Molecular characterization of heteroatomic compounds in a high-temperature coal tar using three mass spectrometers

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ABSTRACT

A high-temperature coal tar (HTCT) was extracted by petroleum ether (PE) and the extract (denoted by PE-HTCT) was characterized using three mass spectrometers to obtain and compare molecular compositional information. Gas chromatography/mass spectrometry detected molecules with low molecular weight and polarity such as hydrocarbons. A time-of-flight MS coupled with an atmospheric solids analysis probe ion source realized rapid and in-situ analysis of compounds with mid-polarity in PE-HTCT without sample pretreatment. An electrospray ionization (ESI) Orbitrap MS was used to characterize heteroatom-containing compounds in PE-HTCT. Most heteroatomic species identified by ESI-Orbitrap MS contained oxygen, nitrogen, or both atoms, and the total percentage of both O_o and N_n species was approximate 13%. Ketene and furan derivatives were identified in O_o class, as well as aliphatic amine compounds, azoles, aniline and pyridine derivatives for N_n class. The combination of three mass spectrometers gave a detailed characterization of coal tar and provided a full view of the corresponding constituents.

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1. Introduction

Coal tar, a byproduct of coal carbonization/gasification, contains complex chemicals that are otherwise difficult to acquire from other fossil fuels such as gas and oil [1]. In general, a wide variety of aromatic chemicals including phenols, polycyclic aromatic hydrocarbons (PAHs) and heterocyclic compounds exist in coal tar, depending on the reaction temperature and the nature of original coals [2]. The complex compositions make coal tar an important feedstock for value-added substances and materials [3]. Meanwhile, carcinogenic components, PAHs, have become one of the most widely measured groups of environmental pollutants [4]. Therefore, to efficiently utilize coal tar with less pollution, it is necessary to first arrive at accurate molecular mass estimate and evaluation of structural features of the coal-derived liquids. Great efforts have been contributed to characterize the mass distribution and molecular structure of coal-derived liquids. The molecular size distributions and functional groups of coal-derived liquids were analyzed by size exclusion chromatography [5] and Fourier transform infrared spectroscopy [6], respectively. The ratio of aromatics/saturates and heteroatom

distribution were determined by X-ray photoelectron spectroscopy [7], nuclear magnetic resonance [8], and X-ray absorption near edge structure [9]. Although the achievements of these analytical methods are really remarkable, revelation of the compositions of coal tar at molecular level is remaining a challenge. International Energy Agency reported coal could rival oil as the world's largest source of energy by 2017 due to the booming demand for steel and cement production, as well as electricity generation [10]. The tremendous demand for coal will facilitate the utilization of coal tar in high efficient ways and re-investigation of molecular compositions of coal tar with recently developed analytical instrumentation and methodology.

Mass spectrometry (MS), in association with a variety of sample inlet systems, has revolutionized the analysis of complex components and should be the most rapidly developed analytical technology in the last 20 years [11]. Around 45% of Pittcon Editors' Awards have honored the inventions in MS field since its establishment in 1996. Various ion sources and mass analyzers have developed that dramatically increase the sensitivity, accuracy and resolution of mass spectrometers.

Herod and co-workers have developed MS methods such as laser desorption (LD)-MS and matrix-assisted laser desorption/ionization (MALDI)-MS for the characterization of heavy hydrocarbons from coal, petroleum and kerogen [12–16]. Broader molecular mass distributions were detected from coal-derived liquids compared to other mass spectrometric techniques [17], because laser desorption ionization could

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ionize molecules with relatively higher molecular mass [18]. Compared to LD-MS, MALDI-MS improves the sensitivity to high-mass material and expands the detection range of molecular mass up to m/z 270,000 for fossil fuels [14,19,20]. At the meantime, the type of mass analyzer most widely used with LD and MALDI is time-of-flight (TOF), which can well separate ions with relative high mass-to-charge ratio (m/z). Herod et al. also investigated two-dimensional gas chromatography (GC × GC) coupled to TOF-MS in the characterization of heavy hydrocarbons. Compared with GC/MS, the procedure certified particularly effective in identification of n-alkanes and other saturates, which accumulate in the recycle solvent [21].

The difficulty in characterization of complex components in coal tar is converting molecules with different polarities into gaseous ions that can be detected while at the same time preserving the properties of interest [22]. In this work, three MS systems with different ion sources and mass analyzers developed in recent years were used to analyze the petroleum ether extract of a high-temperature coal tar (HTCT), which is obtained in the coking process at 1000 °C. GC/MS is a relative traditional MS technique for the analysis of chemicals from fossil fuels [23]. Sample has to be gasified (up to 300 °C) before injecting into electron ionization (EI), the ion source. Thus EI is especially suitable for analyzing small, volatile and thermally stable molecules with low polarities such as the light fraction of coal tar [24]. For nonvolatile and thermally labile components with relatively higher polarities in coal tar, electrospray ionization (ESI) equipped in Orbitrap MS and atmospheric solids analysis probe (ASAP) coupled with TOF-MS applied in this work are better choices. ESI is especially suitable for the ionization of polar heteroatomic species in fossil fuels [25]. ASAP, an ambient ionization technique invented in 2005, can provide in-situ analysis of samples with mid-polarity in various phases with minimum or without sample pretreatment [26]. The characteristics of coal tar such as high viscosity and heterogeneity make a challenge for MS ionization, but can be well resolved by ambient ionization because of its noninvasiveness in sampling [27,28]. The combination of three mass spectrometers gives an overview of the components in coal tar as much as possible.

For the analysis of complex mixture like coal tar, mass analyzer with enough qualitative ability is required. Although the resolving power of quadrupole mass analyzer in GC/MS is much lower than that of TOF and Orbitrap, the fragmentation patterns induced by a highly energetic process in the ion source of GC/MS can facilitate accurate determination of structural features of the compounds [29]. TOF and Orbitrap provide high and ultrahigh resolving power, respectively, for accurate mass measurement to assign elemental compositions of fossil fuels [30,31]. Compared to TOF, Orbitrap is a relatively new mass analyzer commercialized by Thermo–Fisher Scientific as a part of hybrid LTQ Orbitrap instrument in 2005 [32].

Historically, analysis of constituents in coals and coal derivatives required prior time-consuming isolation and involved difficult separation schemes. Fractional distillation and chromatography separate components according to the difference in boiling point and distribution ratio, respectively. Nevertheless, it is hard to distinguish and identify individual component in complex mixtures like coal derivatives [33]. The ultrahigh resolving power of mass analyzer such as Orbitrap (100,000–240,000 at 400 m/z) enables separation and identification of elemental compositions (including isotope m/z peaks) of complicated mixtures. Orbitrap has been proven a powerful mass spectrometer for the examination of a variety of types of chemical systems due to high resolution, high-mass accuracy (2–5 ppm) and good dynamic range (over 10) [34]. Compared to separational methods, MS with ultrahigh resolving power may distinguish compounds at molecular level.

