Qualitative and quantitative analysis of dibenzothiophene, its methylated homologues, and benzonaphthothiophenes in crude oils, coal, and sediment extracts

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ABSTRACT

Polycyclic aromatic sulfur heterocyclics (PASHs) consist mainly of thiophene class compounds, and are the most important organosulfur compounds in crude oils and sediment extracts. Dibenzothiophene (DBT) and its methylated homologues were identified on mass chromatograms by comparison with retention indices published in the literature. Some isomers of dimethyldibenzothiophene and trimethyldibenzothiophene that were tentatively identified in previous reports have been determined here by comparison with calculated retention indices and taking the substitution pattern of the methyl groups into account. The response factors relating that of dibenzothiophene to internal standards were obtained by GC–MS analyses of mixture solutions with different concentration ratios. We concluded that DBT-d8 (octadeutero-dibenzothiophene) is the optimal internal standard for quantitative analyses of the thiophene compound class in oils, coal, and sediment extracts. Calibration experiments for each class of compounds are absolutely necessary when quantifying polycyclic aromatic hydrocarbons and other heterocyclics with a stable isotope labeled internal standard.

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1. Introduction

Except for carbon and hydrogen, sulfur is the most important element in crude oils and ancient sediment extracts. One of the main forms of organosulfur compounds in crude oils is the thiophene moiety where sulfur is incorporated into polycyclic aromatic hydrocarbons (PAHs) to form sulfur heterocycles (PASHs), including benzothiophene (BT), dibenzothiophene (DBT), benzonaphthothiophenes (BNT) and their alkylated homologous series (Fig. 1).

Due to their detrimental effect on the performance of catalysts used during the refining of petroleum, the risk of metal corrosion during the production, transportation and processing of crude oil, and air pollution caused by fossil fuels or emissions after combustion [1], much effort has been expended for the desulfurization of PASHs [2,3]. Furthermore, PASHs have been tested for mutagenicity in the Ames test, and some of them, especially the benzo[b]phenanthro[4,5-bcd]thiophene, were found to exhibit high activities [4].

1.1. Occurrence of PASHs

PASHs have also been applied as important molecular markers in geochemistry and petroleum exploration. Due to the diverse molecular thermodynamic stability of the alkyl substituents at different positions of the DBT carbon skeleton [5,6], the DBTs-related molecular markers have been used by most researchers mainly as maturity indicators [5–13]. In addition, the occurrence and distribution of DBTs are also dependent on source rock and/or sediment types [5,9,12,14–18]. More recently, researchers found that the absolute concentrations of DBTs and the relative abundances of the different isomers of methyl DBTs in petroleum are also controlled by migration processes [19,20]. They are therefore potential molecular parameters to indicate the petroleum migration distances and filling pathways [19,20].

Two methyldibenzothiophene isomers (MDBTs), i.e. 1- and 4-MDBT, were identified by gas chromatography-flame photometric detection (GC-FPD) and gas chromatography–mass spectrometry (GC–MS) [14,15]. Also, three dimethyldibenzothiophene isomers (DMDBTs), i.e. 1,4-, 2,4- and 4,6-DMDBT, have been confirmed by co-injection of synthetic standards in the GC–MS analysis

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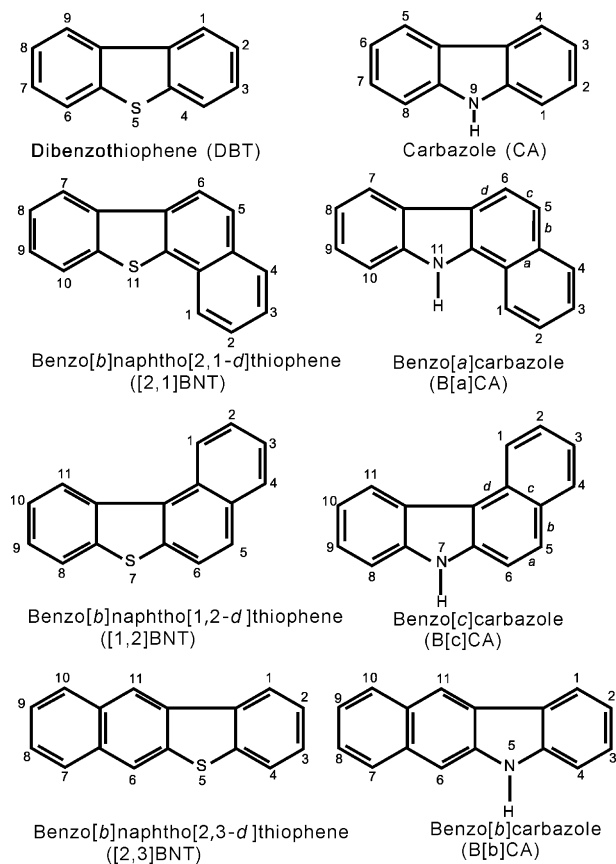
Fig. 1. Structures of aromatic thiophenes and carbazoles discussed in the text.

of aromatic fractions [5,9]. The tentative identification of other DMDBTs in crude oil and ancient sedimentary organic matter has been reported [21]. Due to essentially identical mass spectra of all isomers, a lack of co-injection standards or systemic correlation with gas chromatographic retention indices, the methyl positions of each DMDBT isomer have not been definitely confirmed. Five trimethyldibenzothiophenes (TMDBTs) have tentatively been detected in m/z 226 mass chromatograms [9]. However, their exact chemical structures, i.e. the specific positions of the three methyl groups, have not yet been determined. Up to now, the identification and application of tetramethyldibenzothiophenes (TeMDBTs) in crude oils and ancient sediment extracts have not been reported. The occurrence and distribution of benzonaphthothiophenes (BNTs) have been reported, especially in the case of microbial degradation of PASHs in the environment [22], but up to now, their identification and significance in petroleum geochemistry have not been reported.

Mössner et al. [23] discussed the retention behavior of PASHs on GC columns with different stationary phases. Recently, Schade and Andersson [24] specified a series alkylated dibenzothiophenes by correlation of structure and GC retention indices. This approach provides a feasible way to identify more isomers of PASHs without additional internal reference standards.

1.2. Origin of PASHs

The origin of PASHs in oil and sedimentary organic matter remains one of the primary issues in the organic geochemistry of organosulfur compounds. The BT, DBT and BNT series do not have obvious biological precursors. Due to the insufficient amount of sulfur in organic material from biota to produce the large amounts of sulfur compounds in petroleums, researchers proposed

that a thermal reaction between elemental sulfur and the organic material of a sediment may be responsible for the genesis of the sulfur-containing compounds [25,26].

Thiophene derivatives such as 2,4-diphenylthiophene and phenylbenzothiophenes can be produced from the reaction of ethylbenzene and sulfur under mild thermal conditions [27]. Xia et al. [28] synthesized DBT series from biphenyls in the presence of sulfur through simulation experiments. Other simulation experiments [21] have shown that biphenyl and sulfur can form dibenzothiophene. Similarly, methyl substituted biphenyls reacted to yield the corresponding methyl DBTs. It was suggested that the widespread distribution of dibenzothiophene and alkylated DBTs in sediments and crude oils is the result of a catalytic reaction between biphenyl ring systems and surface-adsorbed sulfur on carbonaceous material [21]. This mechanism was also supported by the geochemical relationship between the isomer distributions of methyl substituted biphenyls and DBTs in crude oils and sediment extracts. Laboratory experiments showed that the BNTs can be formed microbially from benzo[b]thiophenes with *Pseudomonas* [22]. The origin of BNTs in oils, coals and rock extracts, however, has not yet been reported.

1.3. Quantification of PASHs

Quantification of PASHs in oils and sediment extracts has mainly been carried out by comparison of peak areas on mass chromatograms of selected ions in GC–MS with those of authentic standards. Grimmer et al. [29] added 10 μg of picene (molecular formula: $C_{22}H_{14}$; molecular mass: 278.35) as internal standard prior to GC–MS analysis to quantify all PAHs, BTs, DBTs, BNTs, and carbazoles (including the parent compounds and their alkylated homologous series). Other individual PAHs, such as 1,1′-binaphthyl (molecular formula: $C_{20}H_{14}$; molecular mass: 254.33), were also used in the quantitative analyses of PAHs [30]. However, individual perdeuterated PAHs, e.g. phenanthrene-d10 or anthracene-d10 are common internal standards for the quantitative analysis of PAHs and PASHs [21,31,32].

