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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 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.

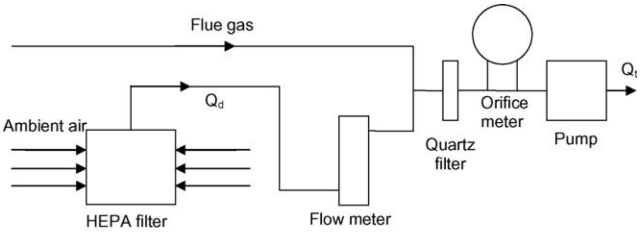

Fig. 1. Schematic of high-volume dilution sampler.

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.

Table 1
GC/AED operating parameters

GC conditions	
Injection port temperature	280 °C
AED transfer line	310 °C
GC capillary column	30 m × 0.25 mm I.D. × 0.25-μm film HP-5 MS
Oven temperature program	40–300 °C at 10 °C/min, hold 10 min
Column flow	1.3 mL/min
Carrier gas	Helium
Injection	20:1 split for fuels; splitless for DPM extracts
Injection volume	1 μL
AED parameters	
Reagent gases	Oxygen, 50 psi; hydrogen, 45 psi
Makeup flow	66 mL/min
Cavity temperature	300 °C
Carbon emission line	179 nm
Sulfur emission line	181 nm

2.4. Analytical standards

Standard compounds listed in Table 2 were prepared in dichloromethane. Thiophene and alkylated thiophenes were from Fisher Scientific, and other PASHs were obtained from a laboratory in Germany (Dr. Jan T. Andersson, Institut für Anorganische und Analytische Chemie, Correns-Str. 30, D-48149 Münster, Germany). Fig. 2 shows the structures for the PASH standards. As a check of method performance, a standard reference material (SRM 2724b, sulfur in diesel fuel oil, with a certified total sulfur content of 426.5 ppm) issued by National Institute of Standards and Technology (NIST) was also used.

3. Results and discussion

3.1. AED response factor

Atomic emission detection should permit a compound independent calibration with surrogate reference compounds that contain the elements of interest. Results with errors of a few percent have been reported when the compounds to be quantified had elemental compositions, retention times, and concentrations similar to the reference compounds [12–15].

In this study, three organosulfur compounds (Table 3) that are most abundant in diesel fuel were chosen as external calibration standards. The sulfur response factor was calculated as the average of the three compounds. The sulfur response factor was not influenced significantly by differences in molecular weight or retention time; the deviation from the average value is about 5% among the three compounds.

The total sulfur in diesel fuel was estimated by integrating the sulfur response from 7 min (the beginning of the sulfur emission) to 25 min for the fuel and 32 min for DPM. The integration

Table 2
List of thiophene standards and related information

No.	Compound	Abbreviation	MW[a]	Formula	b.p. or m.p.[b]
1	Thiophene	T	84	C_4H_4S	84.4 °C (b.p.)
2	2-Methylthiophene	2-MT	98	C_5H_6S	113 °C (b.p.)
3	3-Methylthiophene	3-MT	98	C_5H_6S	114 °C (b.p. 738[c])
4	2,3-Dimethylthiophene	2,3-DMT	112	C_6H_8S	142–144 °C (b.p.)
5	2,5-Dimethylthiophene	2,5-DMT	112	C_6H_8S	134 °C (b.p. 740)
6	2-Ethylthiophene	2-ET	112	C_6H_8S	132–134 °C (b.p.)
7	2-Propylthiophene	2-PT	126	$C_7H_{10}S$	157.5–159.5 °C (b.p.)
8	Benzothiophene	BT	134	C_8H_6S	221–222 °C (b.p.)
9	2-Methylbenzothiophene	2-MBT	148	C_9H_8S	51–52 °C (m.p.)
10	3-Methylbenzothiophene	3-MBT	148	C_9H_8S	125–127 °C (b.p. 25)
11	5-Methylbenzothiophene	5-MBT	148	C_9H_8S	66–67 °C (b.p. 0.6)
12	3,5-Dimethylbenzothiophene	3,5-DMBT	162	$C_{10}H_{10}S$	125–126 °C (b.p. 14); 118–118.5 °C (b.p. 9)
13	2,3,5-Trimethylbenzothiophene	2,3,5-TMBT	162	$C_{11}H_{12}S$	145–146 °C (b.p. 15)
14	2,3,7-Trimethylbenzothiophene	2,3,7-TMBT	162	$C_{11}H_{12}S$	143–144 °C (b.p. 15)
15	2,3,4,7-Tetramethylbenzothiophene	2,3,4,7-TTMBT	176	$C_{12}H_{14}S$	167.5–168 °C (b.p. 14)
16	Dibenzothiophene	DBT	184	$C_{12}H_8S$	332–333 °C (b.p.)
17	4-Methyldibenzothiophene	4-MDBT	198	$C_{13}H_{10}S$	>334 °C (b.p.)
18	4,6-Dimethyldibenzothiophene	4,6-DMDBT	212	$C_{14}H_{12}S$	∼340 °C (b.p.)
19	2,4,6-Trimethyldibenzothiophene	2,4,6-TMDBT	226	$C_{15}H_{14}S$	NA[d]
20	Phenanthro[4,5-*bcd*]thiophene	Ph45T	208	$C_{14}H_8S$	139–140 °C (m.p.)
21	Benzo[*b*]naphtho[1,2-*d*]thiophene	BN12T	234	$C_{16}H_{10}S$	103–104 °C (m.p.)
22	Benzo[*b*]naphtho[2,1-*d*]thiophene	BN21T	234	$C_{16}H_{10}S$	232–234 °C (m.p.)
23	Benzo[*b*]naptho[2,3-*d*]thiophene	BN23T	234	$C_{16}H_{10}S$	158–159 °C (m.p.)
24	Phenanthro[3,4-*b*]thiophene	Ph34T	234	$C_{16}H_{10}S$	82.5–83.5 °C (m.p.)
25	Benzo[*b*]phenanthro[9,10-*d*]thiophene	BPh9,10T	284	$C_{20}H_{12}S$	129–130 °C (m.p.)
26	Diacenaphthothiophene	DiAT	332	$C_{24}H_{12}S$	285–286 °C (m.p.)

