

Automatic Quantitative Analysis of Total Aromatics and Oxygenates in Gasoline Samples Using Comprehensive Two-Dimensional Gas Chromatography (GCxGC) and Time-of-Flight Mass Spectrometry (TOFMS)

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1. Introduction

Increased environmental concerns in the past decade have led to more stringent regulations for the presence of toxic and ozone-forming chemicals in gasoline and other petroleum products. Benzene, toluene, ethylbenzene, xylenes (BTEX), and other US EPA regulated aromatics are naturally present in crude oils and/or are enhanced at refineries in order to increase the octane number for gasoline. Required by the US Clean Air Act Amendments of 1990, oxygen-containing components are also added by the manufactures in reformulated gasoline (RFG). Even though the mechanisms are still not very well known, it appears that the increase in oxygen content decreases CO emissions and has other related air benefits. Currently two different methods are used (ASTM methods 5599 and 5769) to detect and quantify total aromatics and oxygenates in gasoline.

The added resolving power and the increase in peak capacity obtained by comprehensive two-dimensional gas chromatography (GCxGC), enable accurate detection of the two chemical classes in a single analysis. The two different separation mechanisms (boiling point in the first dimension, and polarity in the second dimension) result in a highly organized chromatogram based on analyte chemical class and structure. The very narrow chromatographic peaks obtained from the second separation column require fast acquisition rates for adequate peak characterization. This precludes most of the mass spectrometers, such as quadrupoles and magnetic sectors, from being chosen as detection options for GCxGC. The LECO Pegasus 4D GCxGC-TOFMS system provides fast data acquisition rates of up to 500 spectra/second that can accurately define the narrowest chromatographic peaks. Even though there is a significant increase in peak capacity when using the GCxGC technique, especially in very complex samples, not all components are completely separated. Along with fast data acquisition, TOFMS spectral continuity across the chromatographic profile allows the ChromaTOF software to deconvolute complex coelutions and extract adequate mass spectral information for each of the coeluting peaks.

The purpose of analysis was the fast quantitative analysis of total aromatics and oxygenates in gasoline in a single analysis of 10 minutes performed by GCxGC-TOFMS.

2. Experimental Conditions

GCxGC:

Agilent® 6890 GC equipped with a LECO Thermal Modulator

Primary Column:

DB-5, 10 m, 0.18 mm id, 0.18 µm film thickness

Main Oven Program:

32°C (1 minute hold) to 180°C (1 minute hold) at 10°C/minute

Secondary Column:

DB-WAX, 1 m, 0.1 mm id, 0.1 µm film thickness

Secondary Oven Program:

37°C (1 minute hold) to 180°C (1 minute hold) at 10°C/minute

Inlet Temp: 250°C

Injection Size: 0.1 µl

Split Ratio: 900:1

Carrier Gas: He at a constant flow of 1 ml/min

Modulator Temp:

30°C offset from main oven

Modulation Frequency:

5 seconds with a 0.8 second hot pulse time

MS: LECO Pegasus 4D GCxGC-TOFMS

Ionization: EI at 70eV

Mass Range (u): 20 to 400

Acquisition Rate: 200 spectra/second

Source Temp: 225°C

Standards:

Mixture of 11 oxygen-containing compounds and mixture of 23 hydrocarbons plus four deuterated internal standard as listed in Table 1

3. Results

Figure 1 represents the total ion current chromatogram (TIC) of a gasoline sample spiked with 11 oxygen-containing analytes. The chromatogram is presented as a contour plot with the first dimension retention time represented on the x-axis and the second dimension retention time on the y-axis. In addition to the oxygenated compounds, 23 various hydrocarbons and 1 internal standard are also present in the gasoline sample. Peaks are labeled according to Table 1. As required by ASTM method 5769, 4 additional deuterated internal standards were used for the calibration of the aromatic hydrocarbons present. These 4 analytes are not present in the gasoline sample chromatogram presented in Figure 1.

Table 1. Peak numbers and names for the components presented in Figure 1.