The use of internal standards can yield more accurate quantitative results compared to the external standard strategy. The best internal standards are chemically similar to the target compounds; thus, any loss of the target compound during the analytical procedure is replicated by the loss of internal standard, so it is a self-correcting system [33]. Homologues of an analyte can be used as internal standards, but the best internal standards are isotopically labeled versions of the analyte. Because the oils and sediment extracts contain mixtures of various BT, DBT, BNT and their alkylated homologues, the best internal standard may be DBT substituted with eight deuteriums (dibenzothiophene-d8).

In this paper we identify the series of MDBTs, DMDBTs, TMDBTs, TeMDBTs and BNTs in crude oils, coal and sediment extracts by correlations with retention indices (I_S and I_C) and comparison with co-injections of internal standards in GC–MS analyses. Furthermore, we report the quantitative analysis of PASHs in oils using dibenzothiophene-d8 as an internal standard, and compare the distribution patters of DBTs in oils, coal and sediment extracts.

2. Experimental

All oils (derived from carbonate and lacustrine shale, respectively), coal (semi-bituminous) and sediment (lacustrine shale) extracts were treated with following analytical procedure. Coal and sediment samples (lacustrine shale) ($\approx$80 g) were crushed and extracted for 24 h using a Soxhlet apparatus with 400 ml of dichloromethane and methanol (93:7, v:v) to obtain soluble bitumen. The extracts and oils were deasphaltened using

n-hexane and then fractionated by liquid chromatography using silica gel/alumina columns into saturated and aromatic hydrocarbon fractions using n-hexane with dichloromethane (50:50, v:v) and dichloromethane as respective eluents.

In order to obtain a response factor relating the response of the unlabeled compound to the labeled compound, we must determine a response factor for the internal standard dibenzothiophene-d8 (DBT-d8; molecular formula: $C_{12}D_8S$; molecular mass: 192.31; Purity = 99.5%, Laboratory of Dr. Ehrenstorfer, Augsburg, Germany) against a known amount of unlabeled DBT (molecular formula: $C_{12}H_8S$; molecular mass: 184.26; purity = 98%; Sigma Aldrich) and 4,6-DMDBT (molecular formula: $C_{14}H_{12}S$; molecular mass: 212.31; purity = 97%; Sigma Aldrich). A series of standard mixture solutions of DBT and DBT-d8, and 4,6-DMDBT and DBT-d8 with different concentration ratios were prepared for GC–MS analysis.

A known amount of DBT-d8 internal standard was added to each sample prior to GC–MS analysis. The peak of $C_{12}D_8S$ can be identified in the m/z 192 mass chromatograms, eluting just before the four methylphenanthrene peaks (Fig. 2). The absolute concentrations of DBT can be calculated by using a response factor based on calibration solutions and the peak areas of labeled DBT and unlabeled DBT. Those of alkylated DBTs can also be calculated by using a response factor based on calibration solutions and the peak areas of labeled DBT and unlabeled 4,6-DMDBT.

The GC–MS analyses of the aromatic hydrocarbon fractions and mixture solutions were performed on an Agilent 5975i GC–MS system equipped with an HP-5 MS (5%-phenylmethylpolysiloxane) fused silica capillary column (60 m × 0.32 mm i.d., with a 0.25 μm film thickness). The GC operating conditions were as follows: the temperature was held initially at 80 °C for 1 min, ramped to 310 °C at 3 °C/min, and then kept isothermal for 16 min. Helium was used as the carrier gas. The injector temperature was set to 300 °C. The MS was operated in the electron impact (EI) mode with an ionization energy of 70 eV, and a scan range of 50–600 Da.

3. Results and discussion

3.1. Identification of methyl- and dimethyldibenzothiophene isomers

The commonly used retention index system (designated as I_C by [24]) for temperature programmed GC conditions for polycyclic aromatic compounds is based on a series of aromatic hydrocarbon retention markers (benzene, naphthalene, phenanthrene, chrysene and picene) with different numbers of aromatic rings [34].

Schade and Andersson [24] proposed an alternate retention index system (I_S) based on sulfur-containing aromatic compounds. The I_S values are based on the retention markers thiophene (I_S = 100.00, one ring), benzothiophene (I_S = 100.00, two rings), dibenzothiophene (300.00, three rings), benzo[b]naphtho[2,1-d]thiophene (400.00, four rings), and benzophenanthro[2,1-d]thiophene (500.00, five rings). The I values for both systems are calculated using the following equation:

$$I = 100 \times \frac{(t_{Rx} - t_{Rz})}{(t_{Rz+1} - t_{Rz})} + 100 \times z \qquad (1)$$

where t_R is the retention time, x is the target compound, and z and $z + 1$ are the number of aromatic rings in the retention marker compounds eluting immediately before and after the target compound [24].

For methyldibenzothiophenes, z is 3, and t_{Rz} is the retention time of DBT and phenanthrene (Phen). For example, for the coal sample in this study, t_{Rz} is 40.976 and 41.874 for DBT and Phen, respectively, and t_{Rz+1} the retention time of benzo[b]naphtho[2,1-d]thiophene ([2,1]BNT) and chrysene, is 60.431 and 62.517, respectively (Table 1 and Fig. 3). The I_S and I_C of a coal sample from
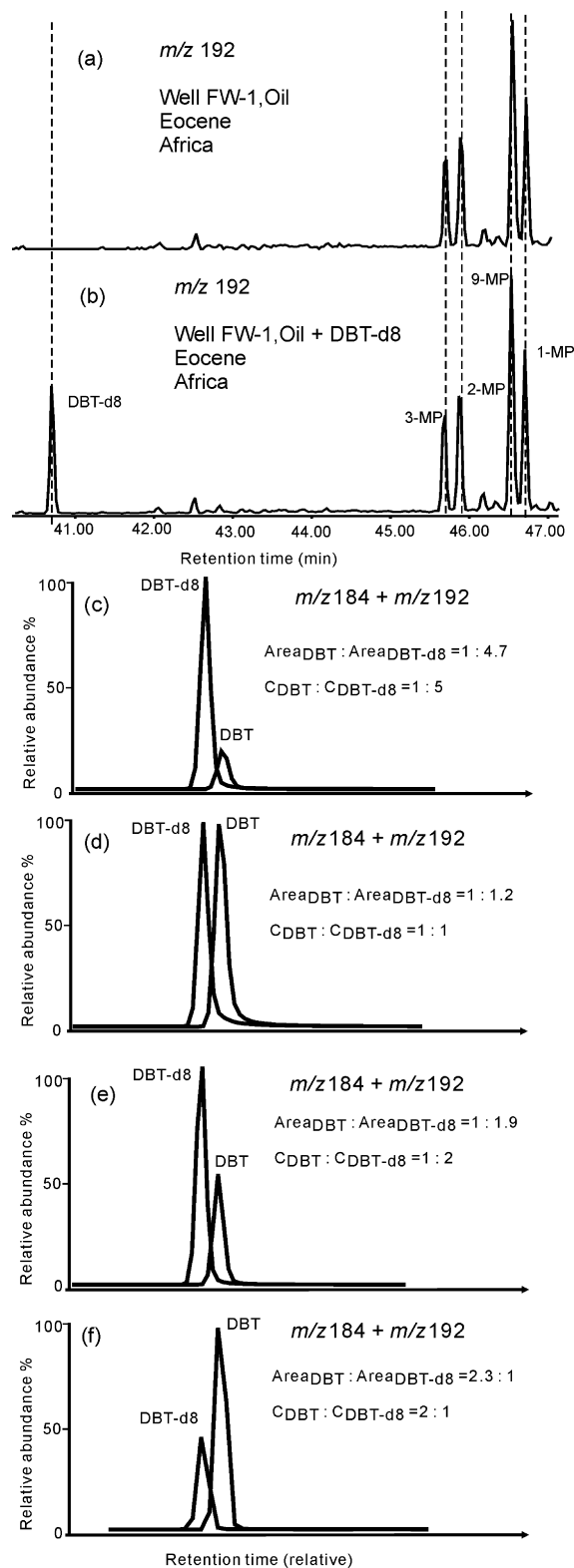
Fig. 2. Correlation of m/z 192 mass chromatograms of the aromatic fraction of an oil for (a) without and (b) with co-injection of the internal standard DBT-d8; (c) and (d): mass chromatograms of m/z 184 and m/z 192 showing the relative peak intensities of DBT and DBT-d8 for different concentration ratios. Area$_{DBT}$: the peak area of DBT in m/z 184 mass chromatogram; Area$_{DBT-d8}$: the peak area of DBT-d8 in m/z 192; C_{DBT}, C_{DBT-d8}: concentrations of DBT and DBT-d8 in their mixture solutions.