In this paper, GC/MS, ASAP-TOF MS and ESI-Orbitrap MS were applied for the analysis and comparison of the components in an extract of HTCT. The combination of three MS systems gave a detailed characterization of coal tar and provided a full view of the corresponding constituents.

2. Experimental

2.1. Sample preparation

HTCT was collected from Qitaihe Coking Plant (Heilongjiang, China) and the corresponding proximate and ultimate analyses of HTCT are shown in Table 1. At room temperature, 2 g HTCT was exhaustively extracted with 100 mL petroleum ether (PE, boiling range 60–90 °C) under ultrasonic condition for half an hour. PE used in the experiments was commercial analytical reagent (Xilong Chemical Co., Ltd, Guangdong, China) and distilled prior to use with a rotary evaporator (R-134, Büchi Labortechnik AG, Flawil, Switzerland). The extractable species were collected and condensed using the rotary evaporator to remove the solvent and obtain the extract (PE-HTCT).

2.2. Calculation of extraction yield

$$E = \frac{W_1}{(100 - M_{ad} - A_{ad}) \times W/100} \times 100\% \tag{1}$$

The extraction yield was calculated using Eq. (1) as follows: E is the extraction yield, %; W is the weight of HTCT, g; A_{ad} is the ash of HTCT, %; M_{ad} is the moisture of HTCT, %; and W_1 is the weight of PE-HTCT, g.

2.3. Mass analysis

The first MS system applied to the sample analysis was a GC/MS (Model 7890/5975, Agilent Technologies, USA) equipped with a capillary column coated with HP-5MS (cross-link 5% PH ME siloxane, 60 m length, 0.25 mm inner diameter, and 0.25 μm film thickness) and a quadrupole analyzer with an m/z range from 33 to 500. Helium was used as the carrier gas at a flow rate of 1 mL/min and a split ratio of 20:1.The capillary column was heated at a rate of 5 °C/min from 60 to 300 °C and held at 300 °C for 5 min. The ion source temperature of GC/MS was set at 230 °C and operated in electron impact (70 eV) mode. Data were acquired and processed using Chemstation (E.02.02.1431).

An ASAP (Model ASAP™, IonSense, USA) ion source coupled with a TOF MS (Model G6210, Agilent Technologies, USA) was also used to analyze the coal tar extract. The configuration of ion source has been described previously [35]. A melting point (mp) capillary with 25 mm length and 1.7 mm outer diameter was fixed on the center of a probe. Sample was dipped on the end of the mp capillary and introduced directly into the ion source with the ASAP probe. Corona discharge current and capillary voltage were set to 4.0 μA and 4000 V, respectively. The temperatures of desolvation and drying nitrogen gas with flow rate of 9 L/min were set to 350 °C and 300 °C, respectively. Positive ion mode was chosen and the mass spectra were acquired with m/z from 60 to 1000. Data were processed using the software of Agilent MassHunter WorkStation Qualitative Analysis (Version B.06.00).

An ultrahigh resolution MS (LTQ-Orbitrap XL, Thermo-Fisher Scientific, USA) coupled with an ESI source with positive ion mode was the third MS system to analyze the sample. The source voltage was set to 4.0 kV, the capillary voltage to 35 V, the capillary temperature to 150 °C, and the tube lens voltage offset to 125 V. Flow rates of the

Table 1
Proximate and ultimate analyses of HTCT from Qitaihe (wt.%).

Proximate analysis		Ultimate analysis (daf)				
M_{ad}	A_d	C	H	N	S	O_{diff}
1.53	0.13	90.61	6.09	0.99	0.59	1.72

Daf: dry and ash-free base; M_{ad}: moisture (air dried base); A_d: ash (dry base, i.e., moisture-free base); and diff: by difference.
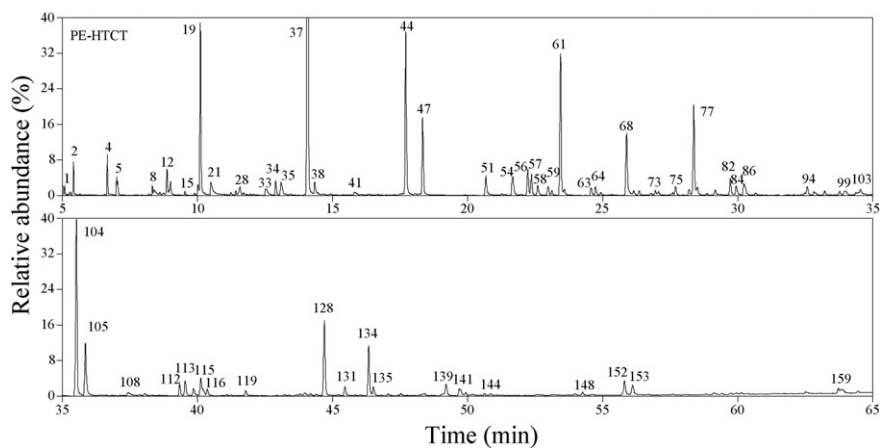
Fig. 1. Total ion chromatograms of the PE-HTCT (37: part of peak).
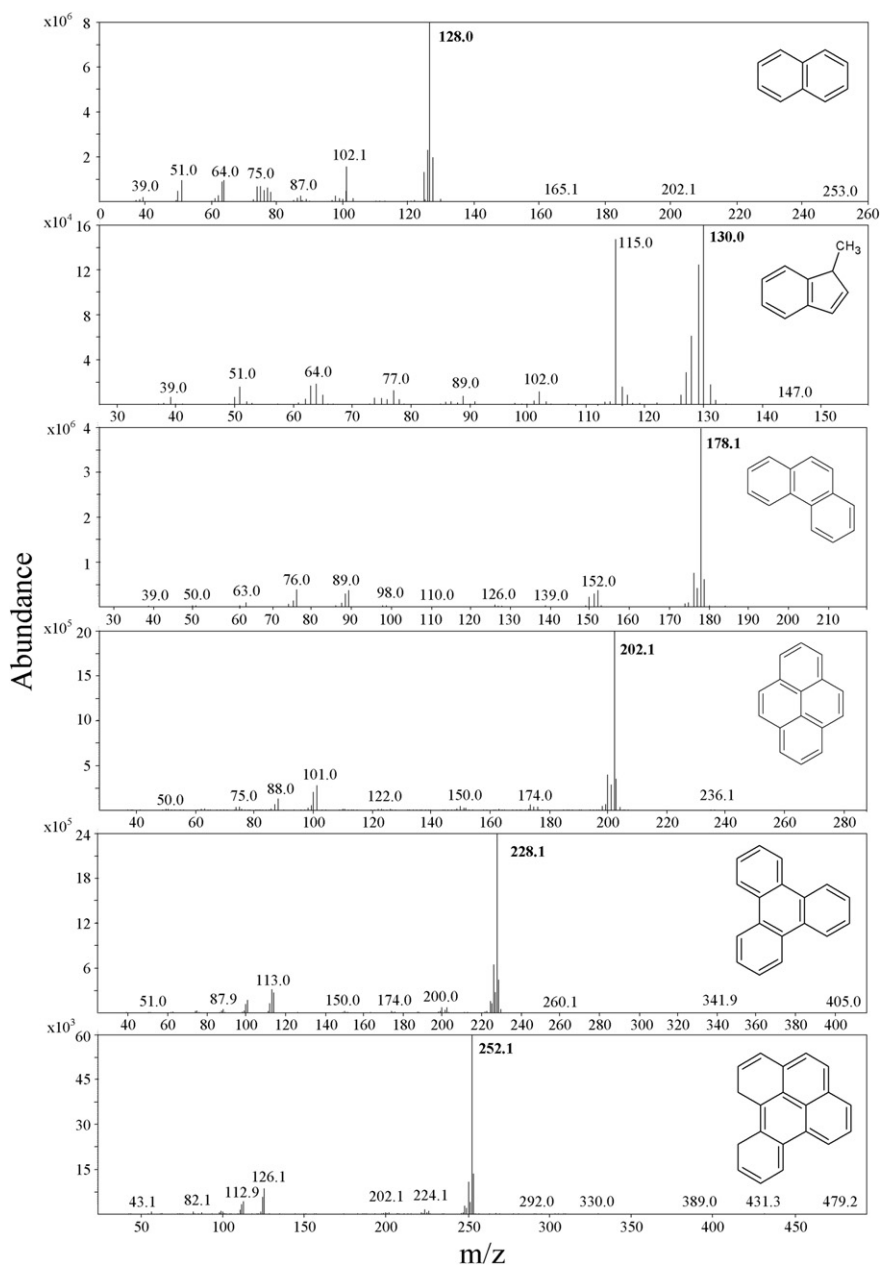