Peak #	Name	Peak #	Name	Peak #	Name
1	Methanol	14	1,2-Dimethoxyethane	28	1,3,5-Trimethylbenzene
2	Ethanol	15	D6 Benzene	29	1-Ethyl-2-methylbenzene
3	Isopropanol	16	Benzene	30	1,2,4-Trimethylbenzene
4	t-Butanol	17	D8 Toluene	31	1,2,3-Trimethylbenzene
5	1-Propanol	18	Toluene	32	Indane
6	MTBE	19	D10 Ethylbenzene	33	Butylbenzene
7	sec-Butanol	20	Ethylbenzene	34	1,4-Diethylbenzene
8	i-Propyl ether	21	m-Xylene	35	1,2-Diethylbenzene
9	i-Butyl alcohol	22	p-Xylene	36	1,2,4,5-Tetramethylbenzene
10	ETBE	23	o-Xylene	37	1,2,3,5-Tetramethylbenzene
11	t-Amyl alcohol	24	i-Propylbenzene	38	D8 Naphthalene
12	1-Butanol	25	n-Propylbenzene	39	Naphthalene
13	t-Amyl ethyl ether	26	1-Ethyl-3-methylbenzene	40	2-Methylnaphthalene
		27	1-Ethyl-4-methylbenzene	41	1-Methylnaphthalene

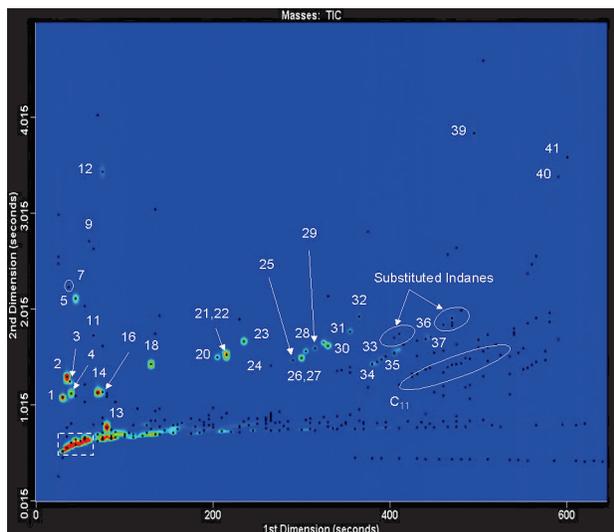


Figure 1. TIC presented as a contour plot for a gasoline sample spiked with 11 oxygenated components. Black dots represent peak markers and names for the labeled peaks are presented in Table 1. The boxed region in the lower left corner is presented in greater detail in Figure 2.

Even though most of the components of interest are well separated in the two-dimensional separation, several coelutions are still present. Figure 2 shows the results obtained for the deconvolution for MTBE, an oxygenated component that elutes in the alkane region of the chromatogram. Spectral data, along with the NIST library match, are also shown in the figure. Accurate deconvolution allows reliable identification and quantification of MTBE in the gasoline sample. The inset of the figure represents the boxed region of Figure 1 presented on a reduced scale.

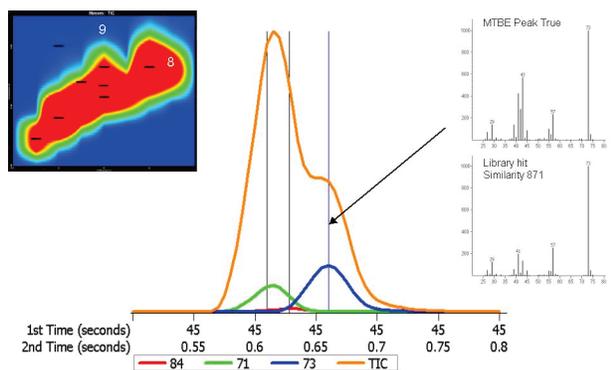


Figure 2. Deconvoluted analyte spectrum as well as NIST library match for MTBE. The chromatogram for the selected region presents the TIC as well as unique ions for the co-eluting components. The inset in the upper left corner represents the TIC chromatogram in the boxed region of the contour plot displayed in Figure 1.