Table 1
Comparison of calculated indices for methyl DBTs in oils, coal and sediment extract with those in the literature.

No.	Ref. [24]		Coal extract			Identification	Well SG1,Lacustrine shale			Identification	Well TP10CX, Oil, Marine carbonate, Tarim Basin			Identification	Well Dugu32, Oil, Lacustrine shale, Liaohe Basin			Identification
	I_S	I_c	t_R	I'_S	I'_c		t_R	I'_S	I'_c		t_R	I'_S	I'_c		t_R	I'_S	I'_c	
	Naph		200.00			200.00		18.637		200.00		17.918		200.00		17.810		200.00	
	Phen		300.00	41.874		300.00		42.409		300.00		41.509		300.00		41.504		300.00	
	DBT	300.00	295.81[a] 296.01[b]	40.976	300.00			41.383	300.00	295.69	DBT	40.541	300.00	295.90	DBT	40.544	300.00	295.96	DBT
1	4-M	317.67	311.92	44.492	318.07	312.68	4-M	44.861	317.85	311.90	4M-	44.072	318.10	312.40	4-M	44.041	317.95	312.29	4M-
2	2-M	321.13	315.11	45.177	321.59	316.00	2-+3-M	45.500	321.13	315.00	2-M	44.742	321.53	315.64	2-+3-M	44.723	321.45	315.62	2-+3-M
3	3-M	321.65	315.51					45.558	321.43	315.28	3-M								
4	1-M	324.87	318.65	45.869	325.15	319.35	1-M	46.351	325.50	319.13	1-M	45.521	325.53	319.41	1-M	45.515	325.51	319.47	1-M
5	4-E	333.06	326.52	47.445	333.25	326.99	4-E	47.911	333.51	326.70	4-E	47.105	333.65	327.07	4-E	47.093	333.61	327.12	4-E
6	4,6-DM	334.25	327.55	47.766	334.90	328.54	4,6-DM	48.184	334.91	328.03	4,6-DM	47.394	335.13	328.47	4,6-DM	47.376	335.07	328.50	4,6-DM
7	2,4-DM	337.76	329.92	48.201	337.14	330.65	2,4-DM	48.628	337.19	330.18	2,4-DM	47.837	337.40	330.62	2,4-DM	47.824	337.37	330.67	2,4-DM
8	2,6-DM	337.36 338.26[b]	330.12 331.28[c]	48.377	338.04	331.50	2,6-DM	48.802	338.08	331.02	2,6-DM	48.019	338.33	331.50	2,6-DM	47.990	338.22	331.48	2,6-DM
9	3,6-DM	337.99 338.38[b]	330.69 331.49[c]	48.494	338.64	332.07	3,6-DM	48.895	338.56	331.48	3,6-DM	48.113	338.81	331.95	3,6-DM	48.069	338.62	331.86	3,6-DM
10	2,8-DM	341.08	333.19	48.920	340.83	334.13	2,8-DM	49.372	341.00	333.79	2,8-DM					48.561	341.15	334.25	2,8-DM
11	2,7-DM	341.13	333.15																
12	3,7-DM	341.20	333.38	49.044	341.47	334.73	2,7-+3,7-DM	49.480	341.56	334.32	2,7-+3,7-DM	48.688	341.76	334.73	2,8-+2,7-+3,7-DM	48.663	341.67	334.74	2,7-+3,7-DM
13	1,6-DM	340.81[c] 339.74[d]	333.71[d] 332.80[e]																
14	1,4-DM	341.85	334.66	49.265	342.61	335.80	1,6-+1,4-DM	49.706	342.72	335.41	1,6-+1,4-DM	48.916	342.93	335.84	1,6-+1,4-DM	48.883	342.80	335.81	1,6-+1,4-DM
15	1,8-DM	343.79 342.8[b]	336.47 335.65[c]																
16	1,3-DM	343.98	336.55																
17	3,4-DM	344.00	336.34	49.672	344.70	337.78	1,3-+3,4-DM	50.125	344.87	337.45	1,3-+3,4-DM	49.324	345.02	337.81	1,3-+3,4-DM	49.315	345.02	337.91	1,3-+3,4-DM
18	1,7-DM	344.59	337.21	49.786	345.28	338.33	1,7-DM	50.262	345.57	338.11	1,7-DM	49.457	345.70	338.45	1,7-DM	49.445	345.69	338.54	1,7-DM
19	2,3-DM	347.11	339.70																
20	1,9-DM	347.24 346.79[b]	340.04 339.49[c]	50.184	347.33	340.26	2,3-+1,9-DM	50.647	347.55	339.98	2,3-+1,9-DM	49.851	347.72	340.36	2,3-+1,9-DM	49.843	347.73	340.47	2,3-+1,9-DM
21	1,2-DM	349.57[c] 348.92[d]	342.05[d] 341.29[e]	50.536	349.14	341.96	1,2-DM	51.010	349.41	341.74	1,2-DM	50.223	349.63	342.16	1,2-DM	50.191	349.51	342.16	1,2-DM
22	4-E-6-M	347.65	340.21	50.270	347.77	340.67	4-E,6-M	50.746	348.06	340.46	4E,6M-TM	49.937	348.16	340.78	4-E,6-M	49.938	348.22	340.93	4E,6M-TM
23	2,4,6-TM	352.47	344.63	51.330	353.22	345.81	2,4,6-TM	51.787	353.40	345.51	2,4,6-TM	50.998	353.60	345.91	2,4,6-TM	50.978	353.55	345.98	2,4,6-TM
24	2,4,8-TM	355.94	347.99	51.873	356.01	348.44	2,4,8-+2,4,7-TM	52.336	356.22	348.18	2,4,8-+2,4,7-TM	51.561	356.49	348.63	2,4,8-+2,4,7-TM	51.530	356.39	348.66	2,4,8-+2,4,7-TM
25	2,4,7-TM	356.00	347.99																
26	1,4,6-TM	357.31	349.02	52.000	356.66	349.05	1,4,6-TM	52.461	356.86	348.78	1,4,6-TM	51.673	357.06	349.18	1,4,6-TM	51.648	356.99	349.23	1,4,6-TM
27	1,4,8-TM	357.91	349.83	52.300	358.21	350.51	1,4,8-TM	52.774	358.47	350.30	1,4,6-TM	51.953	358.50	350.53	1,4,8-TM	51.980	358.70	350.84	1,4,8-TM
28	3,4,6-TM	359.42	350.52	52.389	358.66	350.94	3,4,6-TM	52.873	358.97	350.78	1,4,8-TM	52.077	359.13	351.13	3,4,6-TM	52.054	359.08	351.20	3,4,6-TM
29	1,4,7-TM	360.82	352.62	52.788	360.71	352.87	1,4,7-TM	53.185	360.58	352.30	1,4,8-TM	52.484	361.22	353.10	1,4,7-TM	52.421	360.96	352.98	1,4,7-TM
30	2,6,7-TM	361.96	352.91	52.932	361.45	353.57	2,6,7-TM	53.344	361.39	353.07	1,2,6-TM	52.577	361.70	353.55	2,6,7-TM	52.574	361.75	353.72	2,6,7-TM
31	1,3,7-TM	362.64	354.34	53.338	363.54	355.53		53.701	363.22	354.80	3,4,6-TM	53.017	363.95	355.68	1,3,7-TM				
32	3,4,7-TM	363.49	354.95	53.378	363.75	355.73	3,4,7-TM	53.806	363.76	355.31	3,4,7-TM	53.105	364.40	356.10	3,4,7-TM	52.997	363.92	355.78	1,3,7-+3,4,7-TM
33	1,2,6-TM	364.85[c]	356.48[d]					54.053	365.03	356.51	1,2,6-+2,3,8-TM								
34	2,3,8-TM	365.02[c]	356.22[d]																
35	2,3,7-TM	365.65[c]	356.78[d]	53.811	365.97	357.83	2,3,7-TM	54.400	366.81	358.19	2,3,7-TM[d]	53.510	366.48	358.06	2,3,7-TM	53.497	366.48	358.20	2,3,7-TM
36	1,2,4-TM	365.77	357.30	53.817	366.00	357.85	1,2,4-TM	54.454	367.09	358.45	1,2,4-TM	53.565	366.76	358.33	1,2,4-TM	53.560	366.81	358.51	1,2,4-TM

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Table 1 (Continued)

