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Detection of Oxygenated Components in Diesel by GCxGC x HR-TOFMS

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Introduction

Small amounts of oxygenates are often added to diesel to reduce particle matter in emissions from diesel engines. In most cases, this causes nitrogen oxide emissions to increase. Therefore, it is essential to establish an analytical method for monitoring oxygenates in diesel. This paper describe a new method using GC x GC x HR-TOFMS to analyze oxygenates in diesel samples. A pre-separation and enrichment of oxygenates from hydrocarbon matrix by thin-layer chromatography (TLC) was performed. The method is simple and sensitive.

Experimental

All solvents were of HPLC grade. 100 μ L of diesel sample was applied on a LK5D Silica Gel 150 Å TLC plate (Whattman) and developed with 100% hexane. Spots visible under UV light were cut and back extracted into 200 μ L of ethyl acetate, and centrifuged at 2,000 x g to remove TLC particles. 1 μ L of resulting extract was injected onto a Zoex GC x GC x HR-TOFMS system. The instrument conditions are listed in Table 1. GC Image software was used for data processing.

Table 1. Experimental conditions for GC x GC x HR-TOFMS system

GC x GC	
GC:	Agilent 6890N
Modulator:	Zoex ZX2 loop thermal modulator
Carrier gas:	Не
Oven temperature:	32°C - 240°C @ 2.3°C/min and hold for 20 min
Column:	1. SPB-1 (15m x 0
	2. SupelcoWax (1m x
Injection mode:	splitless
Inlet temperature:	280°C
Inlet Pressure:	125 kPa – 250 kPa @ 1.4 kPa/min
Hot jet temperature:	250°C - 375°C @ 2.5°C/min
Transfer line T:	280°C
MS	
MS:	Zoex HR-TOFMS
Mass resolution:	7,000 FWHM
Data acquisition rate:	100 Hz
Ionization mode:	EI @ 70eV
Ion source temperature:	280°C
Ion source pressure:	7E-6 mbar
TOF pressure:	8E-7 mbar
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Supplier of GCXGC software



Results and Discussion

The high resolution time-of-flight mass spectrometer was tuned to achieve mass resolution of 7,000 (FWHM) and calibrated locally to ensure mass accuracy for each ion better than 2 mmu. Figure 1 shows the 2D total ion chromatogram (TIC) of diesel TLC extract. The TLC extraction removed hydrocarbon interferences, making splitless injection possible for trace level oxygenates. Solvent blanks and TLC plate blanks were also analyzed to ensure that peaks analyzed in the 2D TIC were attributable to the samples, not to backgrounds.



Fig 1. GC x GC x HR-TOFMS total ion chromatogram of diesel TLC extract

Compound	Retention time		NIST search results			
·	l (min)	II (sec)				
			Name Formula Match Rev Proba CA5# Molec Lbr Lbra Ni Sel			
			Ethanol, 2-(2-ethoxyethoxy)- C6H14O3 864 885 92.39 111-9 134 mainlib 14593 227			
A	14.8000	1.9900	Ethane, 1,1'-oxybis[2-ethoxy-] C9H1803 737 764 4.02 112-3 162 mainlb 15009 229			
			Ethanol, 2-(2-(2-ethoxyetho C8H1804 684 699 0.79 112-5 178 mainlib 14925 230 2-Propanol, 1-(2-methoxypro C7H1603 682 711 0.76 13429 146 mainlib 24735 32514			
			2-Propanol, 1-(2-methoxypro C7H1603 663 711 0.76 13429 149 mainlb 24735 32514 Ethanol, 2-ethoxy- C4H1002 678 725 0.61 110-8 90 mainlb 1357 19550			
			2.Proprint 2. Contactor Contactor Contactor 200 1200			
			Name Formula Match F Reverse Probability CAS# Molecula Library LibraryID NIST# Select			
В	47.7333	5.6200	Dibenzofu C12H8O 827 854 81.96 132-64-9 168 mainlb 107679 228192 1(2H)-Acc C12H8O 754 774 11.16 2235-15-6 168 mainlb 107679 128365			
			Nationation - Libro 756 776 776 1110 Libro 1 10 10 10 10 10 10 10 10 10 10 10 10 1			
			1-Naphth C11H6N2 679 662 0.67 38515-13-0 168 mainlb 107697 186244			
D	47.7000	0.0200	9H-Pyrido C11H0N2 673 666 0.53 244-63-3 166 mainlb 107702 233366			
			Naphtho[C11HBN2 665 823 0.39 233-53-4 166 mainlb 107689 261805			
			Name Formula Match.F Reverse Probability CAS# Molecula Library LibraryID NIST# Select			
			6H-OBenzul C13H100 845 872 44.01 229-95-8 182 mainlb 114947 289928 Disenzofu C13H100 809 819 10.87 7320-53-8 182 mainlb 115521 30279			
	53.8667	4.3600	94-Xarth C13H100 806 824 9-61 92-83-1 182 mainle 114951 22819			
	55.6007	4.3000	2,4,6-Cyc C13H100 805 822 9.24 14562-09-5 182 mainlib 114959 241983			
С	E4 6667	1 61 00	24Hydrox C13H100 797 826 6.89 2443-58-5 182 mainlb 115519 133894			
C	54.6667	4.6100	[1,1'-Bph C13H100 795 816 6.35 3218-36-8 182 mainlb 115520 7593 9H-Fluore C13H100 759 779 1.57 1689-64-1 182 mainlb 114946 230895			
	FF 2000	4 7000	9H-Huore C13H100 759 779 1.57 1889-64-1 182 manib 114946 230895 9H-Xanth C22H19NO2 751 772 1.17 349401-3 329 mainlb 114954 277777			
	55.2000	4.7600				

Table 2.	Retention time and NIST library search results for 3 groups of
oxygena	es

The EI mass spectra for the blobs (peaks) circled in Figure 1 were subjected to NIST database for library search. The possible compounds are listed on Table 2. The accurate mass was also measured and the possible elemental compositions for each ion were



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obtained and are listed on Table 3. Combining NIST library search and accurate mass measurement of each ions, all of these trace level oxygenates in diesel sample were unambiguous identified.

Table 3. List of oxygenates identified in diesel

No	R1t (min)	R2t (sec)	Compounds	Fragment ions	Measured m/z	Theoretical m/z	Mass error mmu
А	14.8000	1.	Carbitol	$C_{3}H_{7}O^{+}$ $C_{4}H_{8}O^{+}$ $C_{5}H_{11}O_{2}^{+}$	59.047470 72.056646 103.074939	59.049141 72.056966 103.075356	1.672 0.320 0.417
В	47.7333	5.6200	Dibenzofuran	$C_9 H_5^+ C_{11} H_7^+ C_{12} H_8 O^+$	113.038372 139.054693 168.056720	113.038577 139.054227 168.056966	0.205 -0.466 0.246
С	53.8667 54.6667 55.2000	4.3600 4.6100 4.76	Methyldibenzofuran	$C_{11}H_4O^+ \\ C_{13}H_9O^+ \\ C_{13}H_{10}O^+$	152.026875 181.064847 182.070651	152.025666 181.064791 182.072616	-1.209 -0.056 1.965

Conclusions

A new method for detection of trace level of oxygenates in diesel by comprehensive twodimensional gas chromatography and high-resolution time-of-flight mass spectrometry is described. The method is simple and sensitive.

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