Peculiarities of sulphur functionalities in the Thracian coal province, Bulgaria

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Abstract. The Thracian coal province in Bulgaria is comprised of three main coal basins, Maritza East, Maritza West and Elhovo, with extremely immature coals ($R_r = 0.18$–0.21%). These Miocene-Pliocene aged low rank coals (lignites) are characterized by high ash and sulphur contents, and low calorific values. Temperature programmed reduction/oxidation at atmospheric pressure (AP-TPR/TPO), coupled with on-line mass spectrometer (AP-TPR/TPO-MS) and with an off-line gas chromatograph-mass spectrometer (GC-MS), were applied to the qualitative and semi-quantitative analysis of sulphur functionalities in representative samples from each basin of the coal province. Carbonates and mineral sulphur were removed by preliminary treatment with diluted acids at mild conditions to prevent effects on the TPR kinetograms. This treatment mainly removed the mineral sulphur, and its effects on organic sulphur were insignificant. Most of the organic sulphur in the Thracian lignites occurs in thiophenic structures ($\sim 60\%$). The TPR-MS profiles showed the presence of alkyl and aryl thiols, dialkyl and aryl-alkyl sulphides and thiophenes. The main organic sulphur compounds registered by the off-line AP-TPR-GC-MS were highly volatile compounds (thiols, sulphides, disulphides), alkylated thiophenes, and a lesser proportion of benzothiophenes. The disulphides (-SS-) are relatively abundant in the Maritza East and Elhovo lignites. They are probably the main aliphatic sulphur species in the coal's organic matter. Aliphatic chains with sulphur bridges are also principal structural functionalities in the Maritza West organic matter. Aromatic compounds with two aromatic rings and high degrees of substitution could be key organic structures in the studied lignites.

Key words: coal, organic sulphur functionalities, AP-TPR/TPO-MS, AP-TPR-GC-MS

Introduction

The Thracian coal province is situated in the Balkan Peninsula, Bulgaria, and is filled with sediments of the lower (Paleogene) and upper coal-bearing molasse (Neogene) (Šiškov 1997). It is comprised of three main coal basins: Maritza West, Maritza East, and Elhovo (Fig. 1), all with extremely immature coals. A small coal-bearing deposit in the area of the Gulf of Sozopol also belongs geographically to the Thracian coal province (Kortenski 2002), but it is not included in our study because of its insignificant exploration potential and the unavailability of samples.

The formation of these coals began in the Late Oligocene and continued through the Miocene into the Pliocene. The coal-bearing sediments gradually become younger from west (Maritza West) to east (Elhovo). This is due to the advancing regression that occurred in this direction, and to the formation of the Black Sea (Kojumdgieva 1983) (Fig. 1). Under these conditions the plain became relatively raised following the marine regression. A period of compensating sedimentation caused the formation of thick peat deposits. The second coal seam of the Maritza East deposit (maximum thickness of 25 m) is a good illustration of the long duration of the peat formation processes.

The Thracian low rank coals (lignites), exposed on the surface of the coal-bearing strata, vary in thickness from 45 m (minimum at Maritza-East) to 390 m (maximum at Elhovo). They are characterised by high ash and sulphur contents, and by low calorific values (Šiškov 1997). Nevertheless, Thracian low rank coals are the main source of energy for electricity production in Bulgaria, and their proper characterization is therefore of the most importance. They are mined in opencast excavations, and are burnt in a complex of thermal power stations. The main ecological problem of their use is the emission of sulphur during combustion (Stefanova et al. 2002). Sulphur dioxide emissions from utility and industrial boilers are a cause of acid rains. Therefore, investigating the nature of sulphur in these lignites is important for improving their utilisation. Knowledge of the organic sulphur species and the distribution of organic sulphur in Thracian lignites is currently lacking. The present study is an attempt to begin correcting this situation.

