Identification of nitrogen-polyaromatic compounds in asphaltene from co-processing of coal and petroleum residue using chromatography with mass spectrometry

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Abstract Asphaltene, from co-processing of coal and petroleum residues is one of the most precious and complex molecular mixtures existing, with tremendous economic relevance. Asphaltene was separated by Soxhlet extraction with methylbenzene and then divided into three parts by distillation. Gas chromatography (GC) and high-performance liquid chromatography (HPLC) were coupled with quadrupole time-of-flight mass spectrometry (Q-TOF MS) to separate and characterize organic nitrogen species in the distillates of asphaltene at molecular level. Molecular mass of compounds was mainly distributed from 150 to 600 u. Number of rings plus double bonds (rdb) and synchronous fluorescence spectra indicated that most of the organonitrogen compounds (NPAC) contained heterocyclic aromatic rings, including pyridines, anilines, quinolins, pyrroles, carbazoles and indoles plus various alkyl groups. Constant-wavelength synchronous fluorescence spectrometry (CWSFS) indicated NPAC with 2–3 rings were the main structures of organonitrogen compounds and the corresponding structural information was proposed. Some organic nitrogen isomers were separated and identified by atmospheric pressure chemical ionization (APCI) GC-Q-TOF MS and electrospray ionization (ESI) HPLC-Q-TOF MS. The methodology applied here contained chromatographic injection of the diluted sample using conventional columns sets and Data Analysis 4.2 software. Identifying molecular structures provides a foundation to understand all aspects of coal-derived asphaltene, enabling a first-principles approach to optimize resource utilization.

Keywords Co-processing of coal and petroleum residue · Asphaltene · Heterocyclic aromatic rings · GC-Q-TOF MS · HPLC-FL-Q-TOF MS

1 Introduction

Co-processing of coal and petroleum residues is a promising way for converting coal and petroleum residues into oil and an amount of residues. The content of asphaltene in residues is up to 40%, it is an important precursor to gasification, synthesis carbon materials and asphalt. As complex mixture, it is difficult to separate and identify of composite of asphaltene (Zhang et al. 2002; Ying et al. 2009; Xu et al. 2013). In fact, asphaltene, which is rich in aromatic compounds such as polycyclic aromatic hydrocarbons (PAHs) and believed as the polar fraction, has the N, O, S atoms, some of which substitute the carbon in the aromatic chain normally (Gargiulo et al. 2016). Soxhlet extraction, a nondestructive separation technique, can well separate and enrich compounds with similar solubility and polarity from a mixture. Generally, the residues components are separated into several fractions based on the different solubility in n-hexane (n-heptane), tetrahydrofuran (THF) and toluene. The composition that can be dissolved in benzene or toluene-soluble but undissolved in alkanes-insoluble fraction is defined as asphaltene (Mullins et al. 2012; Wu and Kessler 2015). While the complexity compounds cannot be represented by a single model or representative structure and required accurate perspectives...
distributions and structural features of these residues. One of the most important, understanding the modes of occurrence and distribution of heteroatoms in residues is also necessary for potential application.

N-polyaromatic compounds is widely existed in coal and petroleum residues, it could be used as photoconductors, semiconductors (Plater and Jackson 2003) and they are valuable constituents of pharmacologically active synthetic compounds and agrochemical intermediates (Li et al. 2015; Matzke et al. 2015; Gargiulo et al. 2016). N-polyaromatic compounds (NPAC) generally were classified into two types: neutral pyrrolic and basic pyridinic. The neutral organonitrogen consists of indole, pyrrole, carbazole and their alkylated analogues, while the basic organonitrogen contains pyridines, quinolines, benzoquinolines and their alkylated analogues (da Silva et al. 2014). Thus, it is essential to characterize these structures in order to understand their roles and behaviors, also to find effective approaches to separate and effectively utilize.