Using two different sets of standards at five different concentration levels, calibration curves were built for all 36 analytes of interest. One internal standard was used for the oxygenated components, and 4 deuterated components were used as internal standards for the aromatic hydrocarbons present on the ASTM Method 5769 list. Each calibration point was analyzed in triplicate. Due to severe coelution, the fact that the coeluting components were isomers, and deconvolution was not possible, 6 peaks (3 two-peak coelutions) were quantified as pairs. Masses used for quantitation were chosen according to the ASTM method. Two examples of calibration curves for 1-ethyl-2-methylbenzene and isobutanol are presented in Figures 3 and 4. Summarized results for all 36 analytes are presented in Table 2. Correlation coefficient values (R2) were 0.99 or greater for all analytes.

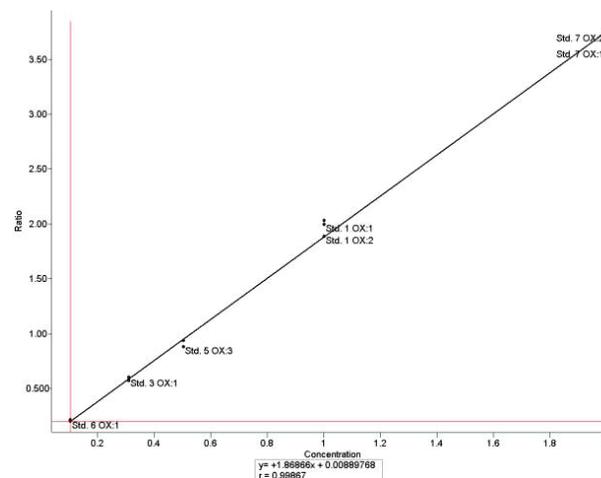


Figure 3. Calibration curve for 1-butanol for a concentration range of 0.105 to 1.998 % wt. 1,2-dimethoxyethane was used as internal standard.

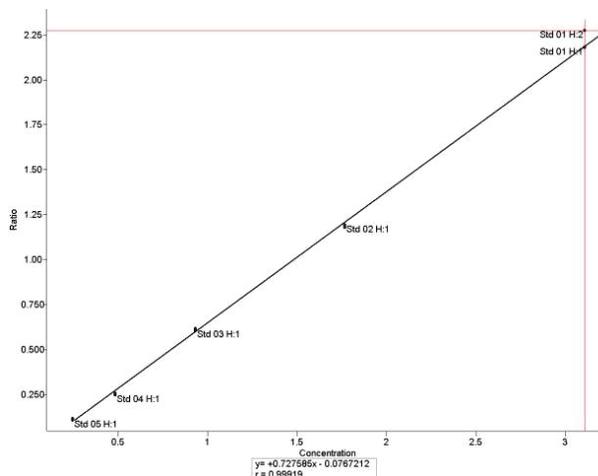


Figure 4. Calibration curve for 1-ethyl-2-methylbenzene for a concentration range of 0.1224 to 4.659 % wt. D10 ethylbenzene was used as internal standard.

The calibration curves obtained were used for the analysis of three gasoline samples obtained from different suppliers and with various octane numbers. Results are presented as a comparison in Table 3. Quantitative results for various levels of benzene substitution were obtained automatically, using either the calibration curves available or the ethylbenzene calibration curve for analytes with no calibration curve available (as per ASTM Method 5769). No oxygen-containing components were present in the samples at levels above the minimum used for calibration.

Table 2. Calibration results for oxygen-containing and EPA regulated aromatics.

