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Determination of polycyclic aromatic sulfur heterocycles in diesel particulate matter and diesel fuel by gas chromatography with atomic emission detection

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Abstract

The sulfur content of diesel fuel is of environmental concern because sulfur can facilitate the formation of diesel particulate matter (DPM) and sulfur dioxide (SO_2) in the exhaust can poison catalytic converters. The US Environmental Protection Agency (EPA) has established more stringent regulations to reduce the sulfur content of diesel fuels in the near future. In this study, various types of organosulfur compounds in DPM extracts and the corresponding fuels have been determined by gas chromatography with atomic emission detection. The diesel fuels used have sulfur contents of 2284 and 433 ppm, respectively, and are labeled as high-sulfur and low-sulfur diesel fuels. The compounds identified are mainly polycyclic aromatic sulfur heterocycles (PASHs). In the fuels tested, trimethylbenzothiophenes (TMBTs), dibenzothiophenes (DBTs), and 4-methyldibenzothiophene (4-MDBT) were the most abundant sulfur compounds, while larger PASH compounds were more abundant in DPM extracts. The high-sulfur diesel fuel contained a larger proportion of PASHs with one or two rings (lighter PASHs). In DPM, the concentrations of total organic sulfur and individual PASHs are higher for the high-sulfur diesel fuel, and the relative percentage of one or two-ring PASHs is higher as well. The influence of engine load on the DPM composition was also examined. With increasing load, the PASH concentration in DPM decreased for lighter PASHs, increased for heavier PASHs, and had a bell-shaped distribution for PASHs in between.

Keywords: PASH; Diesel particulate matter; Diesel fuel; GC/AED; Engine load

1. Introduction

Organic sulfur compounds are the most abundant non-hydrocarbon constituents in petroleum. The sulfur content of petroleum fuels contributes to the formation of sulfur dioxide (SO_2), which causes both acid deposition and poisoning of the catalytic converters in vehicles. An increase in fuel sulfur also results in increased diesel particulate emissions. Fuel sulfur reduction has been mandated by US Environmental Protection Agency (EPA) in the near future.

A large fraction of the organic sulfur in diesel fuels occurs as aromatic structures, especially as alkylated homologues of polycyclic aromatic sulfur heterocycles (PASHs). It was reported that benzothiophene (BT), dibenzothiophene (DBT) and their alkylated homologues are the most abundant organosulfur compounds in diesel fuels [1]. Recently, an increasing interest has been focused on PASHs for several reasons. Some PASHs have been reported for their potential mutagenic and carcinogenic properties [2,3]; some PASHs, especially alkylated DBTs, are difficult to remove in the desulfurization process for production of low-sulfur fuels [4,5]; and some PASHs can be potential indicators of the origin and maturity of crude oils [6].

Given the above-mentioned roles of sulfur compounds, efforts have been placed on the chemical characterization of PASHs in crude oil, diesel fuel, and other petroleum products [1,7,8]. However, there have been few studies on the organosulfur content of diesel particulate matter (DPM), which is regarded as a carcinogen by the EPA [9] and the National Institute for Occupational Safety and Health (NIOSH) [10]. PASHs in DPM can originate directly from the diesel fuel or be generated by the combustion process. They are adsorbed on the DPM, which includes a high number of ultrafine particles, and therefore, penetrate deep into the lung. Thus, the characterization of PASHs and

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other particle-borne organic compounds is important and necessary for evaluating and controlling any adverse health effects associated with DPM exposure. Studies on the PASH content of DPM are difficult because their concentrations are low, there is a great variety of compounds present [11], and quantitative determination of individual PASH isomers in the complex mixture is difficult.

The identification and quantification of individual PASH require selective and sensitive methods of detection. Gas chromatography with atomic emission detection (GC/AED) is a powerful technique that offers high-resolution separation of components in a complex matrix and highly selective spectrometric detection. Its application to the analysis of complex matrices, including petroleum products, has been demonstrated [12–15]. The AED is an element-selective and universal detection that provides relatively constant elemental response factors for different compounds [12–14], which makes a compound independent calibration (CIC) possible. CIC is highly useful because it minimizes the number of analytical standards required and permits quantification of compounds for which no standards exist. CIC is particularly attractive when dealing with highly toxic chemicals because relatively nontoxic surrogates can be used for instrument calibration.