[a] Molecular weight.

[b] b.p., boiling point; m.p., melting point.

[c] b.p. 738 is the boiling point at the pressure of 738 mmHg.

[d] Not available.

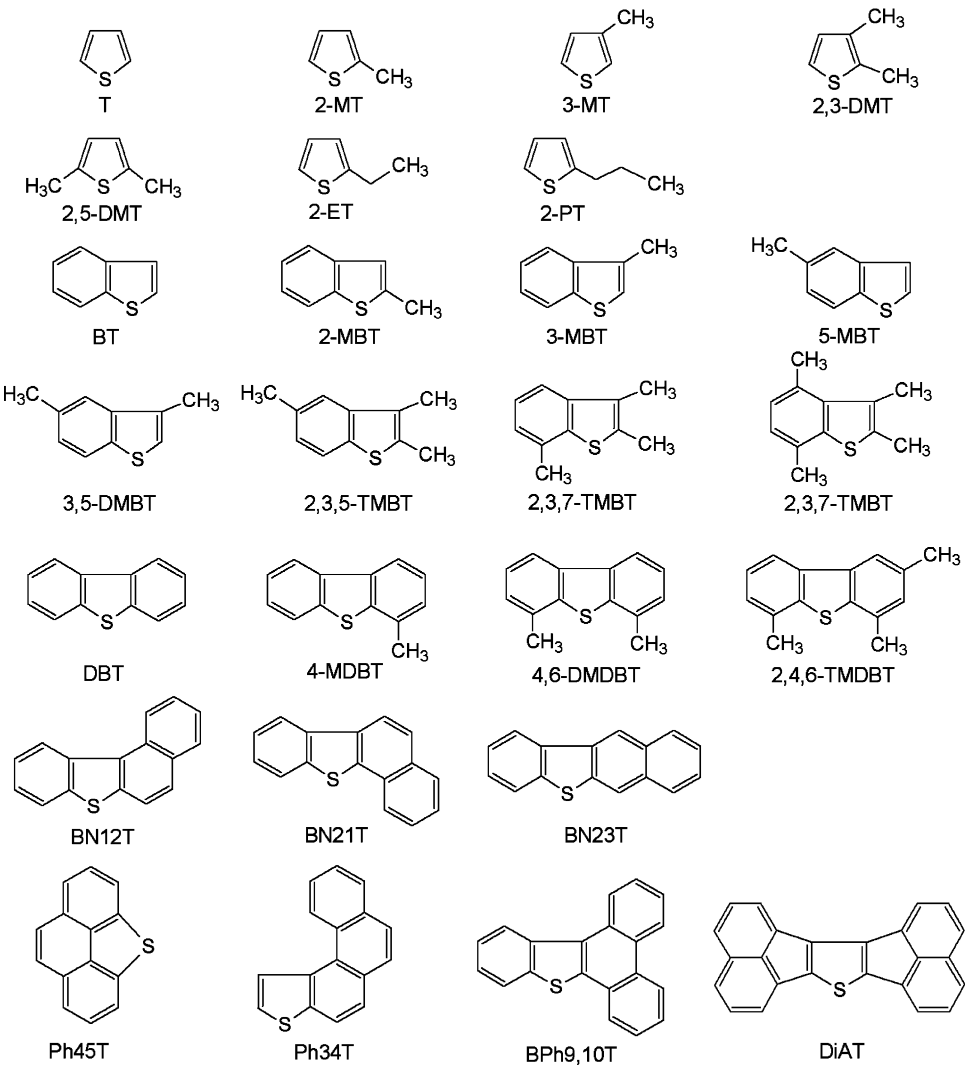

Fig. 2. Structures of PASH standard compounds.