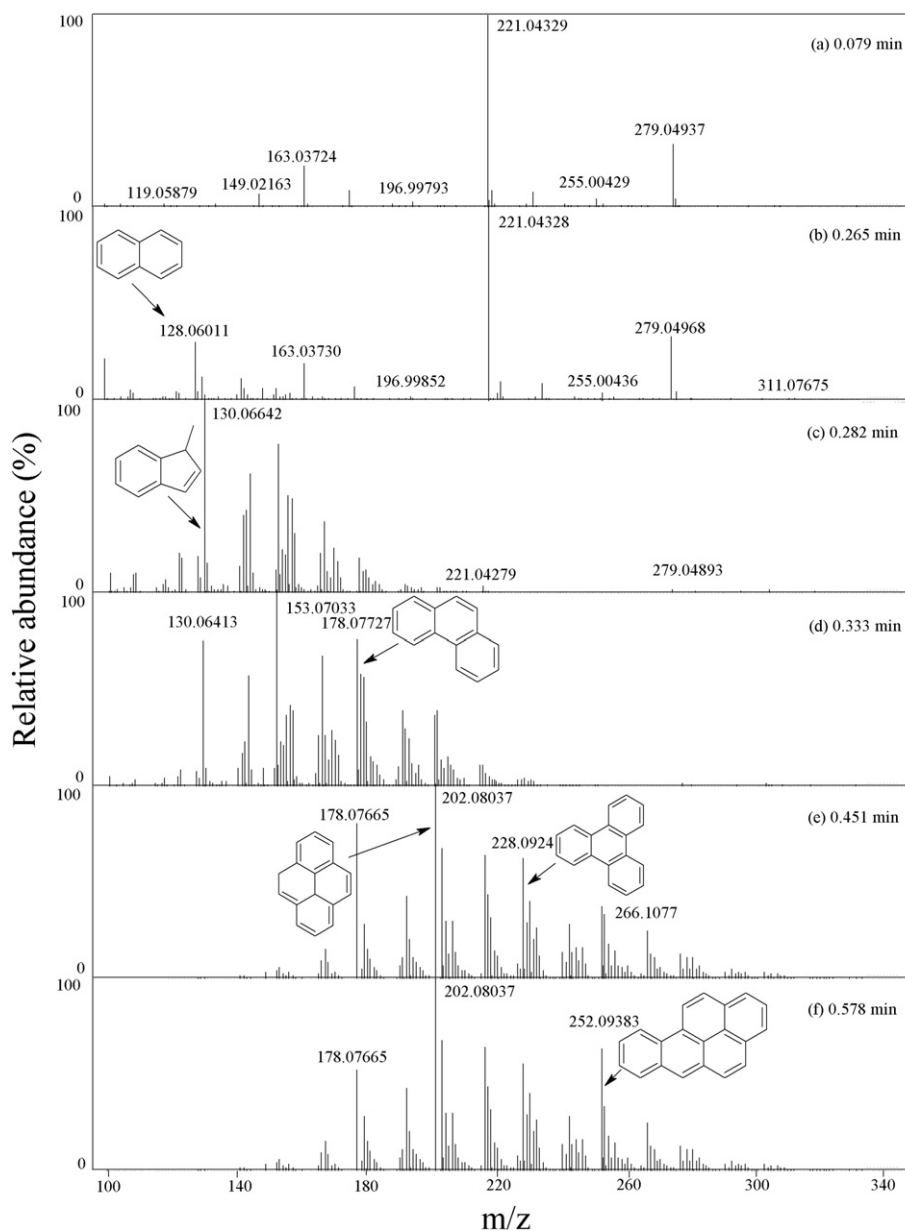**Fig. 2.** Mass spectra of selected compounds in the PE-HTCT obtained by GC/MS.

Fig. 3. Mass spectra of the PE-HTCT obtained using ASAP-TOF MS.

aux gas, sweep gas and sheath gas were set to 0.02, 0.01 and 7 arbitrary unites. The temperatures of vaporizer and capillary were 164.6 °C and 150 °C, respectively. The detected mass weight ranged from 50 to 1000 Da. Thermo Xcalibur 2.2 SP1.48 was used for data processing.

3. Results and discussion

3.1. Characterization using GC/MS

Non-aqueous phase were separated through the ultrasonic extraction for the following GC/MS analysis [36]. According to Eq. (1), the extraction yield of PE-HTCT is around 40%. The total ion chromatograms of PE-HTCT obtained by GC/MS are shown in Fig. 1. A total of 160 compounds were detected and the corresponding chemical information is listed in Table S1. The molecular mass of identified species distributed from 92 to 252 Da and molecular structures for the selected compounds with relatively high content are shown in Fig. 2. Polycyclic aromatic compounds were the major components in PE-HTCT and the three

most highest content compounds were naphthalene, phenanthrene and indene. The aromatics were primarily 1 to 4 aromatic-ring compounds due to depolymerization of macromolecules during coal tar production. The amount of heteroatom-containing compounds was relatively low, which was consistent with the characteristics of GC/MS, not a good detector for polar organic compounds. Some heteroatom-containing compounds with medium polarity such as benzofuran, p-cresol, and dibenzo[b,d]furan (in Fig. 1) were relatively abundant.