No.	Ref. [24]		Coal extract				Well SG1,Lacustrine shale				Well TP10CX, Marine carbonate, Tarim Basin				Well Dugu32, Oil, Lacustrine shale, Liaohe Basin			
	I_S	I_C	t_R	I_S	I_C	Identification	t_R	I_S	I_C	Identification	t_R	I_S	I_C	Identification	t_R	I_S	I_C	Identification
37 1,2,8-TM	367.83[c]	359.24[d]	54.206	368.00	359.74	1,2,8- + 1,2,-TM	54.695	368.33	359.62	1,2,8- + 1,2,7-TM	53.873	368.34	359.82	1,2,8- + 1,2,7-TM	53.763	367.85	359.49	1,2,8- + 1,2,-TM
38 1,2,7-TM	368.46[c]	359.80[d]																
39 4,6-DE	360.94	352.57					53.260	360.96	352.66	4,6-DE				4,6-DE				
40 6-E-2,4-DM	364.65	356.14	53.519	364.47	356.41	6-E,2,4-DM	54.111	365.33	356.79	6-E,2,4-DM	53.202	364.90	356.57	6-E,2,4-DM	53.197	364.94	356.75	6-E,2,4-DM
41 2,4,6,8-TeM	368.33	359.69	54.326	368.62	360.32	2,4,6,8-TeM	54.859	369.17	360.42	2,4,6,8-TeM	54.060	369.30	360.72	2,4,6,8-TeM	54.033	369.23	360.80	2,4,6,8-TeM
42 1,4,6,8-TeM	371.15	362.34	54.673	370.40	362.00	1,4,6,8-TeM	55.150	370.66	361.83	1,4,6,8-TeM	54.389	370.99	362.32	1,4,6,8-TeM	54.364	370.93	362.41	1,4,6,8-TeM
43 2,4,6,7-TeM	375.36	366.40	55.758	375.98	367.26	2,4,6,7-TeM	56.030	375.18	366.10	2,4,6,7-TeM	55.405	376.19	367.23	2,4,6,7-TeM	55.250	375.48	366.71	2,4,6,7-TeM
44 1,3,6,7-TeM	383.16	373.77	57.143	383.10	373.97	1,3,6,7-TeM	57.330	381.85	372.41	1,3,6,7-TeM	56.844	383.57	374.19	1,3,6,7-TeM	56.829	383.59	374.37	1,3,6,7-TeM
45 2,3,7,8-TeM	388.72	378.95	58.058	387.80	378.40	2,3,7,8-TeM					57.764	388.20	378.64		57.750	388.31	378.84	2,3,7,8-TeM
[2,1]BNT	400.00	389.37[b]	60.431	400.00	389.89	[2,1]BNT	60.866	400.00	389.57	[2,1]BNT	60.049	400.00	389.70	[2,1]BNT	60.028	400.00	389.90	[2,1]BNT
[1,2]BNT		392.92[b]	61.045		392.87	[1,2]BNT	61.543		392.86	[1,2]BNT	60.743		393.01	[1,2]BNT	60.507		392.26	[1,2]BNT
[2,3]BNT		395.97[b]	61.638		395.74	[2,3]BNT					61.329		395.89	[2,3]BNT				
Chysene		400.00	62.517		400.00		63.015		400.00		62.178		400.00		62.152		400.00	

Note. n.d., no data. Compounds in the table: Naph, naphthalene; Phen, phenanthrene; DBT, dibenzothiophene; [21]BNT, benzo[b]naphtho[2,1-d]thiophene; 4-M, 4-methyldibenzothiophene; 4,6-DM, 4,6-dimethyldibenzothiophene; 2,4,6-TM, 2,4,6-trimethyldibenzothiophene; 2,4,6,8-TeM, 2,4,6,8-tetramethyldibenzothiophene; 4-E, 4-ethyldibenzothiophene; 4-E-6-M, 4-ethyl-6-methyldibenzothiophene; 4,6-DE, 4,6-diethyldibenzothiophene; 6-E-2,4-DM, 6-ethyl-2,4-dimethyldibenzothiophene.

[a] Retention indices by Lee et al. [35].
[b] Retention indices by Vassilaros et al. [37].
[c] Retention indices measured by Schade and Andersson [24].
[d] Retention indices calculated with Eq. (2).
[e] Retention indices by Mössner et al. [23].

China, an oil and sediment extract from the Liaohe Basin, East China, and an oil sample from the Tarim Basin, Northwest China are listed in Table 1.

Dibenzothiophene can be identified in the mass chromatograms of m/z 184 by comparison of the mass spectrum with that in the NIST or Wiley library of the GC–MS data analysis system, and by comparison of the retention time of DBT standard and retention indices published in the literature [35].

Four compounds can be detected clearly in the mass chromatogram of m/z 198 (Fig. 3b) as 4-methyldibenzothiophene (4-MDBT), 2-MDBT, 3-MDBT and 1-MDBT. Both the values of I_S and I_C of 4-MDBT and 1-MDBT (Table 1) for all samples are similar to those in the literature [24]. These two MDBT isomers have also been identified by co-injection of authentic standards [14]. However, 2-MDBT and 3-MDBT cannot be distinguished based on the minor differences in I_S and I_C of these isomers (the difference is 0.52 and 0.40 for I_S and I_C, respectively, Table 1). However, by comparison of the I_S and I_C values with relative retention times from the literature [9,11], the MDBT isomers can be assigned.

Three dimethyldibenzothiophene isomers (DMDBTs) were identified by co-injection with authentic standards of 4,6-DMDBT, 2,4-DMDBT and 1,4-DMDBT [9]. Other DMDBT isomers (Fig. 4b) were also tentatively identified later [21]. Overall, 4-ethyldibenzothiophene, 4,6-DMDBT and 2,4-DMDBT can be determined in the m/z 212 mass chromatogram without doubt by comparison with the I_S and I_C values and relative retention times in prior literature [21,23]. By comparing the relative retention times in Fig. 4a and f, the compound eluting at 49.044 min for the coal sample of this study is 3,7-DMDBT. The I_S and I_C were also calculated based on Eq. (1) to be 341.47 and 334.73, respectively, consistent with the literature values [24]. However, the I_S and I_C values for 2,7- and 3,7-DMDBT are quite close, with a difference of only 0.07 and 0.23, respectively (Table 1). Thus, they may co-elute in the mass chromatogram. In the mass chromatogram of the oil sample from Tarim Basin, 2,8-DMDBT may co-elute with 2,7- and 3,7-DMDBT (Fig. 4 c), which was confirmed by Mössner et al. [23] in the GC–MS separation experiment of fifteen DMDBT isomers. Thus, 2,8-DMDBT and 2,7-DMDBT cannot be excluded in the peak of 3,7-DMDBT.

According to Asif et al. [21] and Mössner et al. [23], the peak with a retention time of 49.265 min is a mixture of 1,4-, 1,6- and 1,8-DMDBT. But in other reports, it was identified as only 1,4-DMDBT [9,11]. In the oil and coal samples of our study, we report this peak as 1,4- and 1,6-DMDBT (Fig. 4c–f). It is very important to correctly identify this compound, because the 2,4-/1,4-DMDBT and 4,6-/1,4-DMDBT ratios [9] are used as geochemical parameters to assess the thermal maturity of oils or sedimentary organic matter in petroleum geochemistry. However, the indices (I_S and I_C) of the 1,6-DMDBT isomer were not reported in the overview of Schade and Andersson [24].

By using the multiple linear regression (MLR) method, Schade and Andersson [24] proposed an equation to calculate the retention index and provided a set of coefficients describing the contributions from the molecular features.

