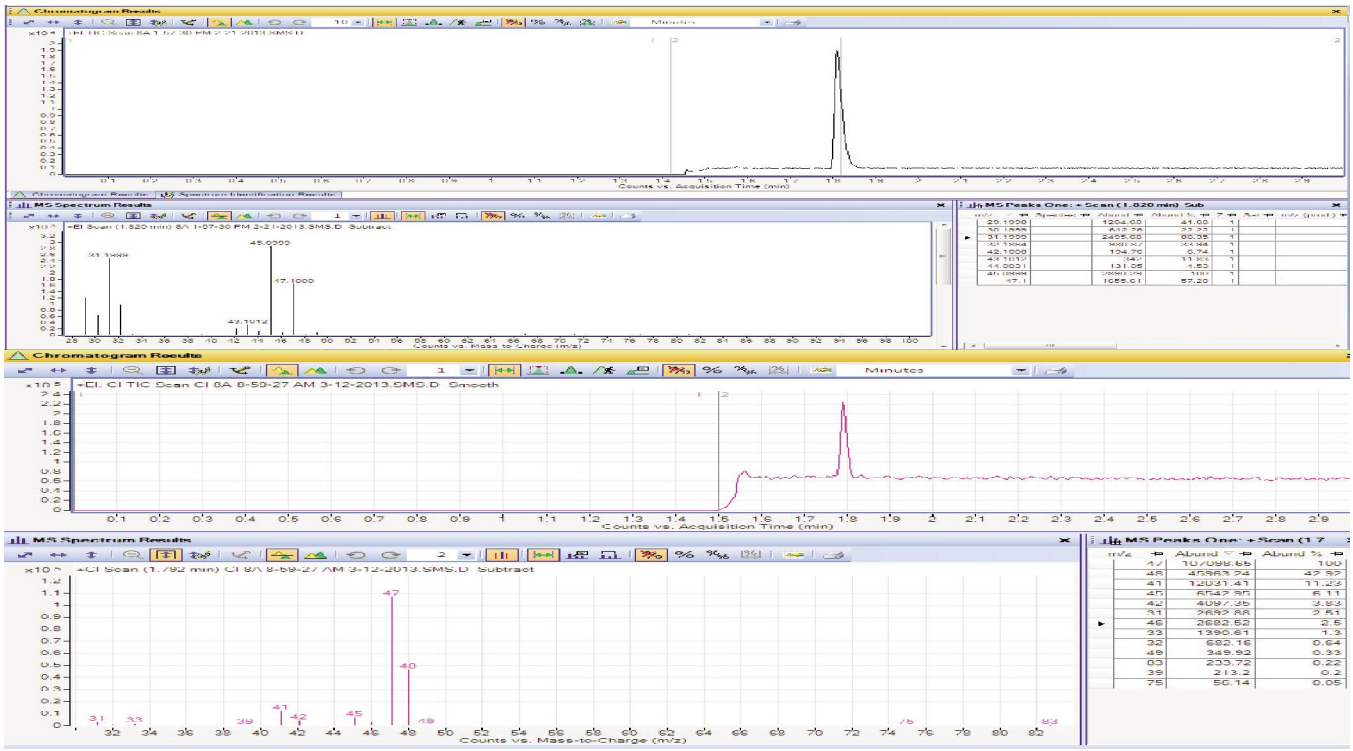

Figure 8. EI and CI chromatogram and spectra of Sample 4, 70:15:15, ^{12}C:1-^{13}C:2-^{13}C.