In this paper, PASHs in two different sulfur-containing diesel fuels (low-sulfur diesel fuel (LSDF) and high-sulfur diesel fuel (HSDF)) and the resultant DPM were identified and quantified by GC with sulfur-selective atomic emission detection. The distribution of PASHs in DPM was investigated under different fuel sulfur and engine load conditions. For the convenience of description, low-molecular weight or lighter PASHs were defined as the PASHs with one or two rings, and high-molecular weight or heavier PASHs were defined as three-, four- or five-ring PASHs. The precision of a CIC was evaluated with a calibration solution containing several PASHs having different structures and molecular weights.

2. Experimental

2.1. Sampling

A Generac diesel generator (1992, Model SD080, model No. 92A-03040-S, direct-injection, turbocharging, compression-ignition) rated at 80 kW, 60 Hz, 100 hp, and 1800 rpm was used as a stationary DPM emission source. A load simulator (Merlin 100 manufactured by SIMPLX) was used to simulate loads by applying steady-state banks of heaters to the generator at 0, 25, 50 and 75 kW, respectively.

Diesel particulate matter was collected on quartz filters with a high-volume dilution sampler (Fig. 1). The total flow rate (Q_t) of this sampler is approximately 300 L/min and was measured with an orifice meter. The flow rate of dilution air (Q_d) was measured with a flow meter (Dwyer). A dilution ratio of 3.4, which was calculated from the two measured flow rates, was achieved with the sampler. Even though the dilution ratio is low relative to other studies [16,17], the dilution sampler provides sufficient dilution air to maintain the exhaust stream at a temperature ranging from 17.2 to 21.7 °C, which is lower than the

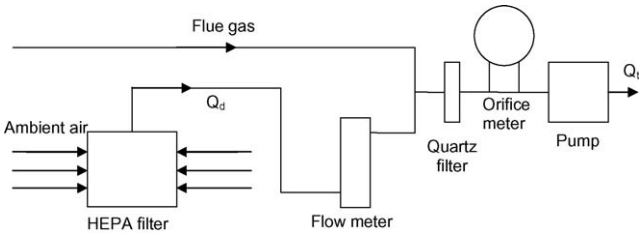

Fig. 1. Schematic of high-volume dilution sampler.

temperature (51.7 °C) required for sample filters when dilution sampling by the Code of Federal Regulations [18]. The DPM samples were taken at four different engine load conditions: 0 (idle condition), 25, 50, and 75 kW. From our previous study [11], it was estimated that the required DPM quantity is 15 mg (for 0 kW) to 30 mg (for 75 kW) to perform the GC/MS analysis. In this study, 50–125 mg DPM was collected on filters for better quantification.

Prior to sampling, the quartz fiber filters used for DPM collection were baked at 550 °C for a minimum of 12 h (to reduce residual carbon levels associated with new filters) and then weighed. After sampling, the filters were dried in a desiccator for 24 h, weighed, and then stored in the refrigerator until the samples were extracted.

2.2. Extraction

The detailed procedure of DPM extraction has been published elsewhere [11]. Briefly, the desiccated filter samples were spiked with deuterated internal standards (naphthalene-d_8 and phenanthrene-d_{10}) prior to extraction to determine the extraction recovery. The concentrations of the standard solutions were about 10 ppm. Samples were then extracted in dichloromethane (DCM) with sonication followed by filtration to remove the insoluble fraction. The extracts were concentrated to about 1 mL for GC/AED analysis. The extraction recovery, determined through the deuterated internal standards, was in the range of 87–98% in this study.

2.3. Analysis

A 6890 GC equipped with a G2350A AED (Agilent Technologies, Palo Alto, CA, USA) was used for quantification of the sulfur components examined in this study. Table 1 lists the GC/AED operating conditions. The HP-5 MS column used in this study and equivalent columns such as DB5-MS have been proven to be effective for PASH separation in several studies [2,6,13]. Both carbon (179 nm) and sulfur (181 nm) selective modes were monitored for all samples. Sulfur determination was based on external and internal standards. For the external standard calibration, the average response factor of a standard solution containing three sulfur compounds at different concentrations was used. As an internal standard, a solution of *t*-butyl disulfide (TBDS) in DCM was spiked into tested fuels and DPM extracts, which were determined to be free of TBDS. Tentative compound identities are based on retention time.