$$I = 300.00 + \alpha_0 + \alpha_{19}n_{19} + \alpha_{28}n_{28} + \alpha_{37}n_{37} + \alpha_{46}n_{46} + \alpha_{or}n_{or}$$
$$+ \alpha_{me}n_{me} + \alpha_{pa}n_{pa} \tag{2}$$

where 300 is the I_S of dibenzothiophene by definition; α_0 is the column intercept, which is 3.83 for HP-5 MS; α_{ij} is the regression coefficient, which is 21.70 for α_{19}, and 15.28 for α_{46}, respectively; and n_{ij} is the number of methyl groups in the positions i or j. For 1,6-DMDBT, both n_1 and n_6 are 1. n_{or} is the number of *ortho*, n_{me} the number of *meta*- and n_{pa} the number of *para* substitutions. For 1,6-DMDBT, n_{or}, n_{me} or n_p is zero because there is no *ortho*-, *meta*- or *para*- substitution in this molecule. By using this equation and
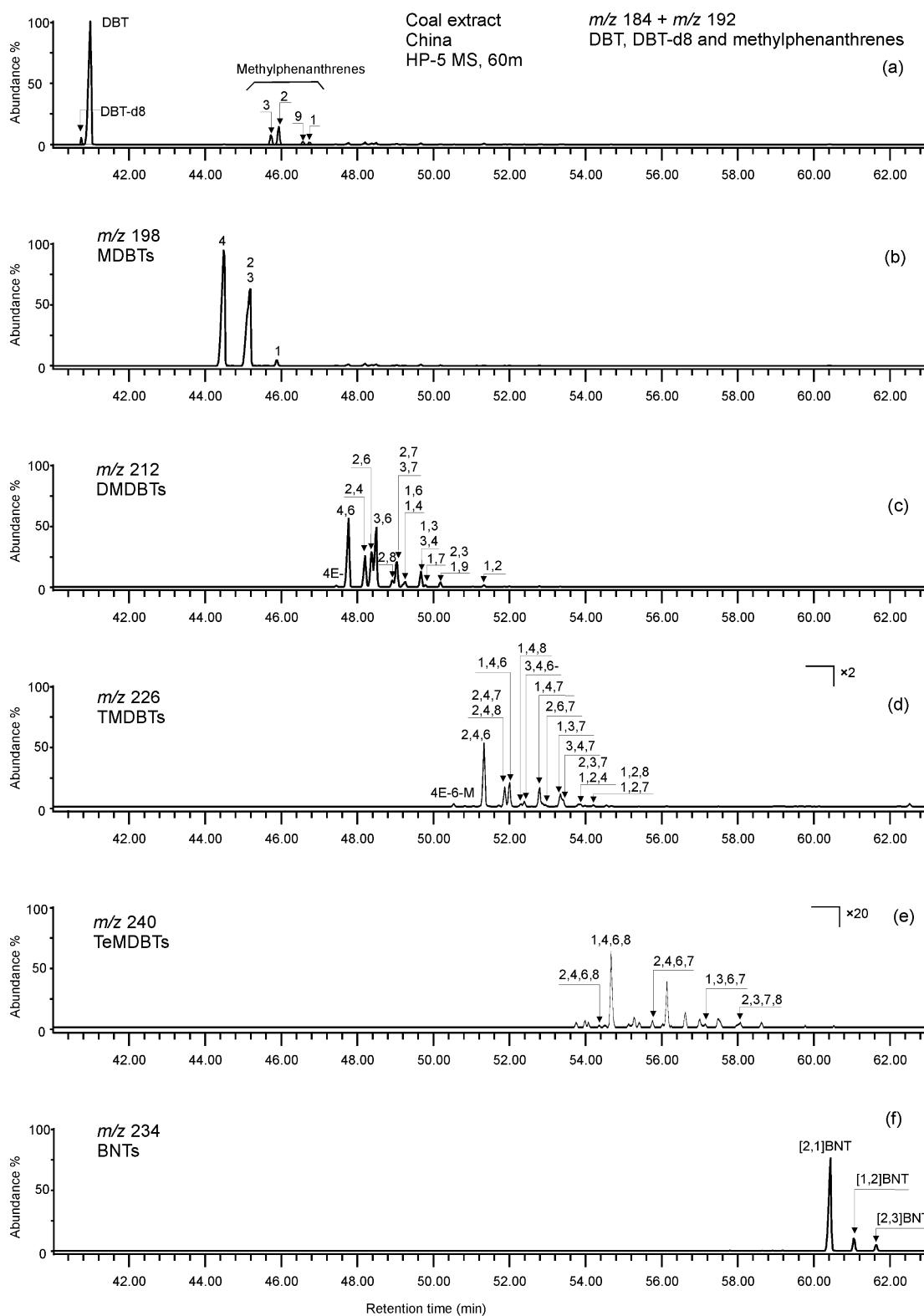
Fig. 3. Identification of dibenzothiophene, methylated homologous series, and benzo[b]naphthothiophenes in a coal extract. Numbers on peaks indicate methyl substitution pattern on DBTs.

parameters, the retention index (I_S) of 1,6-DMDBT can be calculated as 340.81, and by using the same method, the I_C is 333.71, which is about 1.04 and 0.85 lower than that of 1,4-DMDBT, respectively. Thus 1,6-DMDBT is unlikely to co-elute with 1,4-DMDBT based on the Schade and Andersson retention indices [24]. However, the GC–MS separation experiment of fifteen DMDBT isomers

[23] illustrated the co-elution of these two isomers (Fig. 4a). Their I_S and I_C values are also very close to those of 1,4-DMDBT (339.74 vs. 339.51 for I_S and 332.80 vs. 332.53 for I_C) (Table 1). The I_S and I_C for 1,8-DMDBT of 343.79 and 336.47, respectively, are significantly higher than those of 1,4- or 1,6-DMDBT. However, it co-elutes with 1,4-DMDBT and 1,6-DMDBT in the GC–MS separation experiment
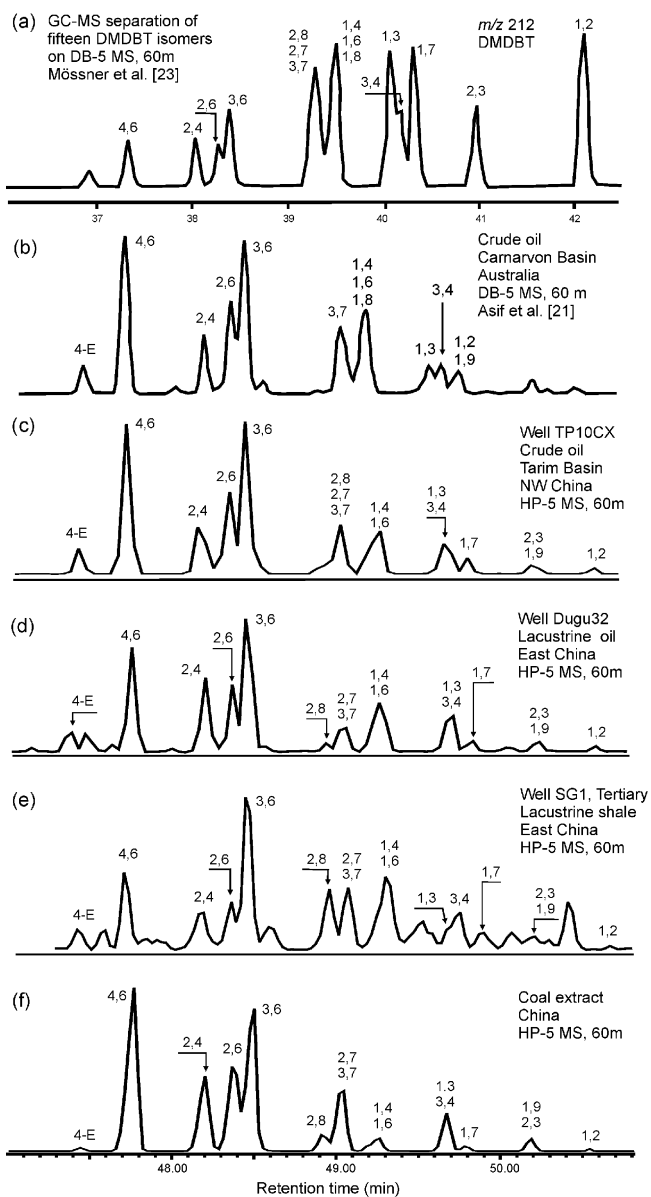
Fig. 4. Identification of dimethyldibenzothiophenes (m/z 212) in crude oils, coal and sediment extracts. Numbers on peaks indicate the methyl substitution pattern on DBT: (a) GC–MS separation of fifteen DMDBT isomers on DB-5 MS [23]; (b) crude oil, Carnarvon Basin, Australia [21]; (c) crude oil, Well TP10CX, Tarim Basin, NW China; (d) crude oil, Well Dugu32, Liaohe Basin, East China; (e) source rock extract, Well SG1, Liaohe Basin, East China; and (f) coal extract, China.

by [23]. Considering the disagreement of retention indices between these two reports, we consider this peak in the m/z 212 mass chromatogram to be a mixture of 1,4- and 1,6-DMDBT until we can obtain further evidence.

DBT has a symmetrical molecular structure (Fig. 1). The 4-position on one aromatic ring is symmetric with the 6-position on the other aromatic ring. Thus, 1,4-DMDBT and 1,6-DMDBT have similar thermodynamic properties, for example the standard molal enthalpy of formation [36]. The thermal maturity parameters of 4,6-/1,4-DMDBT or 2,4-/1,4-DMDBT are based on the thermodynamic stability differences between these isomers. Thus, the co-elution of 1,4- and 1,6-DMDBT has no significant influence on the application of the 4,6-/1,4-DMDBT or 2,4-/1,4-DMDBT maturity parameters.

