

#G02

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

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: He

Oven temperature: 32°C - 240°C @ 2.3°C/min and hold for 20 min

Column: 1. SPB-1 (15m \times 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





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.

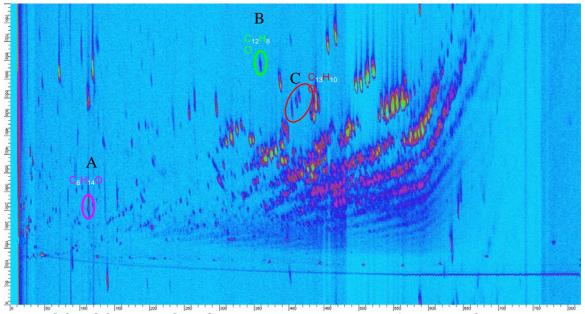


Fig 1. GC x GC x HR-TOFMS total ion chromatogram of diesel TLC extract

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

Compound	Retention time		NIST search results			
-	I (min)	II (sec)				
			Name Formula Match Rev Proba CAS# Molec Libr Libra NI Sel.			
			Ethanol, 2-(2-ethoxyethoxy)- C6H14O3 864 885 92.39 111-9 134 mainlib 14593 227			
Α	14.8000	1.9900	Ethane, 1,1'-oxybis[2-ethoxy-] C8H19O3 737 764 4.02 112-3 162 mainlib 15009 229			
			Ethanol, 2-[2-(2-ethoxyetho C8H18O4 684 699 0.79 112-5 178 mainlib 14925 230			
			2-Propanol, 1-(2-methoxypro C7H16O3 603 711 0.76 13429 148 mainlib 24735 32514			
			Ethanol, 2-ethoxy- C4H1002 678 725 0.61 110.8 90 mainlb 1357 19550			
			3 Protect 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150 150			
В	47.7333	5.6200	Name Formula Match F Reverse Probability CAS# Molecula Library LibraryID NIST# Select			
			Diberzofu C12480 827 854 81.96 132-64-9 168 mainib 107679 228192			
			1(2H)-Acc C12H8O 754 774 11.16 2235-15-6 168 mainlib 107692 128385			
			Naphtho(C12HBO 726 903 3.22 232-95-1 168 marib 107681 6428 1-Naphth C11HBN2 679 662 0.67 38515-13-8 168 marib 107697 196244			
			1-Naprott. C1198V2 6-79 602 0.67 30517-13-9 100 marinb 107/02/ 1862-9-199-Prido. C1198V2 6-73 666 0.53 244-63-3 160 marinb 107/02 23386			
			Naphtho(C11H9N2 665 823 0.39 233-53-4 168 mainlb 107689 261805			
			or must laure			
			Name Formula Match F Reverse Probability CASE Molecula Library LibraryID NISTE Select			
			6H-Obenz C13H10O 845 872 44.01 229-95-8 182 mainlb 114947 280928			
С	50.0007	4.0000	Oberardru C13H10O 609 619 10.87 7320-53-8 102 mainlb 115521 30279 9HXanth C13H10O 806 824 9.61 92-63-1 182 mainlb 114951 228198			
	53.8667	4.3600	2.4,6-Cyc C13H100 805 829 9.24 14562-09-5 182 mainlb 114959 241983			
	E 4 0007	4.04.00	2-Hydrox C13-H0O 797 826 6.59 2443-58-5 182 marib 115519 133894			
	54.6667	4.6100	[1,1'-Bph C13H100 795 816 6.35 3218-36-8 182 mainlib 115520 7583			
			9H-Fluore C13H10O 759 779 1.57 1689-64-1 182 mainlib 114946 230895			
	55.2000	4.7600	9H-Xanth C22H19N02 751 772 1.17 349401-3 329 mainlib 114954 277777			

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



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
Α	14.8000	1.	Carbitol	$C_3H_7O^+$ $C_4H_8O^+$ $C_5H_{11}O_2^+$	59.047470 72.056646 103.074939	59.049141 72.056966 103.075356	1.672 0.320 0.417
В	47.7333	5.6200	Dibenzofuran	$C_9H_5^+$ $C_{11}H_7^+$ $C_{12}H_8O^+$	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.

Headquarters

JSB International Tramstraat 15 5611 CM Eindhoven T +31 (0) 40 251 47 53 F +31 (0) 40 251 47 58

Zoex Europe
Tramstraat 15
5611 CM Eindhoven
T +31 (0) 40 257 39 72
F +31 (0) 40 251 47 58

Sales and Service

Netherlands Apolloweg 2B 8239 DA Lelystad T +31 (0) 320 87 00 18 F +31 (0) 320 87 00 19

Belgium Grensstraat 7 Box 3 1831 Diegem T +32 (0) 2 721 92 11 F +32 (0) 2 720 76 22 Germany Max-Planck-Strasse 4 D-47475 Kamp-Lintfort T +49 (0) 28 42 9280 799 F +49 (0) 28 42 9732 638

UK & Ireland Cedar Court, Grove Park Business Est. White Waltham, Maidenhead Berks, SL6 3LW T +44 (0) 16 288 220 48 F +44 (0) 70 394 006 78

info@go-jsb.com www.go-jsb.com