From the geochemical perspective, the organic sulphur compounds in coal may have formed in an early stage of diagenesis (humification) when bacterial activity decomposed plant debris into premaceral humic substances (Chou 1990). Hydrogen sulphide, elemental sulphur, and polysulphides produced by dissimilarity processes may have reacted with organic matter to form organic sulphur compounds. In the medium- and high-sulphur coals, seawater is also an important source of sulphur. Seawater sulphate, which diffuses into the peat, is reduced by anaerobic, sulphate-reducing bacteria. Reduced sulphur species in interstitial water react with iron and organic matter to form mineral sulphides (mainly pyrite) and organic sulphur compounds. All Thracian coal basins investigated here were generated in continental limnic environments. Such depositional environments, and the presence of high sulphur contents in the coal, indicate a combination of specific paleogeographic, geochemic, and hydrodynamic condi-

Table 1. Lignite characteristics of initial and demineralised samples, in wt%

Parameters Initial samples	Lignites		
	Maritza West	Maritza East	Elhovo
Proximate analysis (wt%)			
W	8.1	7.5	7.8
A^{db}	20.9	14.5	29.8
V^{daf}	58.8	60.9	58.9
Ultimate analysis (wt%)			
C^{daf}	62.8	59.8	56.1
H^{daf}	6.32	6.41	6.25
N^{daf}	0.6	0.67	1.1
S_t^{db}	13.5	3.57	6.26
Sulphur forms (wt%, db)			
Organic (S_o)	4.2	2.10	3.29
Sulphate (S_s)	7.3	0.85	2.36
Pyritic (S_p)	2.0	0.62	0.61
Calorific value (kJ/kg)			
*Q_s^{daf}	22.87	22.31	22.76
Reflectance (%)			
*R_r	0.21	0.20	0.18
Demineralised samples			
S_t db, wt %	4.00	2.05	2.10

* reference (Šiškov 1997)

Figure 1. Location of the Thracian coal-bearing province in Bulgaria: 1 – Maritza West, 2 – Maritza East, 3 – Elhovo.

tions during peat formation. An important factor for the generation high sulphur coal in such environments is the presence of sulphide- and sulphate-rich groundwater, and an exogenic source for the peat swamp. It was under such conditions that the ancient peat bogs of the Thracian coal province existed.

During the past few decades considerable work has been devoted to the study of sulphur contents in fossil fuels (Orr and White 1990). Organic sulphur and its relatively low concentration in fossils has motivated the application of re-

search to more sensitive analytical techniques (Sinninghe Damsté and DeLeeuw 1990). For example, Olivella et al. (2002) used a suite of techniques, including destructive (ASTM standard and Py-GC-MS) and non-destructive (SEM-EDX, XANES and XPS) methods, for comparative sulphur functionality studies. The advantages and drawbacks of the different approaches were discussed as well.

Temperature programmed reduction at atmospheric pressure (AP-TPR) proves to be an effective technique for the specification of organic sulphur forms in coal (Yperman et al. 1999). This method is based on establishing specific sulphur functional groups that become hydrogenated/reduced in a pure H_2 atmosphere into H_2S at specific temperatures. Identification of other evolved gases by extended detection techniques makes it possible to obtain more quantitative and qualitative information about sulphur (Mullens et al. 2003). An improved mass balance after each AP-TPR-MS experiment has been achieved by an extra AP-TPO-MS experiment in pure O_2, in which non reduced/hydrogenated sulphur compounds left in the char or other volatile sulphur compounds are captured in the tar and analyzed (Mullens 2000, Marinov et al. 2004). A variant of AP-TPR coupled off line with GC-MS was used for confirming and extending the information obtained from above mentioned TPR techniques (Marinov et al. 2003).

The aim of the present study is to obtain information about the abundance of organic sulphur forms and compounds in representative samples from Thracian coal province using AP-TPR/TPO-MS and AP-TPR-GC-MS techniques.

Procedures

Representative lignite samples from the Maritza West, Maritza East, and Elhovo deposits were used in this study. The samples were freshly obtained from the mines, and treated under mild conditions with dilute HCl and HNO_3 to remove calcium-containing minerals and inorganic sulphur (Marinov et al. 2003). The removal of these minerals was important, because they could react with the H_2S formed during the TPR experiments, and thus complicate kinetogram interpretation. Demineralised coal samples were consecutively analysed by AP-TPR/TPO-MS and AP-TPR-GC-MS techniques.

