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Full Length Article

Comparison of GC-VUV, GC-FID, and comprehensive two-dimensional GC–MS for the characterization of weathered and unweathered diesel fuels

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ABSTRACT

Characterization of diesel fuels and degraded diesel fuels in the environment is a common issue nowadays. Providing definitive information for litigation regarding determination and distinguishing the origins or sources of fuel spill contamination has been a significant need among the environmental forensics community. Diesel fuels contain more complex chemicals and isomers compared to gasoline. Here, we compare the use of gas chromatography – vacuum ultraviolet spectroscopy (GC-VUV), gas chromatography – flame ionization detection (GC-FID), and comprehensive two-dimensional gas chromatography – mass spectrometry (GC × GC–MS) for diesel fuel and weathered diesel fuel analysis in fingerprinting biomarkers. GC-VUV is a relatively new technique that can rapidly acquire full absorption spectra from 120 to 240 nm. Class information about individual components is readily obtained based on reference to a library of matched spectra. Direct comparison of GC-VUV, GC-FID, and GC × GC–MS was undertaken to identify different classes of compounds and biomarkers. Using GC-VUV, numerous peaks representing minor and major components were classified into different classes by applying spectral filters and, in some cases, spectral deconvolution. Isoprenoid biomarkers, such as pristane and phytane, and their ratios with n-alkanes, C_{17} and C_{18}, respectively, were determined The biomarker ratio results from GC-VUV matched well with both GC-FID and GC × GC–MS. About 5%–20% difference in measured biomarker ratios were obtained for a series of commercial weathered diesel standard samples, which is good enough to allow the discrimination of different weathered diesel samples, according to prior literature.

1. Introduction

Crude oil was formed over a span of millions of years from buried dead and decaying plants and animals that were exposed to high temperatures and pressures in a hypoxic environment. Once extracted from the ground, it can be refined into numerous different types of high value fuels and petrochemical products [1]. Crude oil predominantly contains different classes of hydrocarbons and other chemical compounds. Due to the presence of different temperatures, pressures, and source materials during formation, crude oils obtained from different locations have significantly different chemical signatures. Many different fingerprinting techniques have been reported to visualize these differences [1–4].

Diesel fuel is a high volume refinery product distilled from crude oil. It contains more complex chemical components than gasoline, ranging approximately from C_{10} to C_{22} and including many different isomeric species [5]. The most abundant compounds can be classified into four major hydrocarbon groups, namely paraffins, isoparaffins, naphthenes, and aromatics. The relative abundances of these groups of compounds are very useful for comparing samples of known origin to those from suspected contamination events [6].

Because of the high power-efficiency and economical features of diesel fuel, worldwide demand is very high. Along with the need to transport large volumes of diesel fuel, there exists significant potential for spills into the environment. Diesel fuel spills in soil from leaking underground storage tanks, pipelines, and accidents can cause groundwater contamination and can be toxic to soil microorganisms and plants [7]. Diesel fuel is one of the most acutely toxic oil types; spills can threaten natural marine resources, wildlife, and habitats [8,9]. Therefore, identifying and characterizing diesel spills, and linking them to suspected sources, is an important part of environmental forensics investigations. Fingerprinting multiple classes of compounds and analyzing biomarkers are the most popular methods used [2,10]. Many methods have been developed to analyze diesel fuels; however, there is no perfect routine method that can be applied to fully and readily satisfy the objectives of related forensics investigations

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[2,11].

Several different classes of compounds in diesel fuel, including alkanes, cycloalkanes, alkylbenzenes, alkylnaphthalenes, and anthracene/phenanthrenes, are primary targets for source and age identification measurements [2,6,12]. n-Alkanes, like C_{17} and C_{18}, are the highest abundance compounds in fresh diesel, and isoprenoids are the most predominant in weathered and biodegraded diesel; thus, their ratios can be used to determine the degree of the diesel degradation, the age of a diesel spill, and help to identify the source of spilled diesel [1,13]. Pristane and phytane are the two isoprenoids that serve as biomarker indicators in diesel fuels because of their large abundance and relative ease of measurement [14–16]. Steranes, hopanes, and triterpanes can also be useful biomarkers in petroleum analysis but are less abundant in diesel fuels [12]. Biomarkers further play an important role in oil exploration; however, their presence in complex petroleum mixtures is very low, which makes them difficult to detect [12,17].

Overall, there are several technical challenges with diesel fuel fingerprinting. First, target compounds used to identify suspected sources of the spill can be hard to determine since they can undergo several weathering processes that could change the composition of the oil. These include evaporation, emulsification, dispersion, biodegradation, and photooxidation, among others [2,4]. Second, developing a routine procedure with appropriate detection limits to collect sensitive and high resolution data over time is very important, but is not easy to achieve [3].

One-dimensional gas chromatography (GC) with flame ionization (FID) or mass spectrometry (MS) detection are the most popular methods for fuel forensics; they have been widely applied because they can provide fundamental information for major components. However, when it comes to detailed minor compounds, they may not provide sufficient resolution [12]. Other methods developed for petroleum analysis have featured techniques such as high-performance liquid and supercritical fluid chromatography, as well as infrared, ultraviolet, fluorescence, and nuclear magnetic resonance spectroscopy [4,18]. However, because of the inherent complexity of the sample matrix, none of these methods can provide a comprehensive analysis of diesel fuel.