Mass spectra from GC/MS include the information of both molecular ions and fragmentation patterns, which can determine the structural formula of ionized molecules, especially molecules with low polarity. Shown in Fig. 2 is the mass spectra of selected compounds, PAHs, in the PE-HTCT obtained by GC/MS. Anthracene, 1-methyl-1H-indene, and phenanthrene were precisely recognized with m/z 128.0, 130.0 and 178.1, respectively. Pyrene, triphenylene, and benzo[e]pyrene were also identified. These PAHs were also detected using ASAP-TOF MS (shown in Fig. 3). Sixty seven percent of identified species in the PE-HTCT using GC/MS were non-heteroatomic compounds, which might not reveal the full composition of PE-HTCT due to the
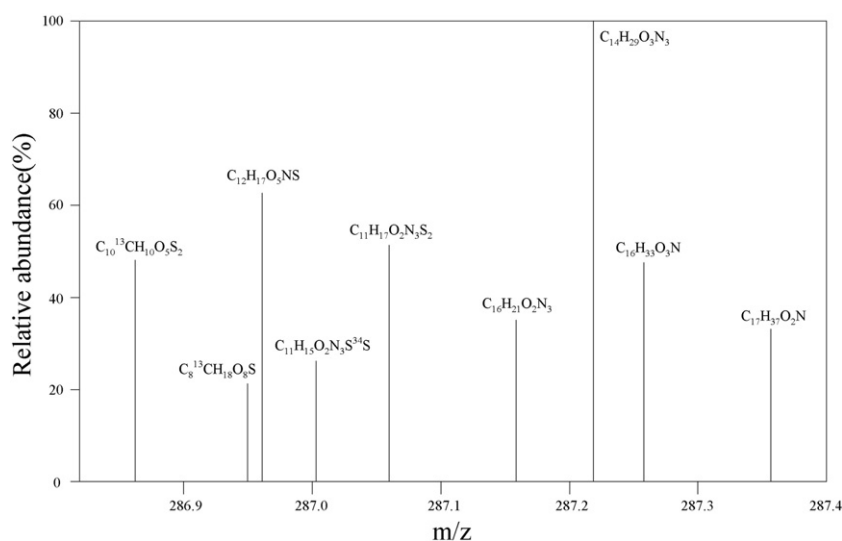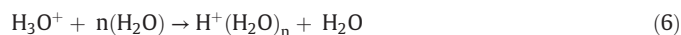
Fig. 4. Mass scale expansion at m/z 287 from the spectrum of ESI-Orbitrap MS.

measurement limit of GC/MS. From the analytical results of ASAP-TOF MS, only nine hydrocarbon compounds were detected. At the meantime, the characteristics of ASAP-TOF MS such as noninvasiveness in sampling can well analyze samples with high viscosity and heterogeneity like PE-HTCT.

3.2. Characterization using ASAP-TOF MS

The temperature of desolvation gas (N_2) in ASAP ion source played a significant role to the response signal of analyte [37]. At low temperature, the signal strength of analyte was low and there were many background signals in the mass spectrum, which hampered the identification of analyte peaks. With the increase of temperature, the signal strength of both associated ions and fragment ions gradually increased. However, if the desolvation gas temperature was too high, molecular association appeared. Therefore, the temperature of desolvation gas was optimized at 350 °C in this work. Temperature of the melting point capillary end loading sample increased from room temperature to 350 °C in 0.5 min, which induced an interesting temperature dependence of mass spectra like the temperature programming in GC/MS. However, unlike GC/MS and other mass spectrometric techniques such as MALDI-MS, the routine time for sample analysis is only tens of seconds for ASAP without sample pretreatment.

The ionization process of ASAP is triggered by corona discharge and the possible ionization mechanism via nitrogen is through the following reactions [38], where A stands for the analyte molecules. Nitrogen radical cation ($N_2^{+\bullet}$) is formed via corona discharge, then $N_2^{+\bullet}$ can react further with N_2 to generate $N_4^{+\bullet}$ (Eqs. (2)–(3)). The following ionization reactions for the analyte may involve either proton transfer (Eqs. (4)–(7)) or charge transfer (Eq. (8)) depending on the trace levels of water vapor in the source region [35].

$$N_2 + e^- \rightarrow N_2^{+\bullet} + 2e^- \tag{2}$$

$$N_2^{+\bullet} + 2N_2 \rightarrow N_4^{+\bullet} + N_2 \tag{3}$$

$$N_4^{+\bullet} + H_2O \rightarrow H_2O^{+\bullet} + 2N_2 \tag{4}$$

$$H_2O^{+\bullet} + H_2O \rightarrow H_3O^+ + OH^\bullet \tag{5}$$

$$H_3O^+ + n(H_2O) \rightarrow H^+(H_2O)_n + H_2O \tag{6}$$

$$H^+(H_2O)_n + A \rightarrow AH^+ + n(H_2O) \tag{7}$$

$$N_2^{+\bullet}/N_4^{+\bullet} + A \rightarrow A^{+\bullet} + 2N_2 \tag{8}$$

As shown in Fig. 3, compounds with low polarities (hydrocarbons) incline to be ionized to obtain radical cations through the way of charge transfer. Compared to ESI, ASAP ionization is not so "soft", because there are a certain number of fragment ions generated in the ionization process, especially from the break of bridged bonds widely existing in HTCT. Therefore, radical cations, protonated molecules and fragment ions increase the complexity of mass spectra of ASAP-MS [35,39].

Shown in Fig. 3(a) is the background spectrum after less than 5 s of the ASAP being inserted into the ion source. The mass spectrum in Fig. 3(b) is similar to that in 3(a), but partial species with molecular weight between 100 and 200 Da were desorbed from HTCT and ionized. With the extension of time up to 27 s (Fig. 3(e)), m/z range of identified species gradually shifted from 100–200 to 200–300. After 27 s, mass spectrum tended to be stable, indicating that the sample temperature reached 350 °C.

Comparing the mass spectra in Figs. 2 and 3, there are both similarities and differences. Although GC/MS and ASAP-TOF MS could detect the same compounds, the later took far less time than the former one. As listed in Table S1 to S5, more compounds were identified under ASAP-MS mode. There was few hydrocarbon compounds detected by
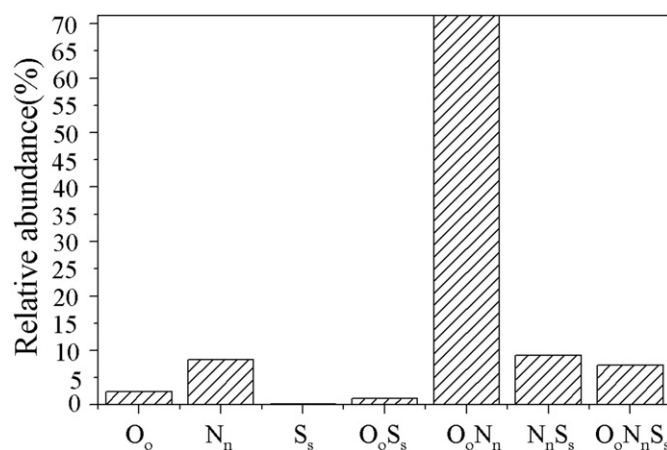

