



## Full Length Article

# Characterization of nitrogen and sulfur-containing species in Zhaotong lignite and its extracts from ultrasonic extraction

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## ABSTRACT

Zhaotong lignite (ZL) was sequentially extracted with cyclohexane, carbon disulfide, methanol, acetone, and isometric carbon disulfide/acetone mixed solvent to afford extracts 1–5 (E<sub>1</sub>–E<sub>5</sub>) under ultrasonic radiation at room temperature. In addition, ZL was characterized with solid-state <sup>13</sup>C nuclear magnetic resonance (SS <sup>13</sup>C NMR), Raman spectrometer and X-ray photoelectron spectrometer (XRPES), while the extracts were analyzed with a gas chromatograph/mass spectrometer along with a positive-ion (PI) and negative-ion (NI) electrospray ionization Fourier transform ion cyclotron resonance mass spectrometer (ESIFTICRMS). According to the characterization with SS <sup>13</sup>C NMR, aliphatic carbons count for 59.5% of all the organic carbons in ZL, and each aromatic cluster contains 2 or 3 aromatic rings on average. The pyrrolic nitrogen and sulfones are the most abundant nitrogen and sulfur forms, respectively, in ZL based on the analysis with XRPES. ESIFTICRMS resolved thousands of basic and non-basic species, and the molecular masses are mainly concentrated in the range of 350–600 and 300–500 *u*, respectively. Acidic S<sub>1</sub>O<sub>3</sub> class species with double bond equivalent values of 3–8 and carbon numbers of 6–39 are dominant species and could be attributed to acidic group-substituted thiophenes. Main nitrogen-containing species detected in the PI mode are basic N<sub>1</sub>O<sub>0–3</sub>, N<sub>2</sub>S<sub>2</sub>, and N<sub>2</sub>O<sub>1–8</sub>S<sub>1–2</sub>. Most of the species were speculated to contain some core structures, such as pyridines, pyrimidines, or pyrazines.

## 1. Introduction

Small molecular components were considered to constitute coal mobile phase [1–3], which has significant influence in coal conversion, such as coal coking [4] and pyrolysis [5]. However, most of their chemical compositions are indefinable due to their compositional complexity and the limitation of analytical instruments. Revealing the compositions and structural features of extractable organic matter at molecular level facilitates the efficient utilization of coals [6–9]. Moreover, since the emissions of NO<sub>x</sub> and SO<sub>x</sub> from coal combustion have brought about serious environmental pollutions, understanding detailed chemical structures of nitrogen-containing organic compounds (NCOCs) and sulfur-containing organic compounds (SCOCs) in coals is of great importance for avoiding the emissions of the species [10,11] and using the species as chemicals.

Although nitrogen and sulfur take up a small proportion in coals, they play an important role in coal properties and structures [12–14].

Multiple direct and non-destructive techniques, such as solid-state <sup>13</sup>C nuclear magnetic resonance (SS <sup>13</sup>C NMR) [15,16] and X-ray photoelectron spectrometer (XRPES) [17,18], were applied to analyzing carbon types and heteroatom forms. In general, nitrogen in coals mainly exists in the form of pyrrolic, pyridonic, amino, quaternary, and pyrrolidonic nitrogens [19]. The sulfur atoms in coals are mainly present in pyrite, sulfates, and SCOCs. SCOCs generally exist in sulfones, thiophenes, mercaptans or thiophenols, and sulfoxides [20]. However, conventional methods cannot provide information on the detailed chemical structures of NCOCs and SCOCs. Gas chromatograph/mass spectrometer (GC/MS) is widely used to analyze soluble coal derivatives (SCDs), but its low sensitivity and the limitation of standard library make it difficult to effectively characterize the heteroatom-containing compounds (HACOCs) in SCDs.

As an efficient and rapidly developed mass spectrometer, Fourier transform ion cyclotron resonance mass spectrometer (FTICRMS) [21–27] possessing high mass accuracy and high sensitivity, has been

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## Nomenclature

CDS	carbon disulfide	FTICRMS	Fourier transform ion cyclotron resonance mass spectrometer
$^{13}\text{C}$ NMR	$^{13}\text{C}$ nuclear magnetic resonance	GC/MS	gas chromatograph/mass spectrometer
CNs	carbon numbers	HACOCs	heteroatom-containing organic compounds
DBE	double bond equivalent	MF	molar fraction
$E_1$ – $E_5$	extracts 1–5	MMs	molecular masses
EBE	electron binding energy	NCOCs	nitrogen-containing organic compounds
ESI	electrospray ionization	$R_1$ – $R_4$	residue 1–4
ESIFTICRMS	electrospray ionization Fourier transform ion cyclotron resonance mass spectrometer	SCDs	soluble coal derivatives
ER	extraction residue	SCOCs	sulfur-containing organic compounds
		XRPEs	X-ray photoelectron spectrometer
		ZL	Zhaotong lignite

widely used in analyzing petroleum [28,29], bio-oil [30,31], and SCDs [32,33], especially in identifying HACOCs [34–36]. Combining FTICRMS with GC/MS and other analytical techniques, more structural information on HACOCs in SCDs was obtained [37–41]. Recently, FTICRMS equipped with electrospray ionization (ESI), i.e., ESIFTICRMS proved to be an effective tool for identifying basic and non-basic species in SCDs [42,43].