endpoint was the point where the sulfur emission fell to the baseline and remained stable. With the average response factor obtained for the three sulfur compounds, the calculated sulfur content of NIST SRM 2724b is 406 ppm, which is a 4.9% deviation from the certified value of 426.5 ppm. Based on the AED results, the sulfur contents of the diesel fuels (LSDF and HSDF) used in this study are 433 and 2284 ppm, respectively. These results are in good agreement with results (400 ppm S for LSDF and 2200 ppm S for HSDF) reported by another laboratory (OKI Analytical, Cincinnati, OH 45212, USA) using ASTM D1552-03 [19] for sulfur analysis. The relative percent difference (RPD) is 3.9% for LSDF and 1.9% for HSDF. Therefore, the accuracy of this approach for total sulfur in the diesel fuels was verified through the analysis of a NIST standard and the comparison with fuel sulfur contents obtained from an ASTM method.

Table 3
Sulfur response factors for three sulfur compounds

Compound	MW[a]	Formula	Response factor[b]	RSD[c] (%) (*n* = 5)
DBT	184.255	$C_{12}H_8S$	54.06	1.8
4-MDBT	198.282	$C_{13}H_{10}S$	52.73	0.7
4,6-DMDBT	212.309	$C_{14}H_{12}S$	52.54	1.1

Results are based on five injections.

[a] Molecular weight.

[b] Area count per nanogram sulfur.

[c] Relative standard deviation.

3.2. PASH speciation in diesel fuel

Carbon (179 nm) and sulfur (181 nm) AED chromatograms for LSDF are shown in Fig. 3. As was done in other studies, both carbon and sulfur selective modes were used to identify the compounds, but with the exception of Fig. 3, only the sulfur chromatograms are provided in other figures. Fig. 4 represents the sulfur chromatogram for HSDF. The total sulfur content and concentration of individual sulfur compounds are listed in Table 4. Samples were screened for 26 different compounds, with eight (T, 2-MT, 3-MT, 2,3-DMT, 2,5-DMT, 2-ET, 2-PT, DiAT) not detected in any of the fuels or DPM extracts. In Table 4, 3-MBT and 5-MBT were identified based on chemical standards. However, coelution may exist for 3- and 4-MBT, and

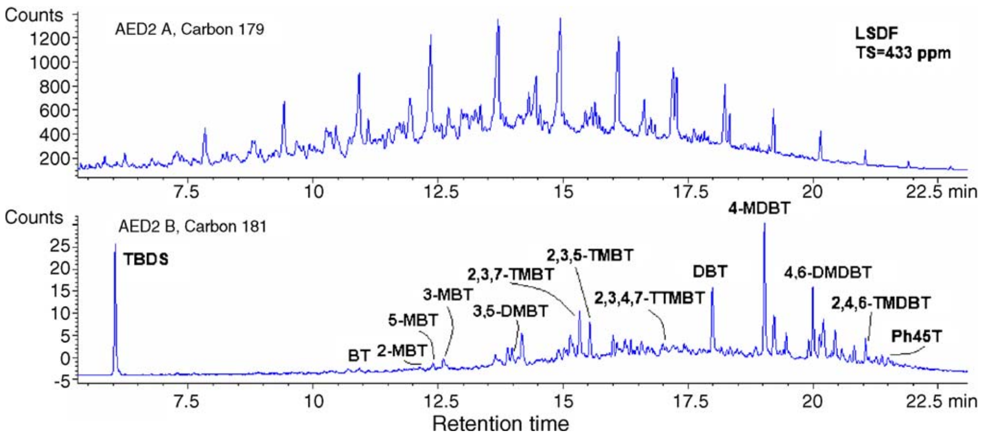

Fig. 3. Carbon (179 nm) and sulfur (181 nm) AED chromatograms for low-sulfur (433 ppm) diesel fuel.

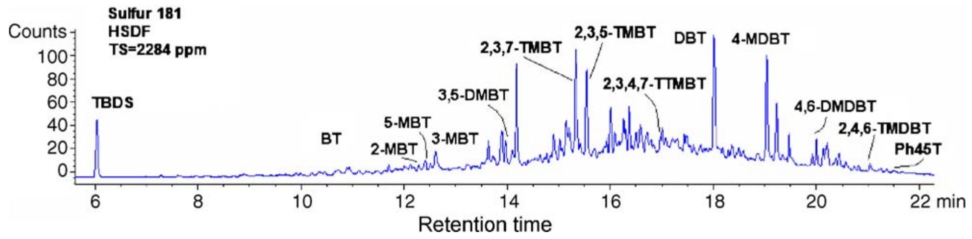

Fig. 4. Sulfur (181 nm) AED chromatogram for high-sulfur (2284 ppm) diesel fuel.

