#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 µL 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 µL of ethyl acetate, and centrifuged at 2,000 x g to remove TLC particles. 1 µL 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 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

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.

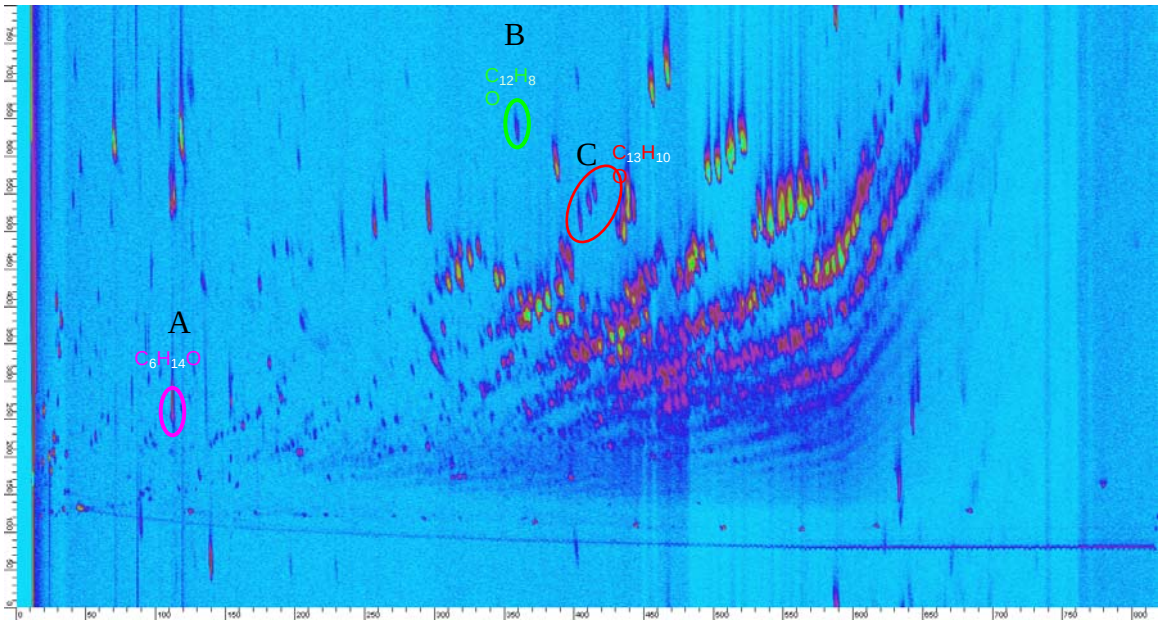
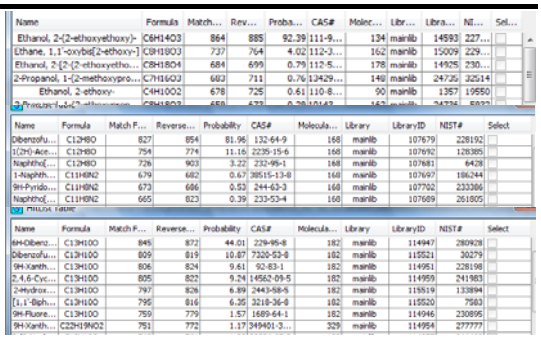


Fig 1. GC x GC x HR-TOFMS total ion chromatogram of diesel TLC extract

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

Compound	Retention time I (min)	Retention time II (sec)	NIST search results
A	14.8000	1.9900	
B	47.7333	5.6200	
C	53.8667	4.3600	
	54.6667	4.6100	
	55.2000	4.7600	

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
A	14.8000	1.	Carbitol	$C_3H_7O^+$	59.047470	59.049141	1.672
				$C_4H_8O^+$	72.056646	72.056966	0.320
				$C_5H_{11}O_2^+$	103.074939	103.075356	0.417
B	47.7333	5.6200	Dibenzofuran	$C_9H_5^+$	113.038372	113.038577	0.205
				$C_{11}H_7^+$	139.054693	139.054227	-0.466
				$C_{12}H_8O^+$	168.056720	168.056966	0.246
C	53.8667	4.3600	Methyldibenzofuran	$C_{11}H_4O^+$	152.026875	152.025666	-1.209
	54.6667	4.6100		$C_{13}H_9O^+$	181.064847	181.064791	-0.056
	55.2000	4.76		$C_{13}H_{10}O^+$	182.070651	182.072616	1.965

Conclusions

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