Rapid Quantitation of Benzene, Toluene, and Total Aromatics in Finished Gasoline by GC-TOFMS

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1. Introduction

The determination of benzene, toluene, and total aromatics in reformulated gasoline (RFG) is of extreme importance to the gasoline refiners because laws exist that limit the amount of emissions of toxic and ozone forming compounds. The emissions performance of a fuel is computed based on a "complex model" which requires the input of certain fuel parameters. One of these parameters is chemical composition. Among the chemical composition parameters, one is total aromatic content of the fuel.

The EPA has established that the determination of benzene, toluene, and total aromatics be done by Gas Chromatography–Mass Spectrometry (GC-MS). In response to this mandate, the American Society for Testing and Materials (ASTM) has developed a standard method for the determination of benzene, toluene, and total aromatics in finished gasolines and designated it as Standard Test Method D5769.

Since the analyses of petroleum products are complicated by the relatively large number of volatile components contained in these mixtures, GCMS analyses of these mixtures typically takes about 30 minutes. Previous analytical conditions have focused on complete chromatographic resolution of as many individual analytes as possible. While all mass spectrometers offer multi-channel detection capabilities that may be used to identify coeluting analytes, slow spectral acquisition rates and under developed software algorithms have minimized the impact of MS detectors on faster GC separation times.

The LECO Pegasus® II GC-TOFMS offers several unique advantages for reducing analysis times. The Pegasus II provides acquisition rates of up to 500 spectra/second to allow accurate definition of the narrowest GC peaks. Fast GC techniques may now be effectively used to reduce separation times without sacrificing data quality. The unique degree of spectral continuity across a chromatographic peak provided by the Pegasus II has allowed the development of several revolutionary software algorithms. The peak find algorithm effectively locates the position of all peaks in the chromatogram including multiple components in complex coelutions. The deconvolution algorithm effectively resolves the mixed mass spectra of the coelution into accurate individual mass spectra for each analyte, including the accurate distribution of signal from masses shared by several components in the coelution.

2. Experimental Conditions

The potential benefit of these unique features of the Pegasus II in gasoline analyses were evaluated using a fast gas chromatographic method for rapid determination of benzene, toluene, and total aromatics in finished gasoline. Advantage was taken of the semi-quantitation features of the Pegasus II software which was developed specifically for Method D5769. The mixture contained 23 quantified analytes commonly found in RFG, plus the semiquantified analytes. The analytical conditions used for the 180 second analysis of this complex mixture are summarized in Table 1. The resulting total ion chromatogram from the separation is shown in Figure 1 with the peak table indicating the analyte, its retention time, and the accuracy of its library search result versus the NIST spectral database summarized in Table 2.

Table 1. Pegasus II GC-TOFMS Conditions for a 3 Minute Analysis of a Reformulated Gasoline Sample.

Detector:	LECO Corporation Pegasus II Time-of-Flight Mass Spectrometer
Transfer Line:	250°C
Source:	200°C
Acquisition Rate:	50 spectra/sec (40 to 200 u)
GC:	Hewlett Packard® 6890*
Column:	DB-1 20 m x 0.1 mm ID, 0.4 µm phase film
Oven:	100°C for 0.25 min., then to 200°C at 100°C/min., then to 250°C at 50°C/min., hold for 0.75 min.
Injector:	250°C
Carrier Gas:	Helium, 0.8 ml/min. constant flow
Sample:	No preparation required. 1µL split (1000:1) injection.

**HP6890 GC is equipped with fast oven temperature ramp capabilities and a high pressure EPC module.*

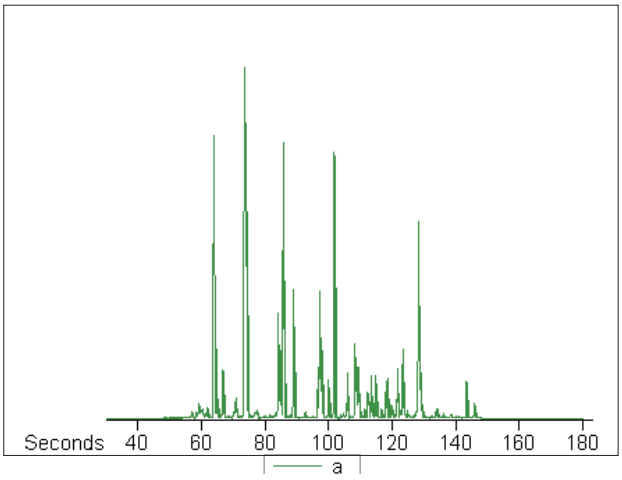

Figure 1. Reformulated Gasoline Analytical Ion Chromatogram (AIC).