Instrumental methods

AP-TPR-MS analyses were performed in the apparatus described previously (Yperman et al. 1999). The samples were placed in the quartz reactor and heated from room temperature to 1025 °C, increased linearly at 5 °C/min. The AP-TPR reactor was coupled on-line with a mass spectrometer (FISONS-VG Thermolab MS) through a capillary heated at 135 °C. The mass spectrometer, equipped with a quadruple analyser, was set at an ionising voltage of 70 eV within the mass range of 12–200 amu.

AP-TPO-MS was applied to the residue to check if any sulphur was left in the AP-TPR treated sample (char and tar). The reactor was the same as in the AP-TPR analysis, but hydrogen was replaced by oxygen. The flow rate of the pure oxygen gas was set at 100 cm^3/min. The SO$_2$ evolution was monitored during linear heating at 20 °C/min from 25 °C to 1100 °C.

AP-TPR-GC-MS experiments were performed using the same AP-TPR reactor. The AP-TPR system was connected off line with the GC-MS to analyse evolving gases (Perkin Elmer Thermal Desorber ATD 400, GC Autosystem XL with capillary column ZB1 15 m × 0.32 mm and film thickness of 3 μm, MS Turbomass).

Results and discussion

The proximate and ultimate analyses of the raw lignites are listed in Table 1. The relatively high sulphate sulphur content of the Maritza West samples (S$_s$ = 1.7%, i.e. 22.7% of S$_t$) and Elhovo sample (S$_s$ = 2.1%, i.e. 35.6% of S$_t$) are noteworthy. The main sulphate mineral in the studied coals is gypsum (CaSO$_4$.2H$_2$O). There are strong links between the comparatively high gypsum contents in the coals and the specific paleogeographic environment during peat formation. The coal-bearing sediments were formed in a typical regressive continental facies near a marine basin (Fig. 1). The sedimentation process occurred in a flat littoral area. The presence of gypsum in the coal layers, and its comparatively high abundance in the upper part of the coal beds, indicates hypergene coal changes. This was caused by the short duration of peat bog after it became covered by sediments (Kortenski and Dimitrov 1990; Markova and Kortenski 2000).

The treatment of samples by diluted acids under mild conditions decreased the sulphur content (Table 1). For all lignites it was found that the mineral sulphur is quantitatively removed, accompanied by a negligible decrease in organic sulphur (i.e. adsorbed or trapped). For the Elhovo samples, the decrease in sulphur content is 64.4% (S$_{mineral}$ = 62.7%), for Maritza East 42.6% (S$_{mineral}$ = 41.2%), and for Maritza West 46.7% (S$_{mineral}$ = 44.0%). As the organic sulphur content is determined by the difference [S$_o$ = S$_t$ − (S$_p$ + S$_s$)], the total sulphur (S$_t$) will be equal to the organic sulphur (S$_o$) as S$_p$ and S$_s$ absent after demineralization treatment.