Fig. 5. Relative abundance of heteroatomic compounds in the PE-HTCT detected by ESI-Orbitrap MS.
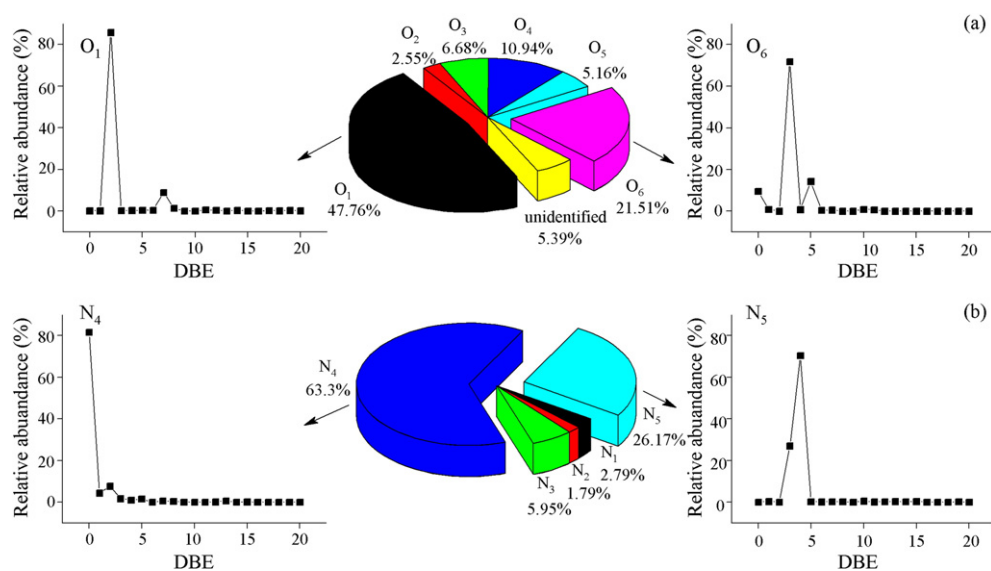
Fig. 6. Relative abundance and DBE distribution of O_o and N_n classes.

ASAP-MS, because ASAP-MS was more suitable for the ionization of medium polar species that did not contain hydrocarbons. The composition of compounds containing heteroatoms was classified according to the chemical formula as O_o, N_n, S_s, O_oN_n, O_oS_s, N_nS_s, and $O_oN_nS_s$. The molecular formula was limited to a maximum of 50 ^{12}C, 102 ^{1}H, 5 ^{14}N, 10 ^{16}O, and 2 ^{32}S atoms. The total relative abundance of both O_o and N_n species identified by ASAP-TOF MS was approximately 13%, but S_s class was not found. The polarity of S_s class is low, and therefore it was relatively difficult to be ionized by ASAP ion source. Since the introduction of oxygen and nitrogen atoms increased the molecular polarity, sulfur-containing compounds (O_oS_s, N_nS_s, and $O_oN_nS_s$ classes) were detected by ASAP-TOF MS and the total relative abundance of them was about 18%. The top 3 highest content compounds ($C_8H_{14}N_2O_2S$, $C_6H_{11}N_5OS$, $C_4H_{11}N_5OS$) accounted for approximate 12% of the total content under ASAP-TOF MS mode and none of them were identified using GC/MS.

3.3. Characterization using ESI-Orbitrap MS

As the resolving power (at m/z 400) of mass analyzer increases from ~15,000 for TOF to >100,000 for Orbitrap, separation and identification of elemental compositions can be realized at molecular level. Thus isotope peaks can be identified by Orbitrap-MS. Shown in Fig. 4 is a mass scale expansion at m/z 287. Nine components were distinctly separated within 0.5 Da, which could not be realized by GC/MS and TOF-MS.

Fig. 5 shows the relative abundance of heteroatomic compounds in the PE-HTCT detected by ESI-Orbitrap MS. Due to the ionization selectivity of ESI source, the relative abundance of sulfur-containing compounds was much less than that of oxygen- and nitrogen-containing compounds. Shown in Fig. 6 is the relative abundance of selected heteroatomic compounds (O_o and N_n classes) in PE-HTCT detected by Orbitrap MS. The relative abundance distribution is determined by
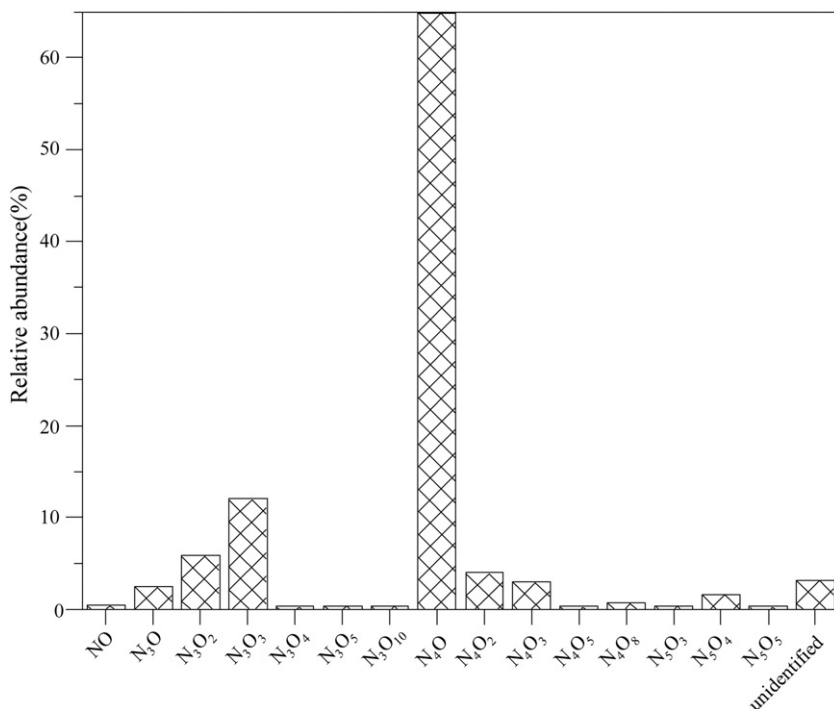

Fig. 7. Relative abundance of N_nO_o species in the PE-HTCT detected by ESI-Orbitrap MS.