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Table 2. Reformulated Gasoline Sample Peak Table.

Peak #	Name	R.T.	Type	Quant Masses	Concentration	Area	Quant S/N
24*	Perdeuterobenzene	63.905	Quantifie	84+83	2.0000 Wt%	8566800	4329.0
25	Benzene	64.125	Quantifie	78	0.82830 Wt%	3446700	4293.1
49	Toluene-d8	73.645	Quantifie	100+99	7.0000 Wt%	14814000	7126.5
51	Toluene	74.125	Quantifie	92	5.2728 Wt%	10029000	11954
67	Ethylbenzene-d10	84.225	Quantifie	116+115	2.0000 Wt%	1763700	1226.1
70	Ethylbenzene	84.945	Quantifie	106	1.0092 Wt%	1224000	1500.1
72	p/m-Xylene	85.825	Quantifie	106	7.7183 Wt%	7069400	7688.1
77	Benzene, 1,2-dimethyl-	89.065	Quantifie	106	2.0000 Wt%	2543500	3604.1
82	Benzene, (1-methylethyl)-	92.765	Quantifie	120	Out of calibration range: 0.015076 Wt%	79161	101.82
86	Benzene, propyl-	96.545	Quantifie	120	0.32940 Wt%	369490	470.87
	Substituted Alylindanes		Summed	117	0.40169 Wt%	5028700	
89	Benzene, 1-ethyl-3-methyl-	97.185	Quantifie	120	1.7395 Wt%	1842600	2756.9
90	Benzene, 1-ethyl-4-methyl-	97.585	Quantifie	120	0.59933 Wt%	638030	955.43
92	Benzene, 1,3,5-trimethyl-	98.025	Quantifie	120	0.69047 Wt%	1114500	1568.1
95	Benzene, 1-ethyl-2-methyl-	99.985	Quantifie	120	0.43756 Wt%	541920	733.22
97	Benzene, 1,2,4-trimethyl-	101.81	Quantifie	120	3.8458 Wt%	4513500	6593.5
	C10 Benzenes		Summed	134	0.74584 Wt%	612530	
105	Benzene, 1,2,3-trimethyl-	105.97	Quantifie	120	0.51858 Wt%	734850	1011.7
107	Indane	108.31	Quantifie	117	0.24323 Wt%	1216900	1638.8
109	Benzene, 1,4-diethyl-	109.23	Quantifie	134	0.82332 Wt%	639190	687.29
111	Benzene, butyl-	109.67	Quantifie	134	0.34047 Wt%	279210	188.78
112	Benzene, 1,2-diethyl-	110.57	Quantifie	134	Out of calibration range: 0.0054306 Wt%	21126	30.951
	C11 Benzenes		Summed	148	0.86021 Wt%	902820	
123	Benzene, 1,2,4,5-tetramethyl	117.97	Quantifie	134	0.27984 Wt%	342660	482.15
125	Benzene, 1,2,3,5-tetramethyl	118.51	Quantifie	134	0.38634 Wt%	505590	705.76
151	Naphthalene-d8	128.31	Quantifie	136+135	1.0000 Wt%	4746800	3444.2
153	Naphthalene	128.75	Quantifie	128	0.34010 Wt%	2113800	3494.8
	C12 Benzenes		Summed	162	0.0059437 Wt%	51996	
175	Naphthalene, 2-methyl-	143.37	Quantifie	142	0.29472 Wt%	739050	985.01
178	Naphthalene, 1-methyl-	145.95	Quantifie	142	0.11998 Wt%	305990	385.95
	Total				41.851 Wt%	76798000	

3. Results

The effectiveness of the peak find and deconvolution algorithms to accurately locate and identify analytes in complex coelutions resulting from the rapid separation conditions used in this analysis can be evaluated in Figure 2. In Figure 2, the positions of all components in a coelution containing five C10 benzene isomers are accurately located by the peak find algorithm. The mass spectra for three of the analytes are accurately resolved from one another by the deconvolution algorithm. Library search results for these mass spectra versus the NIST spectral database are presented in Figure 3. The deconvolution algorithm not only separates out ions unique to the spectra of each analyte but also successfully assigns the appropriate amount of signal to each analyte spectrum for masses that are shared between multiple analytes in the coelution.