Table 4
PASHs in low- and high-sulfur diesel fuels (LSDF and HSDF) and DPM extracts (L0 through H75)

Compound	Formula	Sulfur content[a] (ppm w/w)[b] ± SD (δ; $n=3$)									
		LSDF	HSDF	L0	L25	L50	L75	H0	H25	H50	H75
Total organic sulfur[c]	S	433 ± 9	2284 ± 12	679 ± 32	734 ± 27	819 ± 25	631 ± 35	1585	1599	1349	923
BT	C_8H_6S	1.34 ± 0.05	8.21 ± 0.17	ND[d]	ND	ND	ND	ND	ND	ND	ND
2-MBT	C_9H_8S	0.11 ± 0.02	7.68 ± 0.14	ND	ND	ND	ND	ND	ND	ND	ND
3-MBT[e]	C_9H_8S	3.21 ± 0.09	8.39 ± 0.12	ND	ND	ND	ND	ND	ND	ND	ND
5-MBT[f]	C_9H_8S	2.86 ± 0.13	15.29 ± 0.45	ND	ND	ND	ND	ND	ND	ND	ND
3,5-DMBT	$C_{10}H_{10}S$	3.85 ± 0.16	18.71 ± 0.42	ND	ND	ND	ND	ND	ND	ND	ND
2,3,5-TMBT	$C_{11}H_{12}S$	8.28 ± 0.24	63.56 ± 2.46	ND	ND	ND	ND	2.81	1.93	0.98	1.85
2,3,7-TMBT	$C_{11}H_{12}S$	10.72 ± 0.19	75.91±2.78	ND	ND	ND	ND	3.44	3.40	2.00	1.25
2,3,4,7-TTMBT	$C_{12}H_{14}S$	4.32 ± 0.11	24.36 ± 0.56	1.48 ± 0.15	1.96 ± 0.28	1.53 ± 0.25	1.63 ± 0.22	14.28	12.67	8.52	2.49
DBT	$C_{12}H_8S$	15.23 ± 0.29	83.99 ± 1.92	2.84 ± 0.23	2.68 ± 0.32	1.77 ± 1.89	1.51 ± 1.75	30.29	25.18	11.21	4.41
4-MDBT	$C_{13}H_{10}S$	21.22 ± 0.52	66.78 ± 1.64	9.07 ± 0.68	7.33 ± 0.88	4.71 ± 0.55	3.55 ± 0.41	32.39	26.86	19.81	11.39
4,6-DMDBT	$C_{14}H_{12}S$	10.95 ± 0.31	20.81 ± 0.35	10.30 ± 1.08	12.40 ± 1.03	11.57 ± 1.21	11.34 ± 1.09	22.91	29.28	15.31	8.25
2,4,6-TMDBT	$C_{15}H_{14}S$	4.34 ± 0.15	6.63 ± 0.24	13.37 ± 1.22	34.50 ± 2.94	27.69 ± 2.49	22.38 ± 2.23	28.08	42.40	27.20	18.56
Ph45T[g]	$C_{14}H_8S$	2.08 ± 0.13	3.03 ± 0.12	6.42 ± 0.75	22.39 ± 2.19	14.86 ± 1.78	11.68 ± 0.94	19.05	34.78	17.80	9.55
BN12T	$C_{16}H_{10}S$	ND	ND	0.99 ± 0.37	2.37 ± 0.36	4.09 ± 0.83	5.58 ± 0.63	1.89	3.22	5.54	7.68
BN21T	$C_{16}H_{10}S$	ND	ND	1.13 ± 0.25	2.87 ± 0.43	3.83 ± 0.75	5.11 ± 0.82	1.69	3.06	4.61	6.86
BN23T	$C_{16}H_{10}S$	ND	ND	0.95 ± 0.22	1.74 ± 0.31	2.23 ± 0.41	4.69 ± 0.76	1.50	2.98	4.33	6.49
Ph34T	$C_{16}H_{10}S$	ND	ND	ND	ND	ND	2.25 ± 0.50	ND	0.47	2.48	0.48
BPh9,10T	$C_{20}H_{12}S$	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.81
DiAT	$C_{24}H_{12}S$	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

[a] L or H indicates low- or high-sulfur diesel fuel was used; 0 through 75 is the engine load (kW). For both fuels (LSDF and HSDF) and DPM at LSDF, three sets of samples were collected and injected, but for DPM at HSDF only one set of samples was collected.

[b] The unit for concentration is μg S/g diesel fuel or μg S/g DPM.