Comprehensive two-dimensional gas chromatography (GC × GC) with FID and with MS has also been applied for characterization of diesel and weathered diesel samples [19–21]. GC × GC can provide very detailed information about the various sample constituents due to its potential for increasing peak capacity by an order of magnitude versus one-dimensional GC. It also provides significant insight into the presence of various compound classes, since the signatures of these classes are highly ordered in the GC × GC contour plot [6,22]. However, there are some limitations to GC × GC. GC × GC can be less user-friendly and relatively harder to operate and maintain because of additional hardware and software requirements. Method development challenges include the optimization of the modulator, the modulation time, and the avoidance of wrap around. In addition, the capital equipment and maintenance costs can be quite high. For environmental forensics, these benefits can surely assist law enforcers to solve problems, but it can be difficult for forensic chemists, since they must communicate results to a non-scientific audience (e.g., lawyers and judges), who may not be experts in chemometrics or GC × GC [11,22,23]. Even though advancements in availability and capability of instrumentation and software have been made for GC × GC, one dimensional GC is a much more widely understood and accepted technique in the general and environmental forensics fields.

Vacuum ultraviolet spectroscopy, which has universal detection capabilities [24], coupled with gas chromatography (GC-VUV), has been applied in this research to demonstrate the possibility of its use for resolution of different compound classes and direct speciation of target biomarker compounds in complex diesel samples. Vacuum ultraviolet spectroscopy has been shown to address some limitations of other GC detection techniques due to its added spectral resolution, deconvolution, and quantitative capabilities [24–26]. Various applications have been previously demonstrated using GC-VUV, including those related to permanent gases [25], fatty acid esters [27,28], multiclass pesticides [29], terpenes [30], dimethylnaphthalene isomers [31], and gasoline compound class speciation analysis [32]. Of particular note, the latter work on gasoline compound speciation features a new means for PIONA analysis based on the use of time interval deconvolution (TID). However, diesel fuel is far too complex to currently allow for automated speciation as was performed for gasoline. The VUV spectral library does not yet contain many of the more complex hydrocarbon species present in diesel fuel that would enable such an analysis. That said, researchers have previously applied GC-VUV and GC × GC-VUV to explore some compound classification in diesel fuels [31,33,34].

The aim of this study was to evaluate the unique features of GC-VUV to differentiate and characterize classes of compounds, specifically to fingerprint common biomarkers for age and source identification, in a series of commercial unweathered and weathered diesel fuels. Further, results were compared to those obtained using GC × GC with time-of-flight (TOF) MS and GC-FID, as a means to evaluate different state-of-the-art technologies. By applying different VUV spectral filters, normal alkanes, monoaromatics, and substituted naphthalenes were classified into their respective groups. Dimethylnaphthalenes were also targeted for deconvolution using VUV spectra. Meanwhile, isoprenoid biomarkers pristane and phytane, and their ratios relative to C_{17} and C_{18} n-alkanes, respectively, in the different diesel fuels were determined. Reasonable agreement was observed between results obtained by GC-VUV, GC-FID, and GC × GC-TOFMS, but GC-VUV and GC-FID results were more comparable.

2. Experimental

2.1. Instrumentation and materials

A composite (unweathered, 0%) diesel fuel, as well as 25%, 50% and 75% artificially weathered diesel fuels and a fuel oil degradation mix, which contained heptadecane (C_{17}), octadecane (C_{18}), pristane, and phytane, were obtained from Restek Corporation (Bellefonte, PA). It is worth noting that the commercially obtained 25%, 50%, and 75% diesel fuels were prepared artificially through evaporation, and that they were not all prepared from the same initial diesel fuel sample. An n-alkane standard mixture from C_7 to C_{40} and a n-hydrocarbon mix (C9 and even number hydrocarbons from C_{10} to C_{36}) were also obtained from Sigma-Aldrich (St. Louis, MO). Response factors were determined for heptadecane (C_{17}), octadecane (C_{18}), pristane, and phytane using the fuel oil degradation mix for quantitative determination of biomarker ratios.

A Shimadzu GC-2010 gas chromatograph (Shimadzu Scientific Instruments, Inc., Columbia MD) coupled to a VGA-100 VUV detector (VUV Analytics, Inc., Cedar Park TX) was used to collect GC-VUV data. A Shimadzu GC-17A GC-FID was used to collect GC-FID data.

The column used for GC-VUV was an Rxi-1ms (30 m × 0.25 mm × 0.25 μm) from Restek and a SHRXI-5MS (30 m × 0.25 mm × 0.25 μm) for GC-FID from Shimadzu. Both systems was operated in the constant velocity mode (1.4 mL/min) with helium carrier gas. The GC inlet temperature was set to 275 °C. The injection volume and split ratio were varied for different samples. The GC oven profile was set to start at 40 °C (held for 0.1 min) and then increased to 320 °C at a rate of 6.5 °C/min (held for 5 min). The transfer line and flow cell temperatures for the VUV detector were set to 300 °C, and the make-up gas (nitrogen) pressure was set to 0.25 psi. The data collection rate was set to 2.67 Hz, an acquisition rate that allowed sufficient sampling of each chromatographic peak using the applied GC method.

A LECO Pegasus 4D GC × GC-TOFMS incorporating a dual-stage quad-jet cryogenic modulator and independently-controlled secondary GC oven was used for GC × GC work. Two columns from Restek used