Two broad peaks and several shoulders (Fig. 2) characterize the H$_2$S profiles of the AP-TPR-MS experiments of all three lignites. The first large one with T$_{max}$ around 420 °C for both Maritza samples could be attributed to the hydrogenated sulphidic and disulphidic compounds (Maes et al. 1996, 1997). The second large signal, maximizing at 580–600 °C for the same samples, could be related to diaryl sulphides and simple thiophenes. Two large shoulders at 250–300 °C and 680–700 °C are also apparent for both Maritza samples. The first of these is related to alkyl thiols, while the second is for complex thiophenic sulphur compounds (Maes et al. 1996, Marinov et al. 2004).
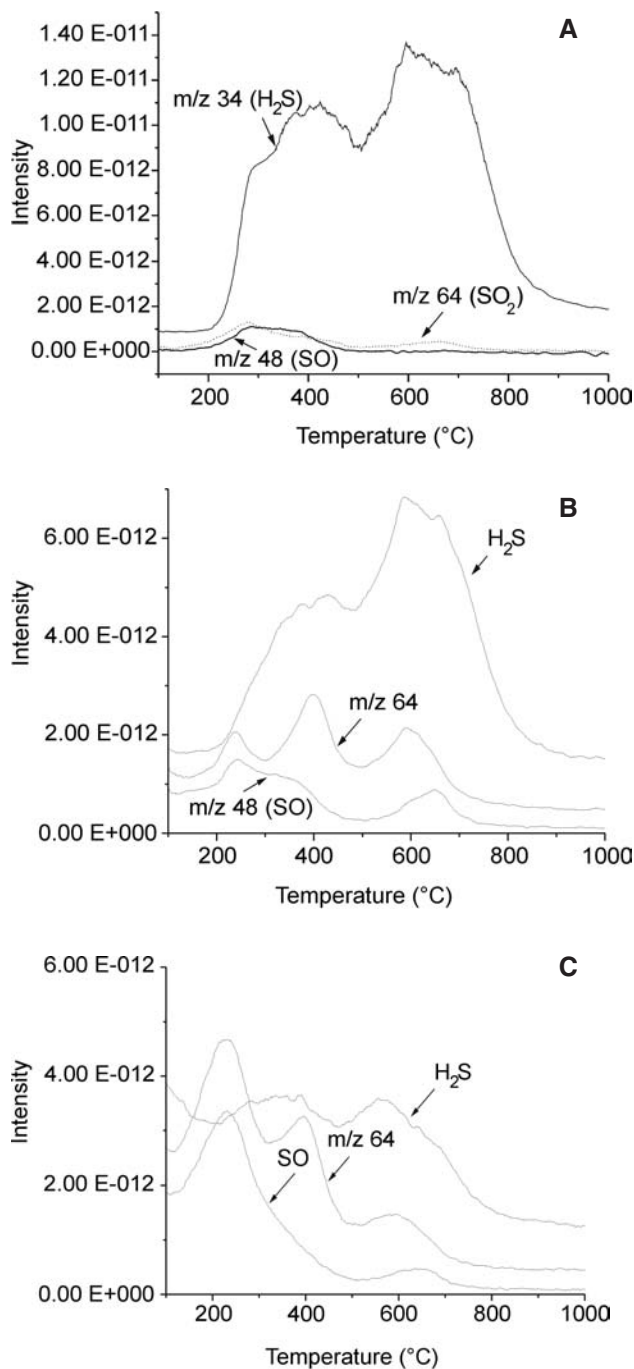

Figure 2. AP-TPR-MS of demineralised Thracian lignites: A – Maritza West, B – Maritza East, C – Elhovo.

In the kinetogram of the Elhovo lignite two main maxima also occur, the first at about 325 °C (starting at 200 °C) and the other at 550 °C. A number of small shoulders/peaks at 275, 435, 505 and 650 °C are also observed. The peaks at 275 °C and 325 °C could be attributed to the presence of alkyl and aryl thiols, while the peak at 435 °C refers to dialkyl and aryl-alkyl sulphides (Marinov et al. 2004). The complex, intense signal at 550 °C is related to diaryl sulphides and to simple thiophenic structures. The shoulder around 650 °C can be assigned to the more complex thiophenic compounds (Maes et al. 1997).

Based on our interpretation of the semi-quantitative TPR-MS data, it is possible to gain more information about the distribution of thiophenic and non-thiophenic organic sulphur forms in the lignite samples. The relatively small amounts of aryl-alkyl sulphides registered by GC-MS in the samples gave us ground for shifting the temperature boundary between thiophenic and non-thiophenic sulphur peak areas on the TPR kinetograms from 620 °C, as determined by Maes et al. (1997), to 500 °C. Most of the organic sulphur in the studied lignites is calculated as thiophenic: 58% for Elhovo and about 61–60% for both Maritza lignites.