GC coupled to different mass spectrometry detectors, including GC-Q-TOF MS, has been proven a powerful tool to separate and analyze complex components in the complex fuel-derived mixtures, such as coal tars, pitches, and petroleum asphaltenes, especially for lower molecular mass (MM) components (Beens et al. 2000; Barman et al. 2001; da Silva et al. 2014).

The majority of the compounds in asphaltene are not volatile enough for GC analysis, HPLC–MS is a better choice with higher molecular mass, and/or lower thermal stability. Reversed-phase (RP) LC accompanied by ESI is commonly used for investigation of polar compounds, like NPAC. It was reported that isomers in beeswax and in coal could be separated and identified using HPLC with PAH column in CH$_3$OH system (Ares et al. 2015; You et al. 2015). These compounds in asphaltene were usually detected by UV or diode array (Smith et al. 2009; Zubkova 2011), fluorescence (George et al. 2010; Zubkova 2011) (FL) and MS detectors (Smith et al. 2009). Researchers (Wang et al. 2013) speculated that coal asphaltene liquefied at different temperatures consisted of similar aromatic structure, mainly 2–3 rings condensed nucleuses, by UV–Vis absorption spectra of coal asphalten in THF solvent. CWSFS, which differs from the common fluorescence method and scans excitation wavelength and emission wavelength synchronously, is widely used to elucidate the fundamental properties of polycyclic aromatic hydrocarbons of complex mixtures like asphaltenes (Goncalves et al. 2004; Abdallah and Yang 2012; Pereira et al. 2014; Wu and Kessler 2015). It has better selectivity, higher sensitivity and less interference than UV–Vis absorption spectra. CWSFS presents the size of aromatic nucleuses of asphaltenes, and the increase of asphaltene aromaticity leads to the increase of fluorescence intensity. Fluorescence spectroscopy is not a very sensitive method, containing fluorophore (George et al. 2010). Sometimes deviation exists when molecular diameter of the asphaltene is measured by Fluorescence depolarization (FD) study (Abdallah and Yang 2012). With high qualitative ability and mass accuracy, Time-of-flight mass (TOF) analyzer can well separate and identify the elemental composition and chemical information, including carbon number, heteroatom content and isotopic distributions. Polar molecules (polar heteratomic species, basic compounds with quinolones and pyridines rings) could be ionized by ESI source; while lower polarity molecules and neutral nitrogen species with pyrroles, indoles and carbazoles rings could be ionized by APCI source. Roussis et al. who first directly measured high-molecular-weight petroleum compounds reported bimodal asphaltene molecular weights of 300 < $m/z$ < 20,000 using a hybrid magnetic sector–TOF tandem mass spectrometer (McKenna et al. 2013). However, there are many isomers with monomeric molecular weight and molecular aggregation in asphaltene, it is difficult to characterize these molecules by MS analysis.

In this work, the GC-APCI-Q-TOF MS and HPLC-FL-ESI-Q-TOF MS were applied in the speciation of NPAC of asphaltene derived from co-processing coal and oil residues. The asphaltene was subjected to distillation instead of column chromatography which was normally complex and the attendant risk of sample loss (da Silva et al. 2014). We also got several cleaner mass spectra to verify the isomers. Analytical information such as retention times, $m/z$, error, msiga as well as rdb was used to identify the compounds. Fluorescence spectra were complementary to predict the aromatic structures of asphaltenes that were mainly inferred by the rdb values.

2 Materials and methods

2.1 Chemicals and sample

Coal sample was collected from Shenfu coal mine. Petroleum slurry was from Shijiazhuang Refining & Chemical. THF, hexane and methylbenzene were commercial analytical reagents supplied from Sinopharm (China) and were further distilled before use. Methanol and acetonitrile were purchased from Thermo Fisher scientific (USA) with purity above 99.9%.