[c] Total sulfur was calculated by integrating the entire sulfur response as one peak. Integration began where the sulfur emission line increased from baseline or at the beginning of the first peak (7 min for both diesel fuel and DPM). The final integration point was designated after the sulfur emission returned to baseline and remained stable (25 min for diesel fuel and 32 min for DPM). The standard temperature program indicated in Table 1 was used.

[d] ND (not detected) indicates result below the minimum detectable level (MDL). MDLs are based on results for a test mixture (Agilent part 8500-5067). The specification for sulfur 181 is 2 pg/s. The MDL for our laboratory was typically about 0.5 pg/s, or 1 pg S for a peak having a 2-s width (at half height).

[e] The coelution between 3- and 4-MBT may occur.

[f] The coelution between 5- and 6-MBT may occur.

[g] This peak is assigned as Ph45T based on the retention time of a standard compound. It is possible that this peak also contains a C_3-DBT because C_3-DBTs can also elute in this region. Currently, we do not have a C_3-DBT standard to examine this possibility.

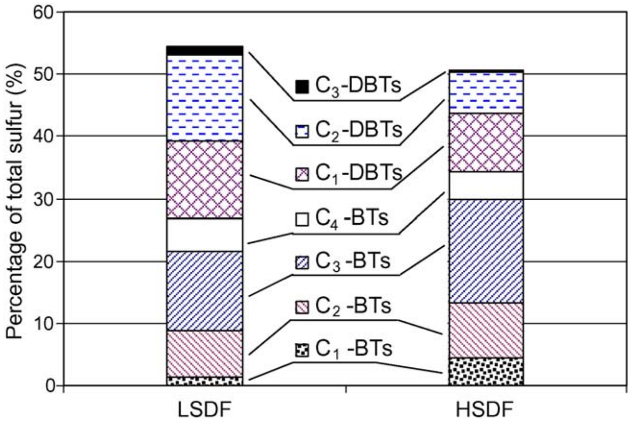

Fig. 5. Possible alkylated PASH groups in low- and high-sulfur diesel fuels (LSDF and HSDF, respectively).

for 5- and 6-MBT, which was reported by Depauw and Froment [20].

The chromatograms for both LSDF and HSDF indicate a large number of alkylated PASH isomers exist in the two fuels. Although we don't have standards for each of the peaks, an isomer grouping method can be used to categorize these compounds into several groups according to their retention times and other properties [6]. The following possible groups can be assigned based on this comparison: C_1-BTs (12.0–13.0 min), C_2-BTs (13.5-14.5 min), C_3-BTs (14.6–15.8 min), C_4-MBTs (16.8–17.2 min), C_1-DBTs (18.8–19.6 min), C_2-DBTs (19.6–20.9 min), and C_3-DBTs (21.0–22.0 min). These groups account for more than 50% of the total sulfur in diesel fuel, with C_2-DBTs as the largest fraction for LSDF and C_3-BTs for HSDF (Fig. 5). Compared to previously reported chromatograms [6] for crude oil, the grouping pattern of diesel fuel resembles the middle fraction of crude oil.

For most diesel fuels, the sulfur content is 0.01–0.5% by weight. Currently, the EPA is proposing stringent regulations for the sulfur content of diesel fuels. For highway diesel fuel, sulfur content will be reduced from 500 to 15 ppmv on June 1, 2006 [21]. For non-road applications, the current EPA regulation is 3400 ppmv, but it will be reduced to 500 ppmv in 2007 and further to 15 ppmv in 2010 [22]. As the total sulfur content of diesel fuel is reduced from high to low, the distribution of organosulfur compounds also changes, as illustrated in Fig. 6. In Fig. 6, the concentration was normalized by total sulfur content in diesel fuel, which is different from Table 4.

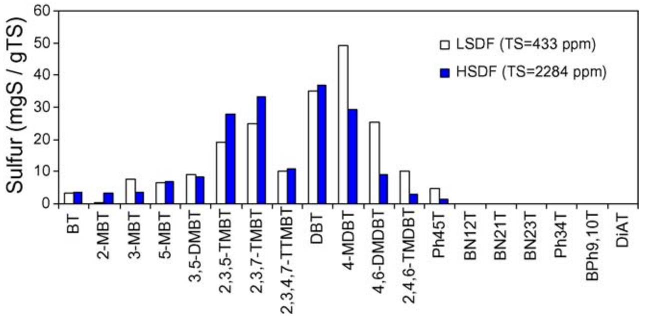

Fig. 6. PASH distribution in low- and high-sulfur diesel fuels (LSDF and HSDF, respectively).