In this investigation, we examined the chemical structures of HACOCs, especially NCOCs and SCOCs, in the extracts from ultrasonic extraction of Zhaotong lignite (ZL collected from Zhaotong coal mine, Yunnan Province, China) using multiple analytical techniques.

## 2. Experimental

### 2.1. Materials

ZL was pulverized to pass through a 200-mesh sieve (particle size < 74  $\mu\text{m}$ ) followed by desiccation in a vacuum at 80 °C for 24 h before use. The proximate and ultimate analyses of ZL are listed in Table S1. The solvents cyclohexane, carbon disulfide (CDS), methanol, and acetone used in the experiment are analytical reagents and were distilled prior to use.

### 2.2. Sequential ultrasonic extraction of ZL

As shown in Fig. 1, 25 g ZL was extracted with 500 mL cyclohexane in a 1000 mL beaker placed in an ultrasonic bath for 30 min. After stratification, the supernatant was filtrated to filtrate and filter cake. The extraction was repeated until the filtrate was nearly colorless to

ensure that the soluble species were extracted exhaustively. All the filtrates were merged and concentrated using a rotary evaporator to afford extract 1 ( $E_1$ ) and the filter cake was desiccated as residue 1 ( $R_1$ ). With the same treatment,  $R_1$  was sequentially extracted with CDS, methanol, acetone, and isometric CDS/acetone mixed solvent to afford extract 2 ( $E_2$ ) and residue 2 ( $R_2$ ), extract 3 ( $E_3$ ) and residue 3 ( $R_3$ ), extract 4 ( $E_4$ ) and residue 4 ( $R_4$ ), and extract 5 ( $E_5$ ) and final extraction residue (ER), respectively. The sequential ultrasonic extraction was repeated 3 times and the errors for the extract yields are less than 3%.

### 2.3. Analyses of ZL with SS $^{13}\text{C}$ NMR, Raman spectrometer, and XRPEs

ZL was analyzed on a Bruker Avance III spectrometer at a  $^{13}\text{C}$  frequency of 100.63 MHz. A 5 mm diameter zirconia rotor loaded about 200 mg ZL was rotated at 14 kHz. The spectral width, recycle delay time, and contact time were adjusted to 10 kHz, 0.5 s, and 1 ms, respectively. PeakFit software was used to curve fit the  $^{13}\text{C}$  NMR spectrum for getting the information of different carbon types [37].

Raman spectrum of ZL was taken using a Bruker Raman Spectroscopy Senterra with an excitation laser wavelength of 532 nm at room temperature. It was also fitted into D and G peaks.

A Thermo Fisher ESCALAB 250Xi XRPEs was used for characterizing elemental composition on ZL surface. It was operated at 150 W with a monochromatic Al K $\alpha$  X-ray source. All the calculations of electron binding energy (EBE) for nitrogen and sulfur were carried out to the main C 1s peak at 284.8 eV. The peak fitting was performed with PeakFit software for XRPEs [37,40].

### 2.4. Analyses of $E_1$ – $E_5$ with GC/MS and ESIFTICRMS

$E_1$ – $E_5$  were analyzed with a Hewlett-Packard 7890/5975 GC/MS, which is fitted with a capillary column coated with HP-5 (cross-link 5% PH ME siloxane, 60 m length, 0.25 mm inner diameter, 0.25  $\mu\text{m}$  film thickness) and a quadrupole analyzer and operated in electron impact (70 eV) mode. The capillary column was heated at 5 °C  $\text{min}^{-1}$  from 60 to 300 °C and held at 300 °C for 5 min. The data analysis was performed on ChemStation software. Compounds were identified by comparing mass spectra with NIST11 library data.

A Bruker apex-ultra 9.4 T FTICRMS coupled with an ESI source was used to analyze the  $E_1$ – $E_5$ . It was operated in positive ion (PI) and negative ion (NI) modes, respectively. The analytical method and data processing were previously reported elsewhere [44,45].

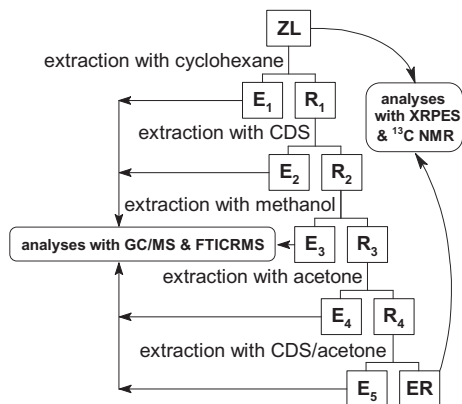


Fig. 1. Procedure for sequential ultrasonic extraction of ZL.

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