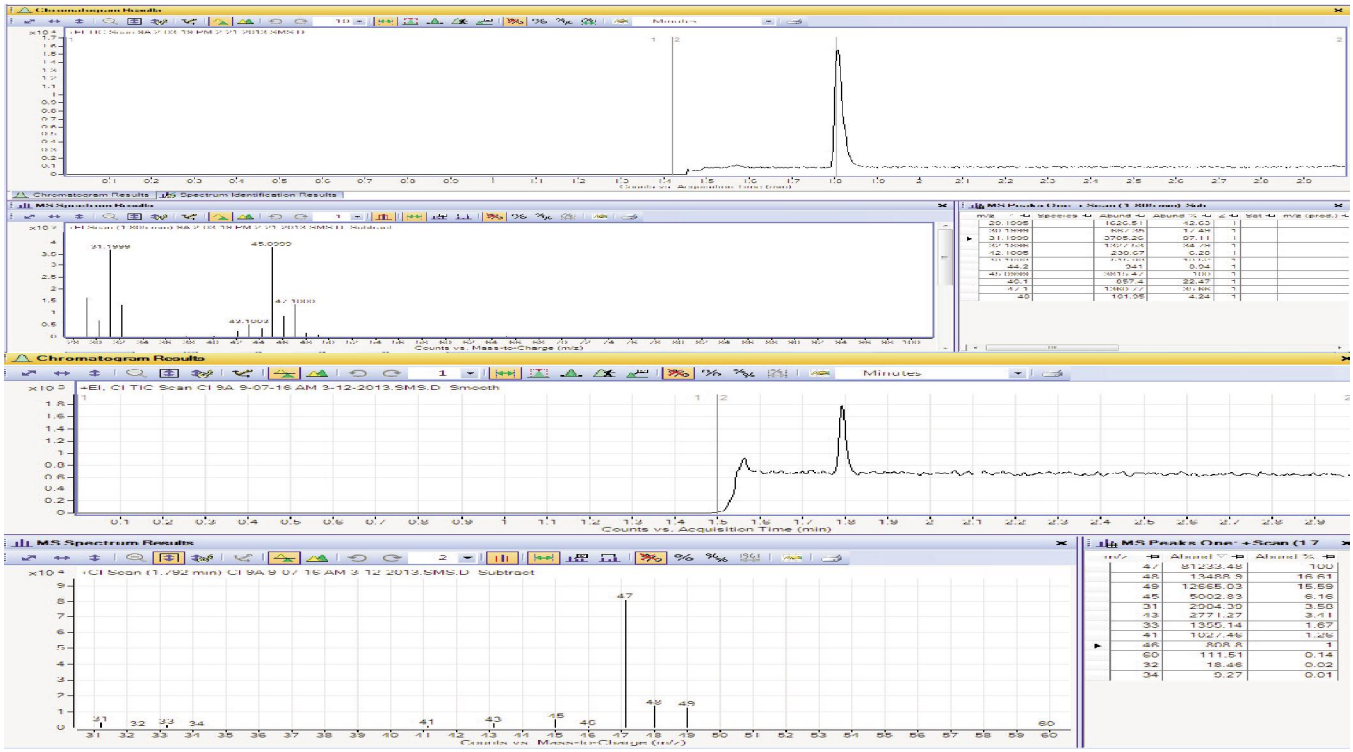

Figure 9. EI and CI chromatogram and spectra of Sample 5, 70:15:15, ^{12}C:1-^{13}C:$^{13}C_2$.