The most abundant PASH species in both the low- and high-sulfur diesel fuels are DBT, 4-MDBT, 2,3,5-TMBT, and 2,3,7-TMBT. In LSDF, 4,6-DMDBT is also one of the major PASHs, whereas its relative abundance in HSDF is low. The concentrations of all the sulfur compounds are higher in HSDF than in LSDF, but the relative abundance of the compounds is different for the two fuels. In the HSDF, the relative abundance of the lighter compounds is higher, while in LSDF, the abundance of heavier compounds is higher (Fig. 6). Based on the chromatograms (Figs. 3 and 4), it also can be seen that there are some lighter sulfur compounds (presuming compounds with shorter retention time are relatively lighter compounds) that are major components of HSDF, which is not the case for LSDF. This is consistent with the results of desulfurization in that lighter compounds are more easily removed from the fuel [5,23]. It is also reasonable to expect that with the future fuel sulfur reduction, the organosulfur species remaining in the fuel will be more inclined toward the heavier (more than three rings) side.

3.3. PASHs in DPM

In diesel emissions, sulfur compounds exist in both gaseous and particulate fractions. Sulfur dioxide is a priority air pollutant regulated under the National Ambient Air Quality Standards. Sulfate (SO_4^{2-}) is thought to play an important role in fine particle formation and the nucleation of organic compounds, including polycyclic aromatic hydrocarbons (PAHs), reportedly through formation of heavy hydrocarbons from reaction between adsorbed sulfuric acid and organic compounds in the exhaust [24–26]. Gas-phase sulfur compounds (SO_2, SO_3) and particulate sulfate (SO_4^{2-}) in diesel exhaust have been investigated, but there have been limited studies on the organosulfur species in DPM and the influence of fuel sulfur on this fraction.

Sulfur 181 AED chromatograms for DPM extracts are shown in Figs. 7 and 8. The large humps in the chromatograms

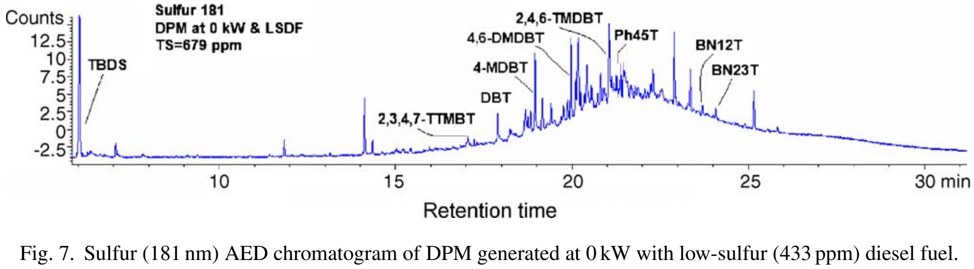

Fig. 7. Sulfur (181 nm) AED chromatogram of DPM generated at 0 kW with low-sulfur (433 ppm) diesel fuel.

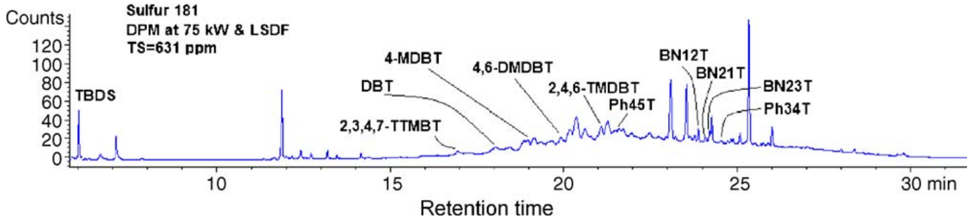

Fig. 8. Sulfur (181 nm) AED chromatogram of DPM generated at 75 kW with low-sulfur (433 ppm) diesel fuel.

(Figs. 7 and 8) represent a much more complex sulfur compound matrix than that of the diesel fuels. DBT, 4-MDBT and 4,6-DMDBT, which are abundant in diesel fuels, are still predominant in DPM under the low load conditions, but there are more high-molecular-weight sulfur compounds present in DPM, especially at the high load condition, which indicates that lighter sulfur compounds are more readily combusted and/or evaporate into the gas phase. Relative to diesel fuel (Fig. 6), the abundance of PASHs is shifted to heavier components. For DPM, most sulfur compounds present in diesel fuel are combusted/evaporate completely, e.g., MBTs and DMBTs. Some heavier PASHs, such as BN12T, BN21T, BN23T, Ph34T and BPh9,10T, appear to be generated during the combustion process. These larger PASHs may increase the toxicity of DPM, as some three-, and especially four- and five-ring species, are known to be mutagenic [27,28].