○ Hydrocarbon   Red: Compounds detected by GC/MS
△ Oxygen-containing compounds   Blue: Compounds detected by ASAP-TOF MS
▽ Nitrogen-containing compounds   Green: Compounds detected by ESI-Orbitrap MS
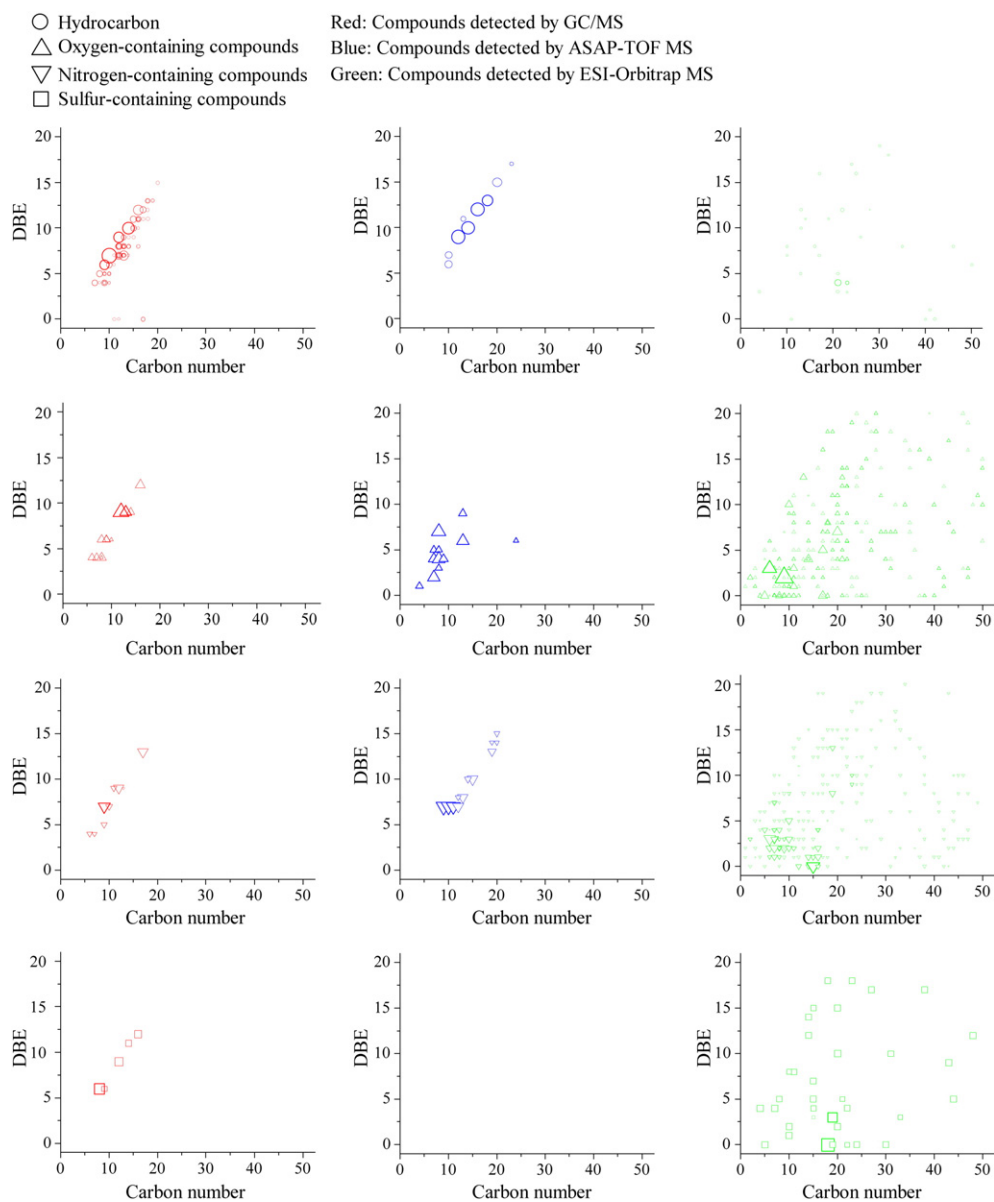□ Sulfur-containing compounds

Fig. 8. DBE versus carbon number of various heteroatom-containing compounds in the PE-HTCT.

dividing the abundance of a specified class of compounds by the sum of abundance of the corresponding heteroatomic class. The accurate molecular formulas are obtained from the mass spectra with high resolution and in turn indicate the degree of unsaturation for molecules, denoted as double bond equivalent (DBE). Each double bond or alicyclic ring increases a DBE number and eliminates two hydrogen atoms. Fig. 6(a) provides detailed information of the relative abundance distribution for oxygen-containing species and shows the DBE distributions for the top 2 O_o classes. Compounds with DBE 2 and 3 were the most abundant organic species identified in O_1 and O_6 classes, respectively. It indicated that most identified species in O_1 and O_6 classes were not aromatics because the minimum DBE number for aromatics is 4. Hence, the unsaturated compounds might be ketene and furan derivatives, respectively, and the former ones were not detected by GC/MS. As shown in Fig. 6(b), the contents of N_4 and N_5 classes were obviously higher than those of other N_n classes. The most abundant species in N_4 class was the saturated ones, which might be aliphatic amine compounds [40]. In N_5 class, most aromatic species were identified with DBE between 3 and 4, which were possibly azoles and aniline/pyridine

derivatives, respectively. Anilines and azoles were detected by neither GC/MS nor ASAP-MS.

Fig. 7 provides a detailed fingerprint of the distribution of relative abundance for O_oN_n class in the PE-HTCT. Evidently most of the O_oN_n compounds mainly contain nitrogen rather than oxygen (N_4O, N_4O_2, N_4O_3, and N_3O_2), and are therefore more basic to exhibit a higher efficiency of ionization under positive ion mode [41,42]. Basic nitrogen compounds (BNCs) mainly include pyridine, quinolone, amide and amine, etc. O_oN_n class should be the predominant BNCs in PE-HTC as shown in Fig. 5. In all of the O_oN_n groups, a series of species with DBE < 4 were detected, suggesting that amines and/or amides exist in each N_nO_o group. N_4O groups are the most abundant components in O_oN_n class, which contains possible amide (DBE < 4) or amine (DBE < 4) in accordance with the DBE value. Oxygen atoms of N_4O may be present in amide or hydroxyl groups.

Analytical results obtained from the three MS systems are compared in Fig. 8. The least amount of compounds was indentified using GC/MS and most of them were hydrocarbons. Although much more species were detected by ASAP-TOF MS and ESI-Orbitrap MS, only a tiny portion

of the species was hydrocarbons. Unlike previous report analyzing coal derived liquids using MALDI-MS [17], carbon number of the compounds detected by GC/MS and ASAP-TOF MS was less than 20 (a relatively low molecular weight compared to molecules identified by MALDI-MS), and the corresponding DBE mainly distributed between 0–10. Furthermore, there was an approximate linear relationship between the DBE value and carbon number, which was also found in middle-temperature coal tar due to the increase of double bond or aromatic ring [43]. Compared to GC/MS and ASAP-TOF MS, ESI-Orbitrap MS was equipped with an ion source specified for polar compounds and a mass analyzer with ultra-high resolution power. Thus much more heteroatomic compounds were detected by ESI-Orbitrap MS, which highly extended the measurement range in both carbon number (mass weight) and DBE (degree of unsaturation) in Fig. 8. In previous work, MALDI-TOF-MS could improve sensitivity to high-mass material but with loss of resolution [20]. For ESI-Orbitrap MS, components with enough molecular weight (up to m/z 6000) could be identified and the sensitivity was kept a high level at the meantime [44].