Asif [31] identified two other DMDBT isomers: 1,2-DMDBT and 1,9-DMDBT, which co-elute in the m/z 212 mass chromatogram (Fig. 4b). Here we calculated the I_S and I_C of 1,2-DMDBT by using the

same equation and parameters as proposed by Schade and Andersson [24]. They are 349.57 and 342.05, respectively, the highest among all the DMDBT isomers (Table 1). The differences in I_S and I_C between 1,2- and 1,9-DMDBT are 2.33 and 2.01, respectively; therefore, their co-elution on GC is not possible. In the GC–MS separation experiment [23], 1,2-DMDBT has also the highest retention time (Fig. 4a). However, the I_S and I_C of 1,9-DMDBT are very close to those of 2,3-DMDBT (347.24 vs. 347.11 for I_S, and 340.04 vs. 339.70 for I_C, respectively, Table 1). So we assigned the peak of 2,3-DMDBT in Fig. 4f at 50.184 min as a mixture of 2,3- and 1,9-DMDBT (Table 1). The original peak assignment of 1,2- and 1,9-DMDBT reported in the literature [21] may be 1,7-DMDBT.

3.2. Identification of trimethyl- and tetramethyldibenzothiophene isomers

The identification and application of trimethyldibenzothiophenes (TMDBTs) and tetramethyldibenzothiophenes (TeMDBTs) in oils and ancient sedimentary organic matter have only been mentioned tentatively in previous reports. Chakhmakhchev et al. [9] detected seven TMDBT isomers in oils. However, the specific positions of the four methyl groups for each isomer were not confirmed. By comparison with the I_S and I_C values, several TMDBT isomers have been tentatively identified in the m/z 226 mass chromatograms in this study (Fig. 5). Among these compounds 2,4,6-TMDBT may correspond to peak 3, and 1,4,8- and 3,4,6-TMDBT may correspond to peak 5 reported by Chakhmakhchev et al. [9].

Five TeMDBTs and one ethyldimethyldibenzothiophene were tentatively identified in the m/z 240 mass chromatograms (Fig. 6) by comparing the I_S and I_C values with those reported by Schade and Andersson [24]. The complete identification and application of TeMDBTs in oils and ancient organic matter needs further study.

3.3. Identification of benzo[b]naphthothiophene isomers

The GC retention behavior of the benzo[b]naphthothiophenes and their alkylated derivatives on different stationary phases were reported previously [23]. In this study, the three isomers of benzo[b]naphtho[2,1-d]thiophene (abbreviated as [2,1]BNT), benzo[b]naphtho[1,2-d]thiophene ([1,2]BNT), and benzo[b]naphtho[2,3-d]thiophene ([2,3] BNT) were detected in oils by co-injection of authentic internal standards (Purity > 99.0%, Laboratory of Dr. Ehrenstorfer, Augsburg, Germany) in the GC–MS analysis of the aromatic fractions. The I_C values calculated by PAHs retention system (Table 1) for these three BNT isomers also correlate well with those published in the literature [37].

The [2,1]BNT and [1,2]BNT isomers have similar structures to those of benzo[a]carbazole (B[a]CA) and benzo[c]carbazole (B[c]CA) (Fig. 1) which occur in oils at significant quantities. Like benzo[b]carbazole, benzo[b]naphtho[2,3-d]thiophene is usually present at very low concentrations or below the detection limit in regular GC–MS analyses.

The ratio of B[a]CA/(B[a]CA + B[c]CA) in oils has been used as an empirical measurement for determining their relative secondary migration distances. The main proposed mechanism is that the more rod-shaped B[a]CA relative to the sub-spherical B[c]CA is preferentially removed from oils onto clay minerals and into solid organic matter in the carrier bed [38]. The chemical structures of [2,1]BNT and [1,2]BNT are quite similar to those of B[a]CA and B[c]CA, respectively (Fig. 1). As suggested by Larter et al. [38] functionalized aromatic compounds with polarity/shape differences between isomers may be suitable molecular indicators for monitoring oil migration. Therefore, [2,1]BNT/([2,1]BNT + [1,2]BNT) ratio
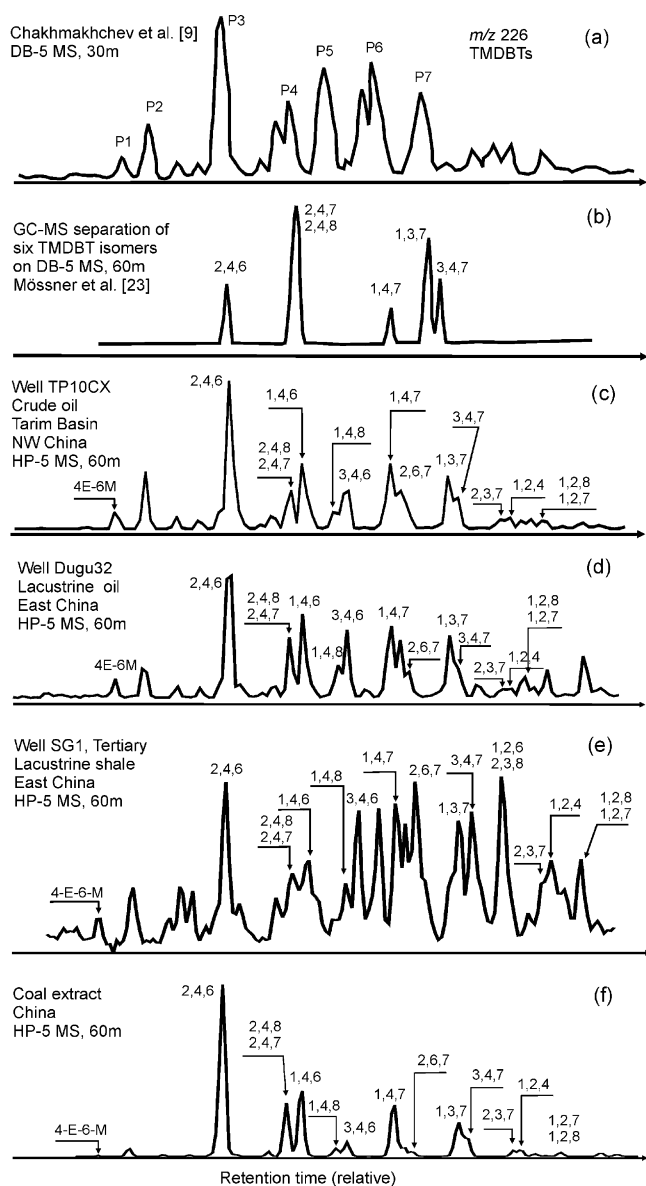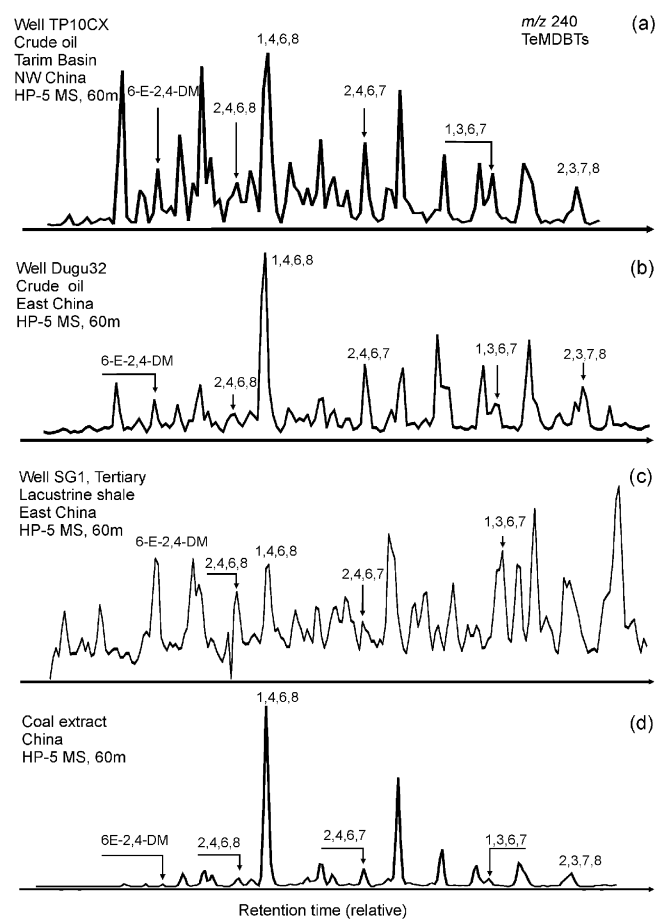
Fig. 5. Identification of trimethyldibenzothiophenes (*m/z* 226) in crude oils, coal and sediment extract. Numbers on peaks indicate the methyl substitution pattern on DBT: (a) crude oil [9]; (b) GC–MS separation of six TMDBT isomers on DB-5 MS [23]; (c) crude oil, Well TP10CX, Tarim Basin, NW China; (d) crude oil, Well Dugu32, Liaohe Basin, East China; (e) source rock extract, Well SG1, Liaohe Basin, East China; and (f) coal extract, China.