3.4. Total organic sulfur in DPM

Results for the total organic sulfur (TOS) in DPM emissions from LSDF and HSDF under different engine loads are shown in Fig. 9. As evidenced by these figures, fuel sulfur content has a significant effect on the concentrations of total organic sulfur and sulfur compounds in DPM. When fuel sulfur was increased from 433 to 2284 ppm, the total organic sulfur in DPM increased from 679 to 1585 ppm at 0 kW (Fig. 9). The effect of fuel sulfur on the DPM sulfur content is less dramatic at high load, increasing from 631 to 923 ppm at 75 kW (Fig. 9). As fuel sulfur was increased from 433 to 2284 ppm, the amount of individual compounds in DPM increased by two to nine times (Table 4). As reported, when fuel sulfur was reduced from 0.2 to 0.05%, a 7–12% reduction in particulate mass can be obtained [29]. Relative to DPM mass, the amount of sulfur compounds is much more affected by the change in fuel sulfur content.

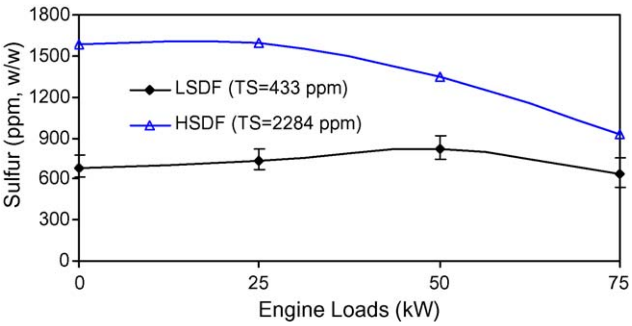

Fig. 9. Total organic sulfur in DPM generated under various loads.

3.5. Effect of fuel sulfur on DPM PASH distribution

The effect of fuel sulfur on the distribution of organosulfur in DPM is similar for each load condition for LSDF and HSDF. Fig. 10 shows the PASH distribution for DPM from different sulfur containing fuel. DPM at 25 and 75 kW are used as examples to illustrate that the general trend of PASH distribution varies less with loads than with the fuel sulfur content. In Fig. 10, the PASH concentration was normalized by total organic sulfur content in DPM. Fig. 10 indicates a significant influence on the distribution of sulfur compounds by fuel sulfur content. With low-sulfur diesel fuel, the distribution curves are sharp, with 2,4,6-TMDBT as the most abundant PASH. While for DPM from HSDF, the curves are broader (more uniformed distribution). In addition to 2,4,6-TMDBT, 4-MDBT, 4,6-DMDBT, 2,4,6-TMDBT, and Ph45T are all major PASH products. This distribution suggests that DPM generated from HSDF contains more PASHs with lower molecular weights relative to LSDF. The presence (Fig. 10) of heavier PASHs (i.e., BPh9,10T) was observed at maximum load in DPM from HSDF, but not from LSDF. This may indicate a greater possibility of forming higher molecular weight PASHs when the sulfur concentration is higher.

3.6. Effect of engine load on DPM PASH distribution

With both fuels, engine load affects the distribution of sulfur compounds. Although to a less extent, engine load can affect PASH distribution due to the variations in fuel usage rate, excess oxygen and combustion temperature, etc. at each load. In the chromatograms (Figs. 7 and 8), an obvious shift to heavier sulfur compounds is observed at high load, with most of the lighter compounds being absent. Fig. 11 illustrates three different types of PASH distributions in DPM as load is increased from 0 to 75 kW.

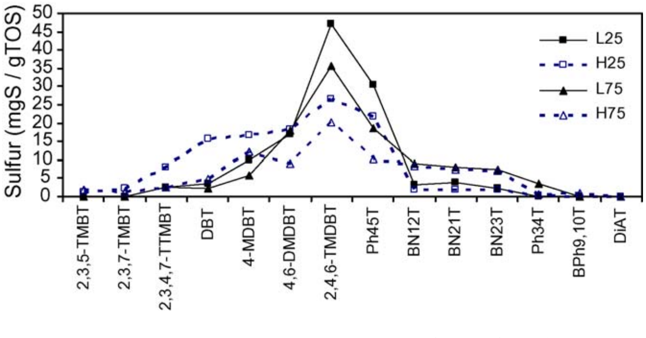

Fig. 10. Organosulfur distribution in DPM under 25 and 75 kW for LSDF (L) and HSDF (H).

