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Mass spectrometric analyses of biomarkers and oxygen-containing species in petroleum ether-extractable portions from two Chinese coals

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HIGHLIGHTS

- Biomarkers, especially sterenes, were enriched into E_{SSBC} and E_{ML}.
- O_xN_2 class species are predominant in E_{SSBC} and E_{ML}.
- All the detected species have long alkyl side chains (LASCs).
- Twining actions play important role in extracting LASC-containing species with petroleum ether.
- Oxygen atoms exist in furan rings, R–O–R′, RCOOR′, and RCOR′ in the species detected in positive-ion mode.

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ABSTRACT

Shaerhu subbituminous coal (SSBC) and Mengdong lignite (ML) were extracted with petroleum ether under ultrasonication at room temperature to obtain E_{SSBC} and E_{ML}, respectively. The extracts were analyzed with a gas chromatograph/mass spectrometer and a positive-ion electrospray ionization Fourier transform ion cyclotron resonance mass spectrometer to characterize biomarkers and oxygen-containing species. The biomarkers consist of a homologous series of alkanes and sterenes. The biomarker distributions provide important information on the main origins and microorganism degradation of organic matter in SSBC and ML. Oxygen-containing species, including O_2–O_4, O_2N_2, and O_1N_2 class species, are predominant in the extracts with double bond equivalent (DBE) values of 2–28 and carbon numbers (CNs) of 15–50. The oxygen atoms exist in furan rings, R–O–R′, RCOOR′, and RCOR′ (R and R′ denote an alkyl or aryl group). The species in E_{ML} have more varied DBE values and CNs compared with those in E_{SSBC}. Most of the O_xN_2 ($x = 1$–2) class species have larger DBE values and CNs than the O_x class species, which might be an evidence for more abundant intermolecular associations, such as hydrogen bonds, among the O_xN_2 class species than among the O_x class species.

1. Introduction

Low-rank coals are rich in heteroatom-containing aromatics, so the utilization process is accompanied by the low thermal efficiency and serious pollution inevitably. Therefore, low-rank coals cannot be used as clean fuels. On the other hand, many aromatics, especially heteroatom-containing ones, are value-added chemicals. They were employed as ligands of fluorescence probe and DNA [1,2] and raw materials of nano electronic devices and solar cells [3–5], and used to synthesize dyes, conducting polymers and polyester materials [4,6–9]. In addition, sterenes could be used as pharmaceuticals or pharmaceutical intermediate [10]. Synthesizing these aromatics is difficult with many steps [11,12], however, the aromatics are abundant in coals. Hence, it is imperative to develop non-fuel uses for producing chemicals from coals. For this purpose, understanding the composition and structure of organic matter in coals is of crucial importance.

Gas chromatograph/mass spectrometer (GC/MS) is one of effective tools for characterizing detailed molecular structures of relatively volatile and less polar unknown compounds in coals and their derivatives [13–15]. However, it is improper for analyzing less volatile and/or strongly polar species which abound in low-rank coals due to their high oxygen content. In addition, the common existence of intermolecular interactions, such as hydrogen bonds, leads to higher apparent molecular masses in extracts,

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Nomenclature

CN	carbon number
DBE	double bond equivalent
ESI	electrospray ionization
FTICRMS	Fourier transform ion cyclotron resonance mass spectrometer
GC/MS	gas chromatograph/mass spectrometer
ML	Mengdong lignite
SSBC	Shaerhu subbituminous coal

which may be beyond the detection range (usually up to 500 *u*) of GC/MS. Hence, GC/MS could not provide a comprehensive analysis of the extracts involving all kinds of species. Electrospray ionization (ESI) coupled to Fourier transform ion cyclotron resonance mass spectrometer (FTICRMS) broadens the detection range of GC/MS to 1000 *u* or even larger due to its good respond to macromolecules. In addition, ESI has high selectivity for ionizing polar species in complex mixtures [16,17].

