Determination of polycyclic aromatic hydrocarbons and fatty acid methyl esters in diesel fuel by comprehensively coupled (supercritical fluid × gas) chromatography

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Abstract

Historically, diesel fuel from petroleum sources consisted of aliphatic hydrocarbons, but it may now contain polycyclic aromatic hydrocarbon (PAH) and fatty acid methyl esters (FAME). PAHs might originate from the refining process, or might be blended in to increase the density or cetane number to comply with standards. FAMEs are blended in because it reduces the carbon footprint of the fuel, and because it helps meet the lubricity requirement.

Keywords: supercritical fluid chromatography, diesel, fatty acid methyl esters, polycyclic aromatic hydrocarbons, biodiesel

1. Introduction

Fuel for compression-ignition engines (diesel fuel) was traditionally obtained from petroleum sources. Today these traditional fuels are being blended with and replaced by diesel fuel from biological sources. To be sold on the open market, these fuels must comply with certain technical requirements, set by standards organizations such as ASTM and CEN. Because of

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the complexity of diesel fuel obtained from petroleum sources (petrodiesel) the chemical composition of the fuel is in general not prescribed. Instead, a compliant fuel must pass certain distillation tests. There are two exceptions: the amount of polycyclic aromatic hydrocarbons (PAHs) and fatty acid methyl esters (FAMEs) are subject to upper limits.

PAHs are natural constituents of petrodiesel. They are noxious pollutants, and therefore regulators try to reduce the exposure of humans to PAHs by limiting their emission into the environment. Since a major source of PAH emissions is internal combustion engines, one way to limit emissions is to limit the amount in diesel fuels. A full discussion on PAH sources is beyond the scope of this paper.

FAMEs are not found in petroleum but are blended with petrodiesel. FAMEs are usually obtained by the transesterification of plant oils with methanol. The resulting product can be used as a diesel fuel and is called biodiesel. The primary benefit of the blending of FAMEs is that it lowers the carbon footprint of the fuel, but it can also improve the lubricity of high-paraffinic diesel (1). Diesel for sale in the Eurpean Union can contain up to 7 % FAMEs. Any concentration of biodiesel makes a diesel fuel but, higher concentrations are regulated as blends.

The amount of PAHs in diesel can be determined by a fluorescent indicator absorption (FIA) test (ASTM D1319, (2)), but this method is labour-intensive. Another method is a liquid chromatography method (EN 12916:2006) with refractive index detection, and the method prescribed by ASTM D2425 requires a mass spectrometer. The method ASTM D5168 is a supercritical fluid chromatography (SFC) method with flame ionization detection (FID). Because the FID responds to number of carbon and has a large dynamic range atoms in the sample FID methods are preferable for quantification.

The prescribed methods for determining FAMEs in diesel is an infra-red absorption method, ASTM D7806-12. This method is liable to interference from FAMEs degradation products that might accumulate during storage (3).

The SFC-FID method ASTM 5186-19 claims that FAMEs interfere with the method. Weber et al. (4) claims that FAMEs 'foul' the column. This is contrary to experience: FAMEs do elute from silica columns with neat CO_2 as mobile phase (5). But the capacity factors (k' values) of the PAHs are less than 0.05, while the capacity factors of the FAMEs are greater than 0.8**To do** [1]. If a number of determinations of PAHs in FAME-containing diesel fuel are done in sequence without allowing the FAMEs to elute, the

FAMEs will start eluting during the PAH determination and cause interference. To address this problem The California Air Resources Board (ARB) has published a standard operating procedure (SOP) (6) based on a publication by Diehl and DiSanzo (7) that combines the determination of PAHs with FAMEs. In this procedure SFC-FID is used to determine the PAHs, and then the column is back-flushed to determine total FAMEs. This solves the problem of FAMEs interfering with the PAHs determination and simultaneously quantifies the FAMEs.

The information produced by this method is the total amount of FAMEs and the total amounts of mono-, di-, and tri+ aromatics. This information suffices for monitoring compliance, but extending the method by comprehensively coupling a fast gas chromatograph (GC) to the SFC provides a richly patterned chromatogram that can help solve process control and supply chain problems. The orthogonality of SFC and GC is high: on SFC with bare silica as a stationary phase and neat carbon dioxide as a mobile phase PAHs are separated according to the number of rings in their structure, and the FAMEs are separated according to the number of double bonds, whereas all GC separations are primarily according to volatility. Therefore determining PAHs and FAMEs make an ideal combination for comprehensively coupled (supercritical fluid × gas) chromatography. If — using the ARB SOP as a basis — the FAMEs are not back-flushed but all the compounds are allowed to elute, and the SFC is comprehensively coupled to gas chromatography (GC), the ^{1}D (SFC) dimension will separate the PAHs into their classes, and the FAMES according to the number of double bonds. The ^{2}D (GC) separation will separate the compounds in each PAH and FAME class further, according to their volatility. The resulting chromatogram contains patterns that are rich in information.

2. Material and methods

3. Results

Figure 1 shows some results.

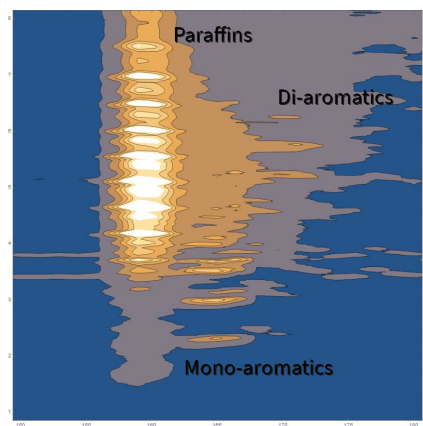## 4. Discussion

5. Conclusion

Acknowledgements

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Figure 1: . A contour plot of an SFCxGC chromatogram, showing the hydrocarbons in detail

To do. . .

☐   1 (p. 2): Use k' values from own experiments

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