Nearly all organic sulphur is reduced/hydrogenated under AP-TPR conditions. Only minor amounts of oxidised organic sulphur compounds are present in the lignites as indicated by m/z 64 (SO_2) and m/z 48 (SO) profiles (Fig. 2). For the Maritza West samples, only some small amounts of sulphatic acids and sulphones could be detected (temperature range for m/z 48 and 64 between 200 °C and 450 °C). For the Maritza East samples, more intense signals are found for m/z 48 and 64; these refer to sulphatic acids (at around 250 °C), sulphones (at around 350 °C), and sulphoxides (at around 650 °C). Elhovo m/z 64 and 48, when exhibiting the same trend, refer to sulphatic acids (225 °C) and sulphoxides (650 °C). It should be kept in mind that m/z 64 could have experienced interference from the contribution of an alkyl fragment $[C_5H_4^+]$ (Mullens et al. 2003). On the other hand, methylthiol (CH_3SH, M^+ 48) might influence the m/z 48 profile. For higher rank coals,

SO_2 and SO profiles overlap when they correspond only to oxidised sulphur forms, but this is not the case in our study. Additionally, oxidised sulphur groups are also partly reduced in AP-TPR media. The AP-TPO-MS experiments demonstrated that after the AP-TPR procedure some organic sulphur compounds are left in the char or are trapped in the tar fraction in the reactor.

The AP-TPR experiments coupled with off-line GC-MS analyses were performed at the same experimental conditions. The volatiles in the temperature region from 250 °C to 700 °C, at 50 °C step intervals, were analysed. A typical GC-MS kinetogram is illustrated in Fig. 3. There are a great variety of individual compounds. Sulphur compounds were further analysed in more detail. The relative intensities of different sulphur-containing compounds in the three lignites are given as a function of temperature in Fig. 4. The main organic sulphur compounds for all lignite samples were highly volatile compounds (thiols, sulphides, disulphides), alkylated thiophenes, and, to a lesser extent, benzothiophenes. The following common sulphur species were determined by selective ion monitoring (SIM):

- aliphatic sulphur-containing compounds, i.e. thiols, CH_3SH (m/z 47); dialkylsulphide, CH_3SCH_3 (m/z 62); dialkyldisulphide, CH_3SSCH_3 (m/z 94); and thiolanes (m/z 88 + 14n);
- aromatic sulphur-containing compounds, i.e. thiophenes, Th, (m/z 84 + 14n); and benzo[b]thiophenes, BzTh, (m/z 134 + 14n).
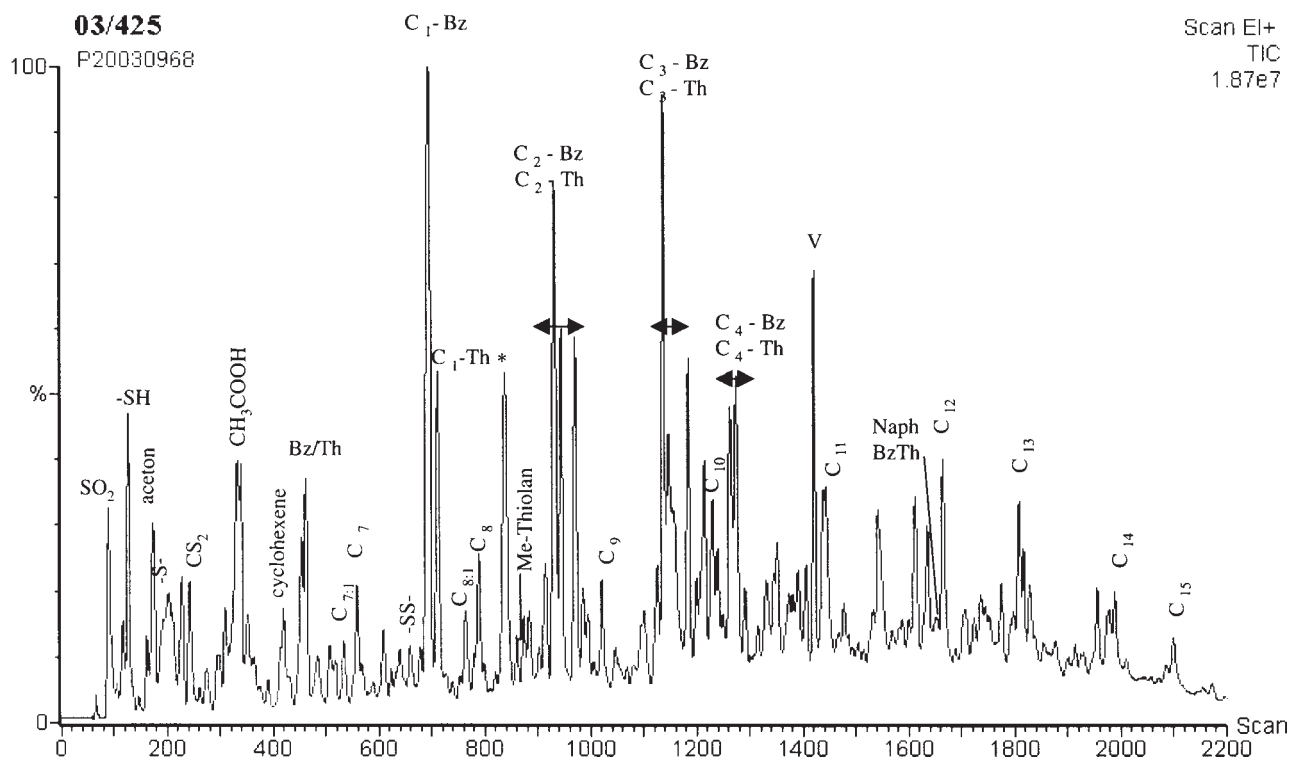