Analyte	R ²	Quant Mass	Curve Order	Internal Std.	Conc. Range (%wt)
Methanol	0.9956	31	1	1,2-Dimethoxyethane	0.101 - 5.01
Ethanol	0.9936	45	1	1,2-Dimethoxyethane	1.01 - 12.002
Isopropanol	0.9936	45	1	1,2-Dimethoxyethane	0.101 - 2.00
t-Butanol	0.9941	59	1	1,2-Dimethoxyethane	0.101 - 1.996
1-Propanol	0.9955	31	1	1,2-Dimethoxyethane	0.199 - 2.002
MTBE	0.9866	73	1	1,2-Dimethoxyethane	1.036 - 17
sec-Butanol	0.9939	45	1	1,2-Dimethoxyethane	0.1 - 2.495
i-Propyl ether	0.9927	45	1	1,2-Dimethoxyethane	0.102 - 2.018
i-Butyl alcohol	0.9963	43	1	1,2-Dimethoxyethane	0.1 - 2.002
ETBE	0.9926	31	1	1,2-Dimethoxyethane	1.038 - 18.48
t-Amyl alcohol	0.9973	73	1	1,2-Dimethoxyethane	0.1 - 2.005
1-Butanol	0.9978	31	1	1,2-Dimethoxyethane	0.105 - 1.998
t-Amyl ethyl ether	0.9922	87	1	1,2-Dimethoxyethane	1.024 - 17.948
Benzene	0.9980	78	1	D6 Benzene	0.2056 - 7.8225
Toluene	0.9970	92	1	D8 Toluene	0.755 - 28.725
Ethylbenzene	0.9946	106	1	D10 Ethylbenzene	0.2033 - 7.734
m+p-Xylene	0.9974	106	2	D10 Ethylbenzene	0.4759 - 18.105
o-Xylene	0.9914	106	1	D10 Ethylbenzene	0.2496 - 9.3435
i-Propylbenzene	0.9991	120	1	D10 Ethylbenzene	0.1216 - 4.626
n-Propylbenzene	0.9983	120	1	D10 Ethylbenzene	0.1217 - 4.629
1-Ethyl-3(and 4)-methylbenzene	0.9949	120	1	D10 Ethylbenzene	0.2469 - 9.3915
1,3,5-Trimethylbenzene	0.9988	120	1	D10 Ethylbenzene	0.1234 - 4.695
1-Ethyl-2-methylbenzene	0.9992	120	1	D10 Ethylbenzene	0.1224 - 4.659
1,2,4-Trimethylbenzene	0.9982	120	1	D10 Ethylbenzene	0.2062 - 7.842
1,2,3-Trimethylbenzene	0.9989	120	1	D10 Ethylbenzene	0.1280 - 4.869
Indane	0.9974	117	2	D10 Ethylbenzene	0.1439 - 5.475
Butylbenzene+1,4-Diethylbenzene	0.9981	134	2	D8 Naphthalene	0.2461 - 9.3585
1,2-Diethylbenzene	0.9964	134	2	D8 Naphthalene	0.1285 - 4.8405
1,2,4,5-Tetramethylbenzene	0.9996	134	1	D8 Naphthalene	0.0929 - 3.5205
1,2,3,5-Tetramethylbenzene	0.9996	134	1	D8 Naphthalene	0.0863 - 3.279
Naphthalene	0.9925	128	1	D8 Naphthalene	0.0925 - 3.5175
2-Methylnaphthalene	0.9980	142	1	D8 Naphthalene	0.0933 - 3.7365
1-Methylnaphthalene	0.9983	142	1	D8 Naphthalene	0.0924 - 3.516

Table 3. Comparison of chemical-class composition of three gasoline samples obtained from different sources (numbers in parenthesis indicate different suppliers). No oxygen-containing components were detected in the samples.

	% Weight		
	87 (1)	87 (2)	93 (2)
Benzene	0.63	1.975	0.3
Toluene	9.075	17.895	0.385
Ethylbenzene	0.94	0.16	< 0.2
m+p-Xylene	3.4	1.09	0.72
o-Xylene	1.55	0.45	0.42
Total BTEX	5.89	1.7	1.14
C8 benzene	5.895	1.71	1.15
C9 benzene	5.565	2.8	12.91
C10 benzene	1.75	1.13	3.335
C11 benzene	< 0.2	< 0.2	< 0.2
C12 benzene	< 0.2	< 0.2	< 0.2
Naphthalene	0.33	0.25	0.46
Methyl naphthalenes	0.55	0.505	0.39
Total Aromatics	25.3	27.555	20.165

4. Conclusions

The increase in peak capacity obtained by using the GCxGC-TOFMS Pegasus 4D system allowed identification and calibration of 36 components from two different chemical classes in an analysis time of 10 minutes. For cases where complete separation of the analytes of interest was not achieved, the Deconvolution algorithm of the ChromaTOF software extracted the necessary information for the coeluted components to achieve peak identification as well as analyte quantification. The method was used for the analysis of 3 different commercial samples. Peak finding, analyte identification, and quantification in the two dimensional chromatogram were accomplished automatically with the ChromaTOF software.