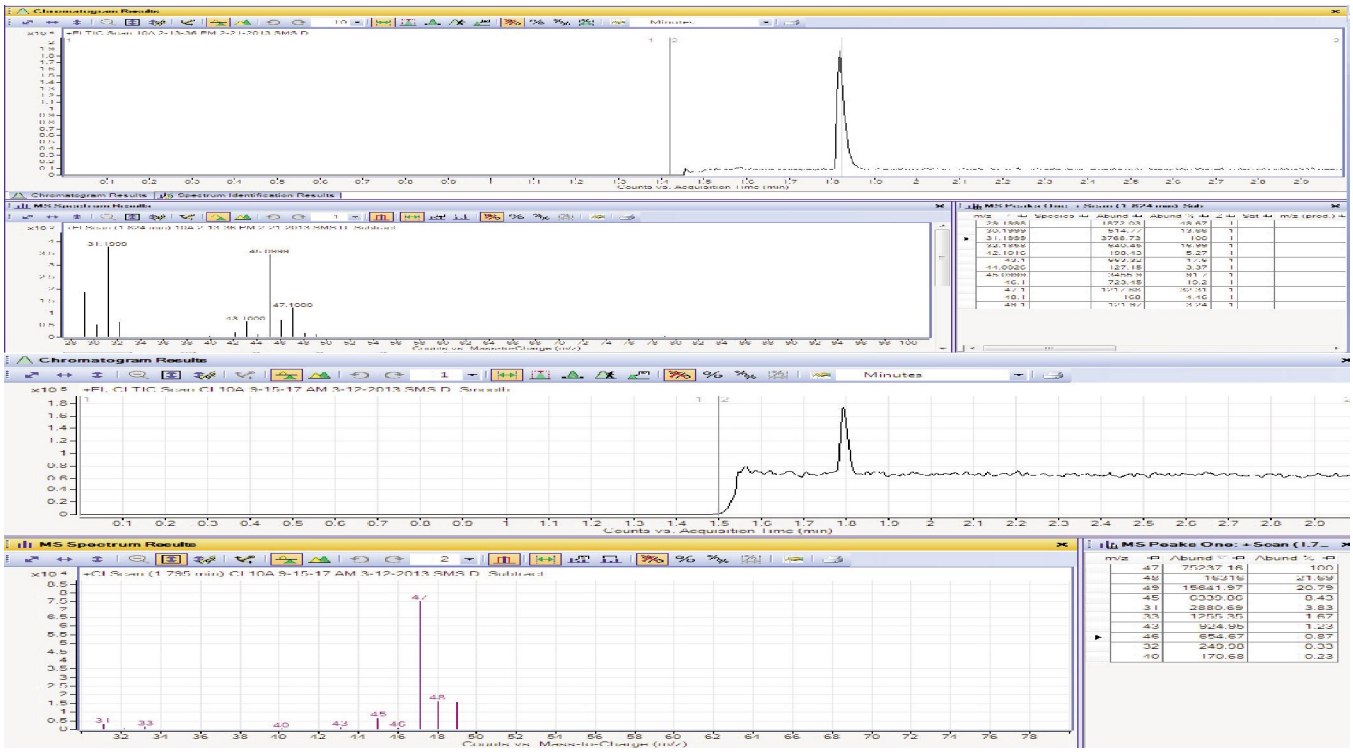

Figure 10. EI and CI chromatogram and spectra of Sample 6, 70:15:15, ^{12}C:2-^{13}C:$^{13}C_2$