High-resolution MS can provide a detailed fingerprint of chemical composition for complex mixtures like petroleum and coal derivatives. Both TOF and Orbitrap are high-resolution MS, and it is necessary to compare them for better application in coal chemistry. Shown in Fig. S1 is the comparison of physical and analytical features of TOF and Orbitrap. Theoretically, the resolving power of TOF is unlimited if the flight path for ions is prolonged. But the flight path extention is limited by instrumental design. Multipass TOF are capable of ultrahigh resolution ($R \geq 100{,}000$), which is very close to that of Orbitrap. However, a certain degree of ions can be lost during the multi-reflection process, inducing the missing of MS peaks for trace components in coal derivatives. Thus the resolving power of TOF is inversely proportional to the detection limit. Compared to TOF, Orbitrap can realize the characterization of more abundant species in complex mixtures like petroleum and coal derivatives as a routine method [45,46].

4. Conclusions

Three MS systems were applied in the characterization of PE-HTCT to give an overview of the components as much as possible. Sixty seven percent of identified species in the PE-HTCT using GC/MS were hydrocarbons, but only a tiny portion of hydrocarbons was detected by ASAP-TOF MS and ESI-Orbitrap MS, which were better choices for the identification of heteroatom-containing compounds. The relative abundance of sulfur-containing compounds (O_oS_s, N_nS_s, and $O_oN_nS_s$ classes) indentified by ASAP-TOF MS was about 18%, but S_s class was not found. It indicates that the introduction of oxygen and nitrogen atoms increased the molecular polarity. With ultrahigh resolving power, Orbitrap MS isolates and identifies individual compounds in coal tar without prior time-consuming separation. Much more molecular information was obtained and highly extended the measurement range in both carbon number (mass weight) and DBE (degree of unsaturation). Due to the ionization selectivity of ESI source, the relative abundance of detected sulfur-containing compounds was much less than that of oxygen- and nitrogen-containing compounds. Each analyzer has both advantages and defects, and complementary advantages can promote better understanding of heteroatomic compounds at molecular levels.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.fuproc.2015.04.020.

References

[1] M. Granda, C. Blanco, P. Alvarez, J.W. Patrick, R. Menéndez, Chemicals from coal coking, Chem. Rev. 114 (2014) 1608–1636.
[2] M. Zander, Aspects of coal tar chemistry/a review, Polycycl. Aromat. Compd. 7 (1995) 209–221.
[3] H. Borwitzky, G. Schomburg, Separation and identification of polynuclear aromatic compounds in coal tar by using glass capillary chromatography including combined gas chromatography–mass spectrometry, J. Chromatogr. A 170 (1979) 99–124.
[4] S.A. Wise, B.A. Benner, G.D. Byrd, S.N. Chesler, R.E. Rebbert, M.M. Schantz, Determination of polycyclic aromatic hydrocarbons in a coal tar standard reference material, Anal. Chem. 60 (1988) 887–894.
[5] D.W. Hausler, L.T. Taylor, Size exclusion chromatography of organically bound metals and coal-derived materials with inductively coupled plasma atomic emission spectrometric detection, Anal. Chem. 53 (1981) 1227–1231.
[6] K.S. Seshadri, D.C. Young, D.C. Cronauer, Characterization of coal liquids by 13C N.M.R. and FT-I.R. spectroscopy-fractions of oils of SRC-I and asphaltenes and preasphaltenes of SRC-I and SRC-II, Fuel 64 (1985) 22–28.
[7] K.D. Bartle, D.L. Perry, S. Wallace, The functionality of nitrogen in coal and derived liquids: an XPS study, Fuel Process. Technol. 15 (1987) 351–361.
[8] D.T. Alien, L. Petrakis, D.W. Grandy, G.R. gavalas, B.C. Gates, Determination of functional groups of coal-derived liquids by N.M.R. and elemental analysis, Fuel 63 (1984) 803–809.
[9] M. Kasrai, J.R. Brown, G.M. Bancroft, K.H. Tan, J.-M. Chen, Characterization of sulphur in coal from sulphur L-edge XANES spectra, Fuel 69 (1990) 411–414.
[10] IEA, Medium-term Coal Market Report 2012, in: OECO (Ed.) International Energy Agency, Paris, 2012.
[11] Z.-H. Wang, The Method of Spectral Technology and Organic Matter (in Chinese), China Light Industry Press, Beijing, 2011.
[12] M.-J. Lázaro, A.A. Herod, M. Cocksedge, M. Domin, R. Kandiyoti, Molecular mass determinations in coal-derived liquids by MALDI mass spectrometry and size-exclusion chromatography, Fuel 76 (1997) 1225–1233.
[13] I. Suelves, C.A. Islas, A.A. Herod, R. Kandiyoti, Comparison of fractionation methods for the structural characterization of petroleum residues, Energy Fuel 15 (2001) 429–437.
[14] A.A. Herod, C.-Z. Li, J.E. Parker, P. John, C.A.F. Johnson, G.P. Smith, P. Humphrey, J.R. Chapman, R. Kandiyoti, D.E. Games, Characterization of coal by matrix-assisted laser desorption ionization mass spectrometry. I. The Argonne coal samples, Rapid Commun. Mass Spectrom. 8 (1994) 808–814.
[15] A.A. Herod, C.-Z. Li, B. Xu, J.E. Parker, C.A.F. Johnson, P. John, G.P. Smith, P. Humphrey, J.R. Chapman, R. Kandiyoti, D.E. Games, Characterization of coal by matrix-assisted laser desorption mass spectrometry. II. Pyrolysis tars and liquefaction extracts from the Argonne coal samples, Rapid Commun. Mass Spectrom. 8 (1994) 815–822.
[16] C.-Z. Li, A.A. Herod, P. John, C.A.F. Johnson, J.E. Parker, G.P. Smith, P. Humphrey, J.R. Chapman, M. Rahman, R.R.F. Kinghorn, R. Kandiyoti, D.E. Games, Characterization of kerogens by matrix-assisted laser desorption ionization mass spectroscopy, Rapid Commun. Mass Spectrom. 8 (1994) 823–828.
[17] M. Millan, T.J. Morgan, M. Behrouzi, F. Karaca, C. Galmes, A.A. Herod, R. Kandiyoti, The high-mass component (>m/z 10 000) of coal tar pitch by matrix-assisted laser desorption/ionisation mass spectrometry and size-exclusion chromatography, Rapid Commun. Mass Spectrom. 19 (2005) 1867–1873.
[18] X. Fan, X.-Y. Wei, Z.-M. Zong, Plume Analysis in Laser Desorption and Ablation, LAP LAMBERT Academic Publishing, Saarbrücken, 2012.
[19] P. John, C.A.F. Johnson, J.E. Parker, G.P. Smith, A.A. Herod, C.-Z. Li, P. Humphrey, J.R. Chapman, R. Kandiyoti, Molecular masses up to 270 000 u in coal and coal-derived products by matrix assisted laser desorption ionization mass spectrometry (MALDI-MS), Fuel 73 (1994) 1606–1616.
[20] A.A. Herod, Y.Q. Zhuo, R. Kandiyoti, Size-exclusion chromatography of large molecules from coal liquids, petroleum residues, soots, biomass tars and humic substances, J. Biochem. Biophys. Methods 56 (2003) 335–361.
[21] J.F. Hamilton, A.C. Lewis, M. Millan, K.D. Bartle, A.A. Herod, R. Kandiyoti, Comprehensive two-dimensional gas chromatography coupled to time-of-flight mass spectrometry of coal liquids produced during a coal liquefaction process, Energy Fuel 21 (2007) 286–294.
[22] X. Fan, L. Chen, S.-Z. Wang, Y. Qing, X.-Y. Wei, Y.-P. Zhao, A.-L. Zheng, J.-L. Zhu, C.-Y. You, Analysis of Geting bituminous coal by electrospray ionization and direct analysis in real time mass spectrometry, Anal. Lett. 47 (2014) 2012–2022.
[23] C. Yang, Z.D. Wang, B.P. Hollebone, X. Peng, M. Fingas, M. Landriault, GC/MS quantitation of diamondoid compounds in crude oils and petroleum products, Environ. Forensic 7 (2006) 377–390.