Figure 3. AP-TPR-GC/MS flue gas composition of Maritza West lignite at 300 °C.
Abbreviations: -SH thiol; -S- dialkylsulphide; -SS- dialkydisulphide; Th thiopehen; Bz benzene; C_n-Bz alkylated benzene; C_n-Th alkylated thiophene; V – methoxy phenol rest of lignin; Napn naphthalene; Bzth benzotiophene; $C_{n:1}/C_n$ alkene/alkane;
* artefact

There was a lack of compounds with sulphur bridges (-S-) in the Maritza East sample, while the Maritza West sample reveals the presence of thiolanes (m/z 88 + 14n). A peculiarity of organic sulphur in the Elhovo and Maritza East samples was the relatively high abundance of disulphides (-SS-) that should be the main aliphatic sulphur species as structural elements for its coal organic matter composition. The Maritza West lignite includes aliphatic chains with sulphur bridges as possible structural arrangements of its organic substance.

Thiophenic aromatic species (i.e. Th and BzTh) had comparable distributions in all of the lignites. There were all homologue series for substituted thiophenes. In Fig. 3 tetra-substituted thiophene C_4-Th was identified, but the series could be extended up to C_7-Th. Benzothiophenes were also alkylated.

All GC-MS spectra showed typical pyrolysis products: alkylated benzenes, C_n-Bz (m/z 78 + 14n), maximizing at toluene; and alkanes/alkenes ($C_7 – C_{15}$) with a maximum at $C_{11}/C_{11:1}$. Some residues of lignin, like methoxy phenols (M^+ 124) and their alkyl analogues, were detected in flue gases (V, in Fig. 3). Aliphatic compounds progressively decreased with increasing temperature. Naphthalenes (Naph) and Benzothiophenes (BzTh) (Figs 3 and 4) appeared with increasing temperature, and are the dominant components in flue gases at temperatures above 500 °C. The identified polycyclic aromatic compounds contain a low number of aromatic rings per molecule (i.e. two aromatic rings with high degree of substitution). This observation could be explained by the immaturity of all coals under consideration here, and is consistent with the above mentioned considerations.