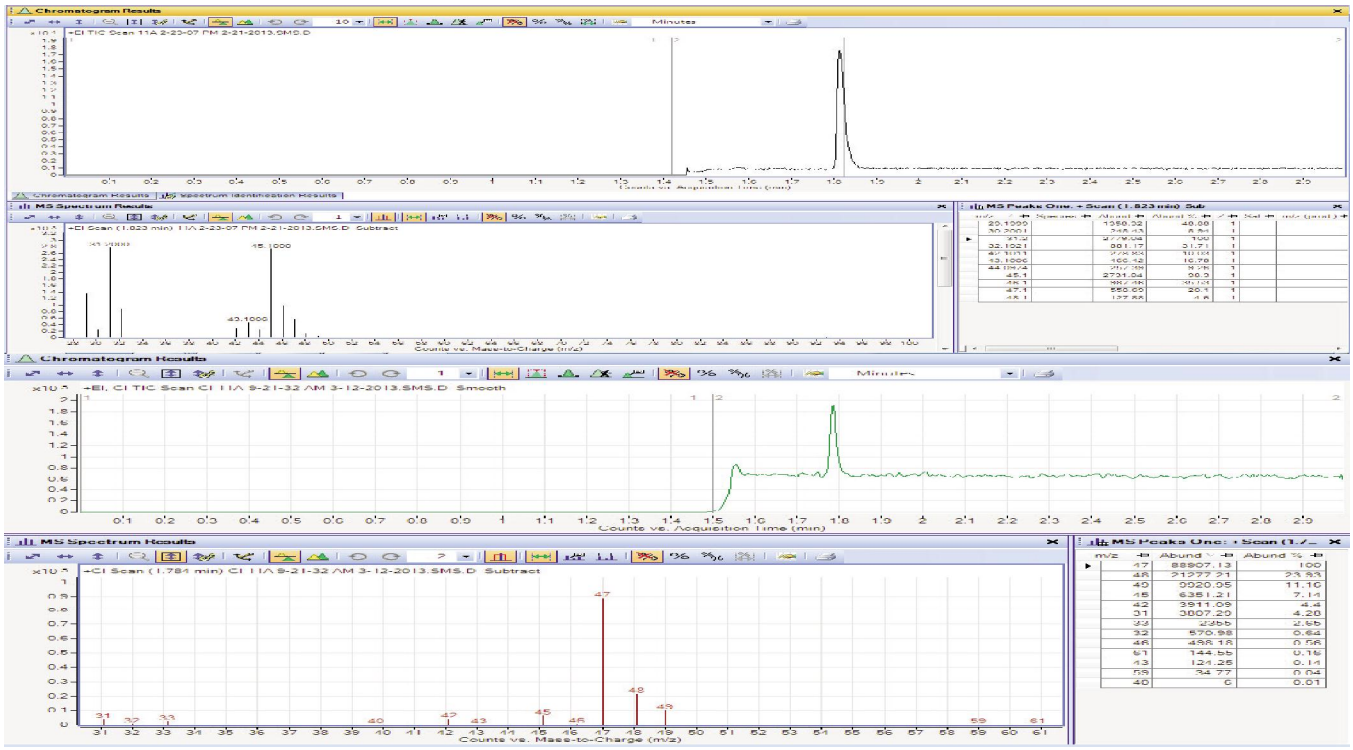

Figure 11. EI and CI chromatogram and spectra of Sample 7, 70:10:10:10, ^{12}C:1-^{13}C:2-^{13}C:$^{13}C_2$

Ten of the most abundant EI ions from the four calibration standards were selected for spectral deconvolution. These ions: (28.2, 29.2, 30.2, 31.2, 32.1, 45.1, 46.1, 47.1, 48.1, and 49) were fitted to spectra of the seven mixture samples using linear least squares. The calculated contribution of each species in the mixtures is given in Table 1.

Table 1. Calculated Contribution of Each Mixture Species

	Native	1-^{13}C	2-^{13}C	$^{13}C_2$	
1	66.9%	26.4%	4.6%	2.1%	70:30 ^{12}C:1-^{13}C
2	70.7%	0.0%	28.2%	1.1%	70:30 ^{12}C:2-^{13}C
3	81.5%	0.0%	1.9%	16.6%	70:30 ^{12}C:^{13}C2
4	70.0%	14.1%	15.5%	0.6%	70:15:15, ^{12}C:1-^{13}C:2-^{13}C
5	75.5%	16.5%	1.5%	6.5%	70:15:15, ^{12}C:1-^{13}C:$^{13}C_2$
6	66.7%	0.0%	12.8%	20.5%	70:15:15, ^{12}C:2-^{13}C:$^{13}C_2$
7	73.9%	12.6%	8.9%	4.6%	70:10:10:10, ^{12}C:1-^{13}C:2-^{13}C:$^{13}C_2$

These results show promise in being able to differentiate between the different isotopomers. This type of mass spectral deconvolution could additionally be applied to the CI results.

Conclusion

For the analysis of isotopically labeled ethanol, the benefits of GC Quadrupole Ion Trap MS cannot be underestimated, in terms of reducing sample matrix interference, improving signal-to-noise and coupling its high selectivity and sensitivity GC/MS Ion Trap provides a more confidence driven solution for isotopically labeled ethanol analysis. GC/MS Quadrupole Ion Trap analysis has the potential to provide an additional degree of confidence in the results obtained. Using the optimized method listed in this application note, a fast, targeted GC/MS method can be used to differentiate and identify the different ^{13}C labeled ethanol's. Two advantages are, the running of EI and CI without any hardware changes and without needing two MS systems, (one for EI and one for CI). Both analyses can be performed in 6 minutes on the same system with appropriate prep ahead of the samples. The use of CI for matrix reduction and identification gives the analyst a higher level of confidence than EI alone.

References

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- "D4806 – Standard Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel"; ASTM International: 100 Barr Harbor Drive, West Conshohocken, PA, USA, 2010.
- "D5501-09 Standard Test Method for Determination of Ethanol Content of Denatured Fuel Ethanol by Gas Chromatography"; ASTM International: 100 Barr Harbor Drive, West Conshohocken, PA, USA, 2010.
- 5990-9927EN Application note- Analysis of Bio-Ethanol by Gas Chromatography; Shannon Coleman, Agilent Technologies, Inc.

Special thanks to Brian Hom, Agilent Technologies, Inc.

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Printed in the USA
May 10, 2013
5991-2355EN

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