Fig. 6. Identification tetramethyldibenzothiophenes (*m/z* 240) in crude oils, coal and sediment extract. Numbers on peaks indicate the methyl substitution pattern on DBT: (a) crude oil, Well TP10CX, Tarim Basin, NW China; (b) crude oil, Well Dugu32, Liaohe Basin, East China; (c) source rock extract, Well SG1, Liaohe Basin, East China; and (d) coal extract, China.

may also be a potential molecular geochemical parameter to indicate oil migration routes and distances.

3.4. Quantitative analysis of DBTs in oils and sediment extracts

Because oil is mixture of numerous complex compounds, we must guarantee that the internal standard DBT-d8 will not interfere with other compounds in the mass chromatograms. Fig. 2a and b illustrate the *m/z* 192 mass chromatogram for an oil sample before and after co-injection of the internal standard DBT-d8, respectively. It is clear that no other compounds co-elute with the DBT-d8 peak in the *m/z* 192 trace.

The second step is to calibrate DBT-d8 against a known amount of unlabeled DBT. This calibration results in a response factor relating the response of the unlabeled DBT to internal standard DBT-d8.

The response factor (RF) can be calculated by the following equation:

$$\text{RF} = \frac{(\text{Area}_{\text{DBT}})/(C_{\text{DBT}})}{(\text{Area}_{\text{DBT-d8}})/(C_{\text{DBT-d8}})} = \left(\frac{\text{Area}_{\text{DBT}}}{\text{Area}_{\text{DBT-d8}}}\right) \times \left(\frac{C_{\text{DBT-d8}}}{C_{\text{DBT}}}\right) \quad (3)$$

Thus, the ratio of the $\text{Area}_{\text{DBT}}/\text{Area}_{\text{DBT-d8}}$ equals the RF multiplied by the concentration ratio of $C_{\text{DBT}}/C_{\text{DBT-d8}}$. A set of $\text{Area}_{\text{DBT}}/\text{Area}_{\text{DBT-d8}}$ ratio data can be obtained by GC–MS analyses of a series of standard solutions with different concentration ratios of DBT to DBT-d8. The relative areas of DBT to DBT-d8 with different concentration ratios are illustrated in Fig. 2c–f. A cross-plot of $\text{Area}_{\text{DBT}}/\text{Area}_{\text{DBT-d8}}$ ratio versus $C_{\text{DBT}}/C_{\text{DBT-d8}}$ ratio is illustrated in Fig. 7a. The coefficient of the equation obtained by the linear regression of the data set is the response factor. Here, the RF relating the response of the unlabeled DBT to the standard DBT-d8 is 1.03. This result is reasonable due to much smaller differences in probabilities for removal of an H or D atom in aromatic systems [39]. The deviation from 1.00 may be due to the differences of the molar mass of unlabeled DBT and DBT-d8. There are more moles of unlabeled DBT in a certain mass of compound than in the same mass of DBT-d8. Therefore it is expected that unlabeled DBT should give a larger signal. The mole mass ratio of DBT-d8 to DBT is 1.04 (192/184 = 1.04), which is very close to the 1.03 measured. Thus, we considered that the DBT and DBT-d8 have generally the same response in GC–MS analysis. The absolute concentrations of DBT in oils or sediment extracts can be obtained simply by co-injection of a known amount of DBT-d8 standard, and
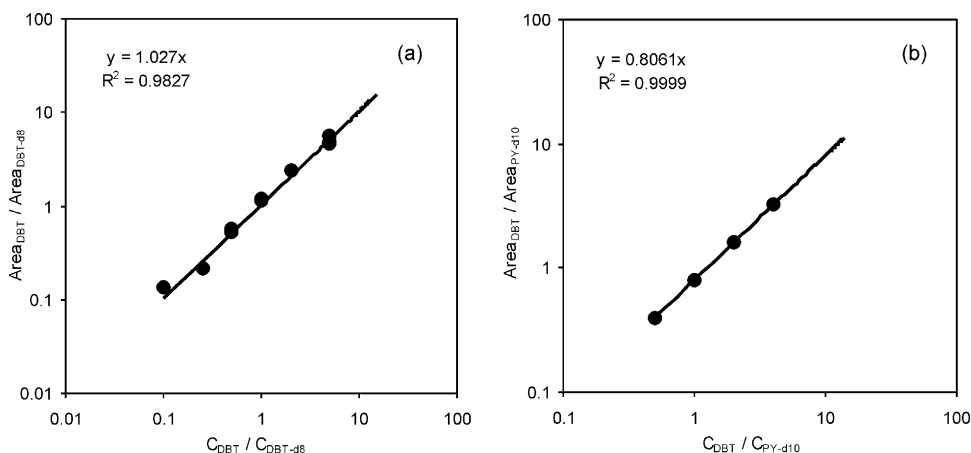
Fig. 7. Cross-plots of: (a) $Area_{DBT}/Area_{DBT-d8}$ versus C_{DBT}/C_{DBT-d8}, and (b) $Area_{DBT}/Area_{PY-d10}$ versus C_{DBT}/C_{PY-d10} showing the response factor relationship.

comparing the peak areas of DBT with those of DBT-d8 without area calibration under the GC–MS conditions in our study.

The internal standard pyrene-d10 (molecular formula: $C_{16}D_{10}$; molecular weight: 212.31; Purity = 99.5%, Laboratory of Dr. Ehrenstorfer, Augsburg, Germany) was used here to examine the response factor of DBT to labeled PAHs. Fig. 7b shows the cross-plot of the $Area_{DBT}/Area_{PY-d10}$ versus C_{DBT}/C_{PY-d10} ratios. The RF relating the response of DBT to pyrene-d10 (PY-d10) is 0.81, which means an area correction of DBT in unknown samples must be calibrated by dividing the area of the DBT peak in the mass chromatogram by 0.81. It can be inferred that different deuterium substituted PAHs many have different response factors to DBT due to their different chemical structures and the occurrence of hetero atoms in the PASHs.

The response factor of 4,6-DMDBT to DBT-d8 can also be obtained by using the same method. A cross-plot of $Area_{4,6-DMDBT}/Area_{DBT-d8}$ ratio versus $C_{4,6-DMDBT}/C_{DBT-d8}$ ratio is illustrated in Fig. 8a. The RF relating the response of the unlabeled 4,6-DMDBT to the standard DBT-d8 is 0.97, which means that DMDBT may have generally same response in GC–MS analysis. The deviation from 1.00 may be due to the differences of the molar mass of unlabeled 4,6-DMDBT and DBT-d8. There are fewer moles of 4,6-DMDBT in a certain mass of compound than in the same mass of DBT-d8. Therefore it is expected that 4,6-DMDBT should give a smaller signal. The mole mass ratio of DBT-d8 to 4,6-DMDBT is 0.91 (192/212 = 0.91), which is very close to the 0.97 measured.

The RF relating the response of 4,6-DMDBT to pyrene-d10 (PY-d10) is 1.14, which means an area correction of methylated DBT in unknown samples must be calibrated by dividing the area of the DBT peak in the mass chromatogram by 1.14.

Thus, the absolute concentrations of alkylated DBT in oils or sediment extracts can be obtained simply by co-injection of a known amount of DBT-d8 standard, and comparing the peak areas of DBT and alkylated DBTs with those of DBT-d8 without area calibration under the GC–MS conditions in our study.

The measured retention data for the methylated DBTs of all samples in this study show excellent correlations with the calculated I values reported by Schade and Andersson [24] with coefficients higher than 0.999 for I_S (Fig. 9).

In our study, except for 2,3,7-TMDBT, 12,4-TMDBT and 1,3,6,7-TeMDBT in lacustrine shale rock extract and 1,3,7-TMDBT isomer in carbonate oil sample from Well TP10CX in the Tarim Basin, the differences between the measured and literature I_S values for all compounds are within ±1.1 index unit. Actually, the measured I_S for some authentic standards, such as [2,1]BNT, [1,2]BNT and [2,3]BNT have −0.66 to 0.53 retention index unit differences from those of literature. Thus, based on our practice experience, the upper limit

for diverging retention indices of ±1.1 is considered to be acceptable.