[24] X. Fan, X.-Y. Wei, Z.-M. Zong, Application of gas chromatography/mass spectrometry in studies on separation and identification of organic species in coals, Fuel 109 (2013) 28–32.
[25] A.A. Herod, Limitations of mass spectrometric methods for the characterization of polydisperse materials, Rapid Commun. Mass Spectrom. 24 (2010) 2507–2519.
[26] C.N. McEwen, R.G. McKay, B.S. Larsen, Analysis of solids, liquids, and biological tissues using solids probe introduction at atmospheric pressure on commercial LC/MS instruments, Anal. Chem. 77 (2005) 7826–7831.
[27] M.-Z. Huang, C.-H. Yuan, S.-C. Cheng, Y.-T. Cho, J. Shiea, Ambient ionization mass spectrometry, Annu. Rev. Anal. Chem. 3 (2010) 43–65.
[28] Y.-G. Wang, X.-Y. Wei, H.-L. Yan, D.-L. Shi, F.-J. Liu, P. Li, X. Fan, Y.-P. Zhao, Z.-M. Zong, Structural features of extraction residues from supercritical methanolysis of two Chinese lignites, Energy Fuel 27 (2013) 4632–4638.
[29] S. Tsuge, H. Ohtani, Structural characterization of polymeric materials by pyrolysis-GC/MS, Polym. Degrad. Stab. 58 (1997) 109–130.
[30] K.-N. Qian, G.J. Dechert, Recent advances in petroleum characterization by GC field ionization time-of-flight high-resolution mass spectrometry, Anal. Chem. 74 (2002) 3977–3983.
[31] A.E. Pomerantz, O.C. Mullins, G. Paul, J. Ruzicka, M. Sanders, Orbitrap mass spectrometry: a proposal for routine analysis of nonvolatile components of petroleum, Energy Fuel 25 (2011) 3077–3082.
[32] A. Makarov, E. Denisov, A. Kholomeev, W. Balschun, O. Lange, K. Strupat, S. Horning, Performance evaluation of a hybrid linearion trap/orbitrap mass spectrometer, Anal. Chem. 78 (2006) 2113–2120.
[33] Z.-G. Wu, Compositional Analysis of Complex Organic Mixtures by Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry, College of Arts and Sciences, Florida State University, United States, 2004. 184.
[34] Q. Hu, R.J. Noll, H. Li, A. Makarov, M. Hardman, R. Graham Cooks, The orbitrap: a new mass spectrometer, J. Mass Spectrom. 40 (2005) 430–443.
[35] S.-Z. Wang, X. Fan, A.-L. Zheng, Y.-G. Wang, Y.-Q. Dou, X.-Y. Wei, Y.-P. Zhao, R.-Y. Wang, Z.-M. Zong, W. Zhao, Evaluation of atmospheric solids analysis probe mass spectrometry for the analysis of coal-related model compounds, Fuel 117 (2014) 556–563.
[36] M. Sun, X.-X. Ma, Q.-X. Yao, R.-C. Wang, Y.-X. Ma, G. Feng, J.-X. Shang, L. Xu, Y.-H. Yang, GC-MS and TG-FTIR study of petroleum ether extract and residue from low temperature coal tar, Energy Fuel 25 (2011) 1140–1145.
[37] C.N. McEwen, Atmospheric-pressure Solids Analysis Probe (ASAP), Encyclopedia of Analytical Chemistry, John Wiley & Sons, Ltd, 2006.
[38] C. Petucci, J. Diffendal, Atmospheric solids analysis probe: a rapid ionization technique for small molecule drugs, J. Mass Spectrom. 43 (2008) 1565–1568.
[39] Y.-G. Wang, X.-Y. Wei, J. Liu, Z.-K. Li, S.-Z. Wang, Y.-H. Wang, G.-J. Kang, X. Fan, Z.-M. Zong, Analysis of some coal-related model compounds and coal derivates with atmospheric solids analysis probe mass spectrometer, Fuel 128 (2014) 302–313.
[40] A.E. Lyuts, V.Z. Gabdrakipov, I.A. Shlygina, V.A. Petropavlov, Photoelectron spectra of saturated nitrogen-containing organic compounds, J. Struct. Chem. 27 (1987) 629–651.
[41] P. Li, Z.-M. Zong, Z.-K. Li, Y.-G. Wang, F.-J. Liu, X.-Y. Wei, Characterization of basic heteroatom-containing organic compounds in liquefaction residue from Shenmu–Fugu subbituminous coal by positive-ion electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry, Fuel Process. Technol. 132 (2015) 91–98.
[42] Z.-K. Li, Z.-M. Zong, H.-L. Yan, Z.-H. Wei, Y. Li, X.-Y. Wei, Identification of basic nitrogen compounds in ethanol-soluble portion from Zhaotong lignite ethanolysis by positive-ion electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry, Fuel 141 (2015) 268–274.
[43] N. Pan, D.-C. Cui, R.-L. Li, Q. Shi, K.H. Chung, H.-Y. Long, Y.-Y. Li, Y.-Y. Zhang, S.-Q. Zhao, C.-M. Xu, Characterization of middle-temperature gasification coal tar. part 1: bulk properties and molecular vompositions of distillates and basic fractions, Energy Fuel 26 (2012) 5719–5728.
[44] M. Scigelova, A. Makarov, Advances in bioanalytical LC-MS using the Orbitrap™ mass analyzer, Bioanalysis 1 (2009) 741–754.
[45] Lu Chen, Xing Fan, Shou-Ze Wang, Teng-Gao Zhu, Xian-Yong Wei, Chang-Chun Zhou, Yun-Peng Zhao, Jing-Pei Cao, Xiao-Yan Zhao, Chun-Yan You, Ji-Liang Zhu, A.-L. Zheng, Molecular characterization of heteroatomic compounds in Shengli lignite extracts using orbitrap mass spectrometry (accepted), Energy Sources Part A (2014).
[46] K.O. Zhurov, A.N. Kozhinov, Y.O. Tsybin, Evaluation of high-field orbitrap Fourier transform mass spectrometer for petroleomics, Energy Fuel 27 (2013) 2974–2983.