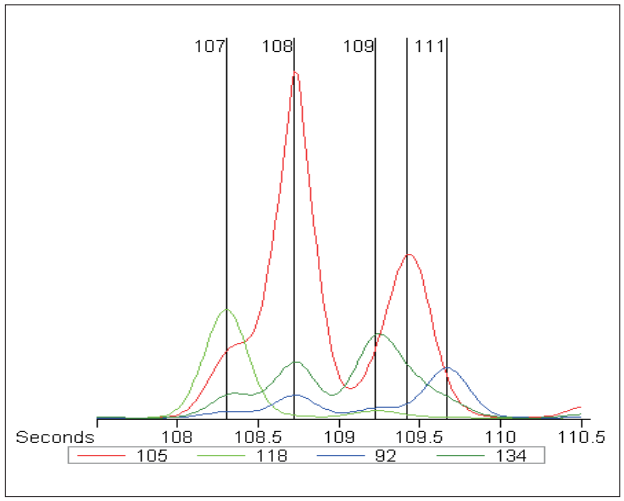
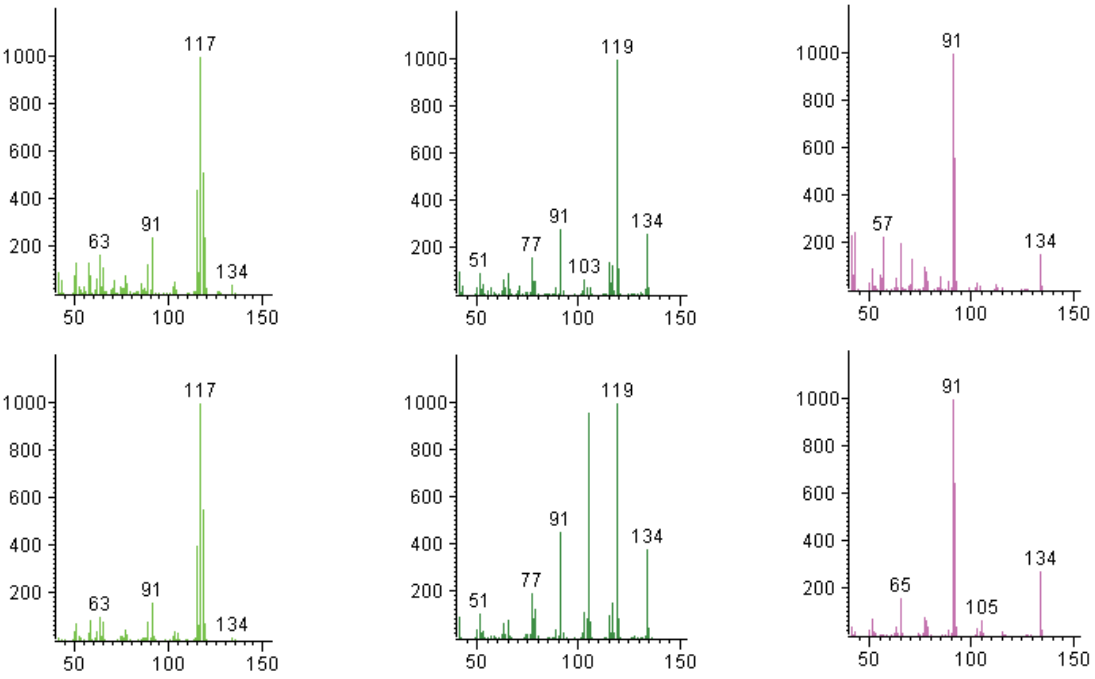


Figure 2. Extracted Ion Profile Chromatogram Showing the Coelution of Indane (107), 1,4-Diethylbenzene (109), and Butylbenzene (111); The markers indicate peak positions as determined by the Pegasus II GC-TOFMS peak find algorithm.



Peak 107; Indane; Similarity 843; Reverse Similarity 885

Peak 109; 1,4-diethyl-benzene; Similarity 897; Reverse Similarity 924.

Peak 111; n-butyl-benzene; Similarity 804; Reverse Similarity 843.

Figure 3. Mass Spectra for Coeluting Components as Determined by the Pegasus II GC-TOFMS Deconvolution Algorithm. Top: Pegasus II spectrum; Bottom: NIST Library spectrum.

4. Conclusions

The combination of fast GC techniques (shorter microbore columns and faster temperature program rates), fast mass spectral acquisition rates, and unique peak find and spectral deconvolution, along with semi-quantitation algorithms allow accurate determination of benzene, toluene and total aromatics in reformulated gasolines in only 3 minutes using the Pegasus II GC-TOFMS. This represents a 10 fold decrease in data acquisition time. The unique software features also significantly reduce data processing time resulting in an overall decrease of analysis time of well over 1 order of magnitude.

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