The concentrations of the total DBTs (including parent, all methyl-, dimethyl- and trimethyldibenzothiophene isomers) and BNTs (including [2,1]BNT, [1,2]BNT and [2,3]BNT) in oils derived from the lacustrine siliciclastic source rocks range from 34 to 380 μg/g oil, with an average of 187 μg/g in the Beibuwan Basin, South China Sea, which is equivalent to about one fifth of the oils from carbonate source rocks in the Tarim Basin, northwest China (Li, unpublished results). Accurate qualitative and quantitative analysis of DBTs and BNTs is vital for their application in studies of depositional environment, thermal maturity of ancient organic matter, and oil migration.

3.5. Comparison of the distribution patterns of DBTs in oils, coal and sediment extracts

In this study, we analyzed two oils sourced from typical marine carbonates and lacustrine shales, respectively, and one lacustrine shale sediment and one coal sample for comparison. Except for minor differences, the distributions of the methyl DBTs have generally similar patterns (Figs. 4–6). They all have relatively high abundances of 2-, 3- and 4-MDBT in the m/z 198 mass chromatograms and 4,6-, 2,4-, 2,6- and 3,6-DMDBTs in the m/z 212 mass chromatograms (Fig. 3). 4-EDBT, 2,3-, 1,9- and 1,2-DMDBTs are present in very low concentrations or even below the detection limit (Fig. 4c–f). This is consistent with their relatively low thermodynamic stability [37]. Among the TMDBTs, 2,4,6-TMDBT is present at higher abundance than the other isomers in these samples (Fig. 5c–f). Budzinski et al. [5] reported that a substituent at the 1-position of DBT is less stable than the 3-position, which is less than the 2-position, and that the 4- and 6-positions are the most stable. Thus, we can infer that 2,4,6-TMDBT is the most stable isomer among all TMDBTs. The high relative abundances of some isomers as for example 4-MDBT or 4,6-DMDBT are mainly controlled by thermal maturity. So they are effective maturity indicators and can be applied to high and over-mature oils [9,10].

Unlike biomarkers in saturated fractions of oils, coals or sediment extracts, thiophene class compounds do not have particular biological precursors. They may be derived from the reaction of other compounds in the sample organic matter. For example, the DBTs may be the products of the reaction of biphenyl and sulfur under mild conditions [21]. Thus, in this study, the various samples do not have distinct differences in their DBT distribution patterns. The relative concentrations of isomers may be controlled by thermal maturity [9–11], and their absolute concentrations may depend on depositional environment [14]. The source type of the
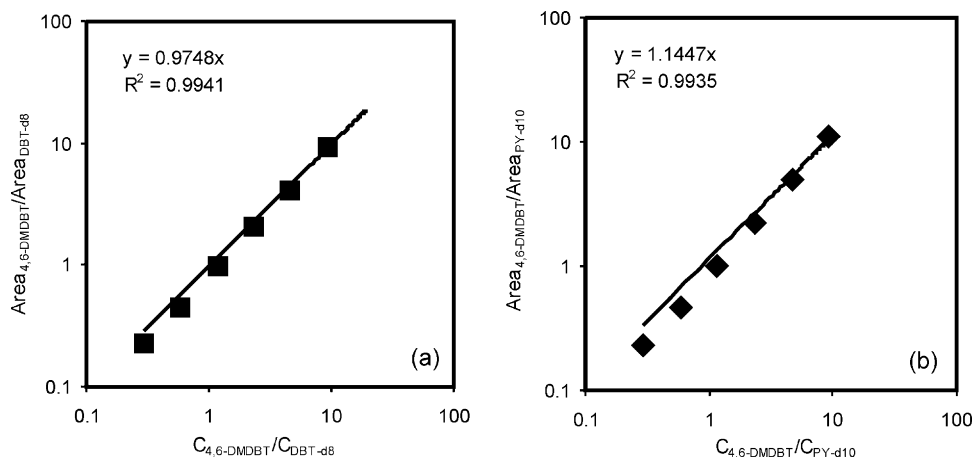
Fig. 8. Cross-plots of: (a) $Area_{4,6-DMDBT}/Area_{DBT-d8}$ versus $C_{4,6-DMDBT}/C_{DBT-d8}$, and (b) $Area_{4,6-DMBT}/Area_{PY-d10}$ versus $C_{4,6-DMDBT}/C_{PY-d10}$ showing the response factor relationship.
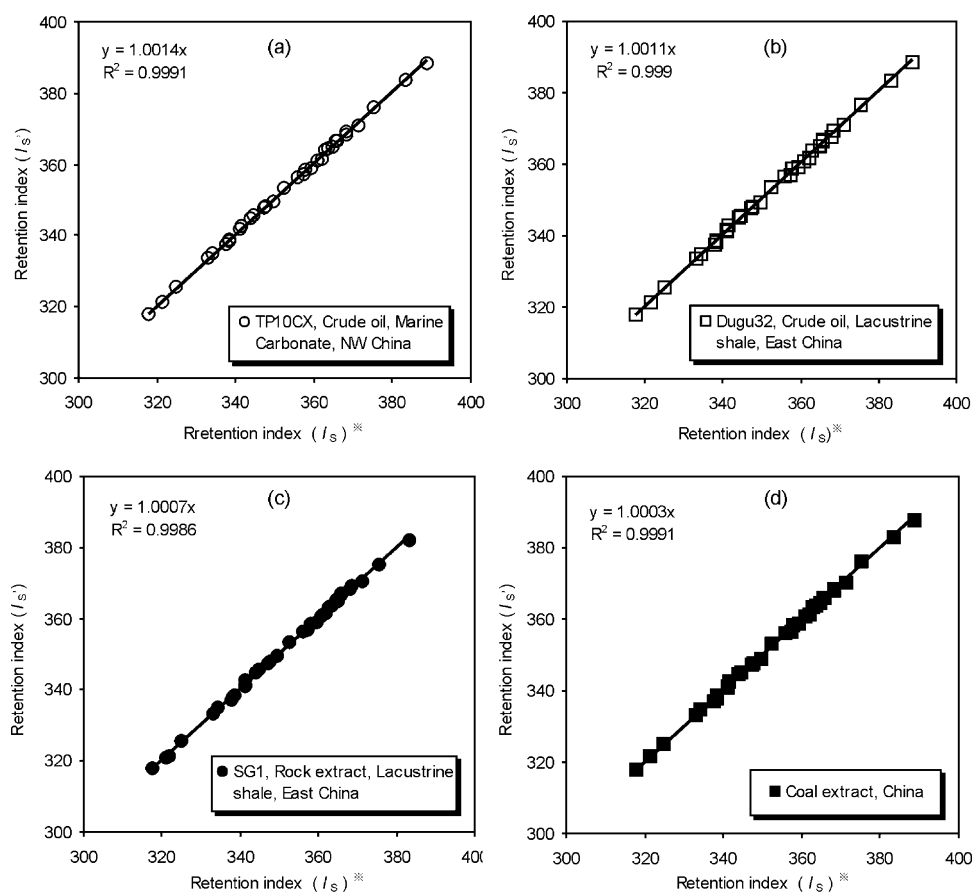

Fig. 9. Measured retention indices (I'_S) from this study versus calculated retention indices (I_S)* reported in reference [24]: (a) crude oil, Well TP10CX, Tarim Basin, NW China; (b) crude oil, Well Dugu32, Liaohe Basin, East China; (c) source rock extract, Well SG1, Liaohe Basin, East China; and (d) coal extract, China.

organic matter may have no significant influence on the DBT distribution.

4. Summary

Dibenzothiophene (DBT) and its methyl-, dimethyl-, trimethyl-, and tetramethyl-homologues have been identified in crude oils, coal, and sediment extracts by comparison of calculated retention indices, I_S and I_C, obtained from PASHs and PAHs, respectively. Three isomers of benzo[b]naphthothiophene have also been

identified by co-injection of reference standards. Some isomers of dimethyldibenzothiophene and trimethyldibenzothiophene that were tentatively identified in previous reports have been definitively assigned here.

The quantitative analysis of dibenzothiophenes in oils was performed by co-injection of deuterium labeled standards. The response factors relating the response of the unlabeled DBT to DBT-d8 and pyrene-d10 were obtained for area calibration of dibenzothiophenes in GC–MS analyses. Due to the same chemical structure and similar GC behavior between deuterated and

hydrogenated PASHs, DBT-d8 is the optimal internal standard for quantitative analysis of the thiophene class compounds in oils, coals and sediment extracts.

Acknowledgements

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