As a powerful analytical tool, ESI FTICRMS has been widely used in recent years [18–25]. Accurate molecular mass and unique molecular formula can be acquired due to the ultrahigh resolution and high mass accuracy of FTICRMS. Therefore, ESI FTICRMS provides an effective approach for analyzing complex compounds in fossil fuels, such as petroleum products [26,27], shale oils [28–30], and bio-oils [31–33]. It has been widely used in analyzing acidic compounds in coal derivates in negative-ion mode [34,35]. However, identification of oxygen-containing species in coals and coal-derived liquids using positive-ion mode was rarely reported.

In the study, two Chinese coals were extracted with petroleum ether under ultrasonication. The extracts were analyzed with GC/MS to investigate the biomarkers and their biotic input, and ESI FTICRMS in positive-ion mode was employed to understand molecular composition of oxygen-containing species in the extracts.

Table 1
Proximate and ultimate analyses (wt.%) of SSBC and ML.

Sample	Proximate analysis			Ultimate analysis (daf)				$S_{t,d}$
	M_{ad}	A_d	VM_{daf}	C	H	N	O[a]	
SSBC	12.20	5.31	37.91	66.81	3.37	0.66	29.09	0.07
ML	8.20	11.11	44.00	59.98	3.01	0.63	36.33	0.06

[a] By difference.

2. Experimental section

2.1. Materials and methods

Shaerhu subbituminous coal (SSBC) and Mengdong lignite (ML) were collected from Shanshan, Xinjiang and Northeastern Inner Mongolia, respectively. They were pulverized to pass through a 200-mesh sieve followed by desiccation in a vacuum at 80 °C for

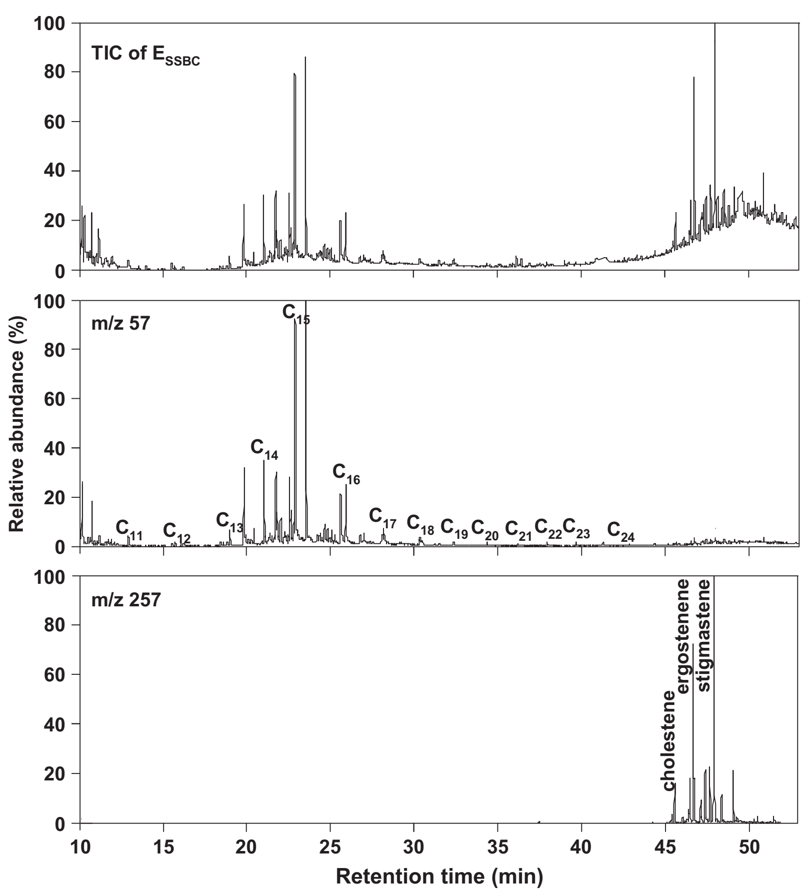

Fig. 1. Total ion chromatogram of E_{SSBC} and selective ion chromatograms of alkanes and sterene in E_{SSBC}.