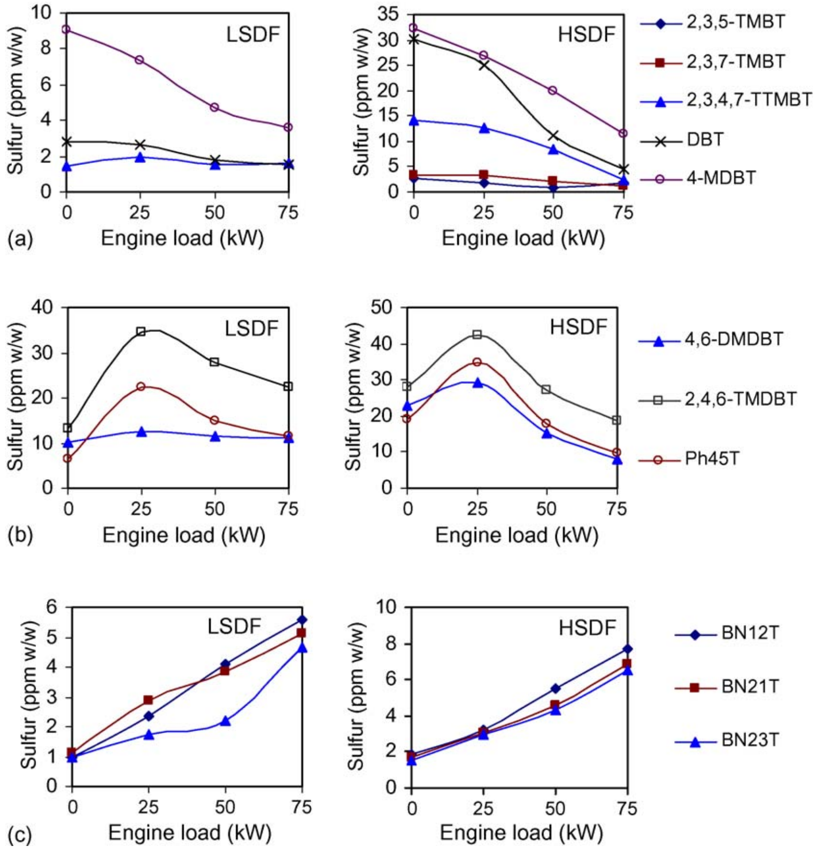

Fig. 11. PASH distribution in DPM generated with LSDF and HSDF under different engine loads: (a) decreasing with load, (b) bell-shaped distribution, (c) increasing with load.

For PASHs with lower molecular weights, such as 2,3,5-TMBT, 2,3,7-TMBT, 2,3,4,7-TTMBT, DBT, and 4-MDBT (2,3,5-TMBT and 2,3,7-TMBT were not found in DPM from LSDF), the concentration was reduced as load increased (Fig. 11a). These PASHs also are present in diesel fuels. As the load was increased, the fuel input increased, which should result in a concentration increase for these lighter PASHs. However, as load increased, the combustion temperature also increased and a greater fraction of the lighter sulfur compounds was completely burned and converted to SO_2 and SO_3. As a result, a lower amount of these PASHs remained in the particulate fraction.

For higher molecular weight PASHs, which include BN12T, BN21T, BN23T, Ph34T and BPh9,10T, the concentration increased with load (Fig. 11c). These heavier PASHs were not present in diesel fuels and are possibly formed during combustion. As the load increased, so did the combustion temperature and fuel input, which may promote the formation of higher molecular weight PASHs.

For intermediate molecular weight PASHs such as 4,6-DMDBT, 2,4,6-TMDBT and Ph45T, a bell-shaped distribution was observed (Fig. 11b). As load was increased from 0 to 75 kW, the concentration first increased and then decreased, with the highest concentration observed at approximately 25 kW. These compounds are present in diesel fuels, and this distribution may be the result of competition between the increase in fuel input and combustion decomposition. As load increased, more fuel input led to a larger amount of PASHs in the DPM, while the increased combustion decomposition lowered the PASH concentration. The combination of both effects resulted in the distribution shown in Fig. 11b.

4. Summary and conclusions

PASHs in LSDF and HSDF and the corresponding DPM emissions were determined by GC/AED. Results for calibration standards and fuels indicated the sulfur response factor in this application is relatively independent of analyte structure. As expected, the PASH concentration and distribution in diesel fuels depends on the sulfur content. The most abundant sulfur species are DBT, C_1-DBTs, and C_3-BTs in both diesel fuels. In low-sulfur diesel fuel, heavier PASHs such as DMDBT are also higher in concentration, which indicates the LSDF contains a larger fraction of heavier components than the HSDF.

Relative to diesel fuels, the most abundant PASHs in DPM were shifted to higher molecular weight compounds. Some heavier PASHs (e.g., BNTs) not found in diesel fuels are present in DPM and are more hazardous. The total organic sulfur and PASH concentration and distribution in DPM are affected by both fuel sulfur and engine load. Higher fuel sulfur led to the following two consequences: higher total organic sulfur in DPM and more PASHs with lower molecular weights in DPM. Engine load is an important factor affecting PASH distribution. With engine load increases, the dominant PASH species in DPM shift to higher molecular weight. Three types of distributions were observed as the engine load was increased from 0 to 75 kW. The concentrations decreased for lighter PASHs and increased for heavier PASHs as load was increased from 0 to 75 kW. For intermediate molecular weight PASHs, a bell-shaped distribution was observed, with the highest concentrations at 25 kW.

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