Conclusions

Total sulphur recovery in the TPR study was not always achieved, although most sulphur compounds were maximally reduced/hydrogenated in discrete temperature regions (Yperman et al. 1999). It was found that oxidised sulphur compounds were hardly reduced, as was demonstrated again by the monitoring of SO_2 and SO by AP-TPR-MS. The AP-TPR-GC-MS analyses also confirmed that some small amounts of volatile sulphur compounds remain unaffected. Therefore the sometimes-poor AP-TPR sulphur recovery balance can be better explained, and thus improved by using extra detection systems.

The key structure of the coal organic matter in low rank coal samples might be aromatic compounds with two rings and a high degree of substitution. About 60% of the organic sulphur in the Thracian low rank coals can be assigned to thiophenic structures. The relatively high proportion of disulphides in the Elhovo and Maritza East samples means that they should be the main aliphatic sulphur species as structural elements for their organic matter composition. Aliphatic chains with sulphur bridges are also important structural elements for the Maritza West organic matter.
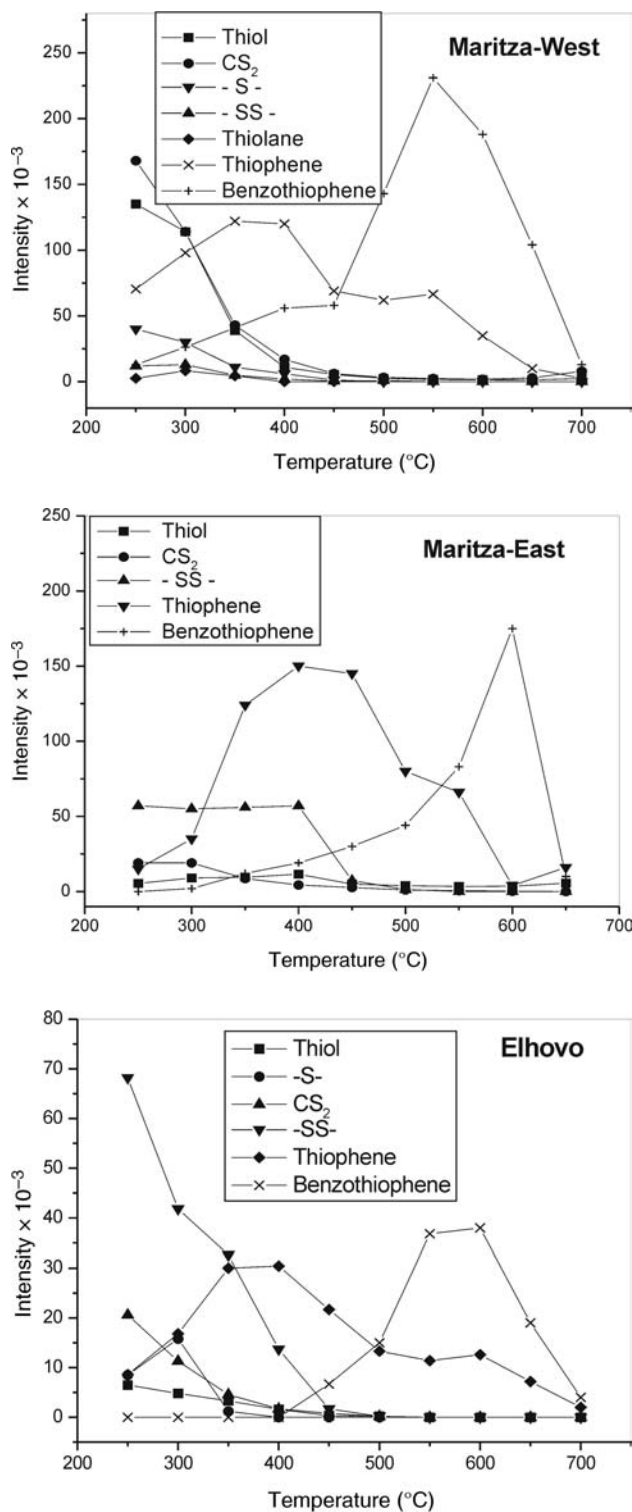

Figure 4. Semi-quantitative distribution of indicated species in different temperature AP-TPR fractions determined by off-line coupled GC-MS in Thracian lignites.

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