2.2 Preparation of asphaltene distillates

The co-processing of coal and oil slurry with a weight ratio of 1:1 was operated at 450 °C and in the pressure of 8 MPa in N$_2$ for 8 h (Wu et al. 2012), and the resultant residue was named COR. COR was treated with hexane for 2 h and
then insoluble substance was extracted with THF by Soxhlet extraction for 8 h. The THF-soluble fraction, called asphalt, was obtained by reduced pressure distillation after removing THF. Asphaltene was got finally by extracting asphalt in methylbenzene with Soxhlet extractor for 8 h and then separated into three parts according to distillation range: fraction a (<100 °C), fraction b (100–200 °C) and fraction c (>200 °C). The fractions were centrifuged and then diluted with methanol before analysis, shown as Fig. 1.

3 Characterizations

3.1 GC-APCI-Q-TOF MS spectrometry

The fraction a and b were analyzed by GC-APCI-Q-TOF MS system, which was performed with a GC-650 (Bruker, German) and a Q-TOF MS spectrometer (Bruker, German) equipped with APCI source. The column set was formed by BR-5ms capillary column (selectivity similar to 5% diphenyl/95% dimethyl polysiloxane) with 30 m length, 0.25 mm internal diameter and 0.25 μm film thickness (Bruker, German). The carrier gas was nitrogen at a flow rate of 1 mL/min. The injection was achieved at 250 °C with a 1:200 split ratio and an injection volume of 1.0 μL. The temperature was kept at 50 °C for 2 min and reached 300 °C at 8 °C/min and for 10 min. In the APCI source, nebulizer pressure, capillary voltage, dry heater, and flow rate of dry gas were set to 3.0 bar, 3000 V, 250 °C and 2.5 L/min, respectively. Data were collected over a mass range of 50–500 Daltons.

3.2 HPLC-FL-ESI-QTOF-MS spectrometry

All distillates, a, b and c, were analyzed by an HPLC (Thermo, USA)-fluorescence spectrophotometer (HITACHI F-7000, Japan)-ESI-QTOF-MS. Samples (5 μL) were injected into the HPLC equipped with a Zorbax PAH column (4.6 mm id × 25 mm; 5 μm particle size, Agilent, USA) by an autosampler with a 0.5 mL/min isocratic elution (80:20 methanol/water) flow rate, and temperature of the column was maintained at 25 °C.

CWSFS was operated as follow: the spectrometer was set to scan at a rate of 240 nm/min with a slit width of 5 nm. Synchronous spectra covered a 240–500 nm range at a constant wavelength difference of 14 nm between emission and excitation wavelengths. PMT voltage was 400 V.

In the ESI source, capillary voltage, nebulizer pressure, dry heater, and flow rate of dry gas were set to 4500 V, 2.0 bar, 350 °C, 220 °C and 10 L/min, respectively. The separated analytes were monitored by the Q-TOF-MS with m/z from 50 to 1000 in positive ion mode.

Elemental Analysis was operated on elemental analyzer (vario M-CUBE, Germany).

4 Results and discussion

4.1 Analysis by double bond equivalence and fluorescence spectra

Asphaltene produced by co-processing of coal and oil slurry accounted for more than 80% (weight percentage) of asphalt, the amount of nitrogen in this asphaltene is about 0.7% which is relatively low compared to coal (varying from 1% to 2%) (Barman et al. 2001; da Silva et al. 2014), many N-polyaromatic compounds were tentatively identified of which mass spectral fragmentation patterns are very unique and easily identified.

Species were detected as protonated molecules: [M + H]^+ ion both in Figs. 2 and 3. Figure 2a, b showed the APCI (+)-Q-TOF MS results for fraction a and b separated by GC. Figure 3a–c showed the ESI (+)-Q-TOF MS spectra of fraction a, b and c separated by HPLC, respectively. More than one hundred peaks were detected, sometimes chromatographic separation was not efficient, but the simultaneous sampling mode and the process of spectral deconvolution of Q-TOF MS produced a mass spectrum more reliable than those produced by scanning mass analyzers, like quadrupole analyzer. Several
compounds may flow out at same time in MS spectra, the paper focused on the compounds with relatively high intensity.

The molecular-mass of N-containing compounds in asphaltene were mainly from 150 to 600. The high resolution mass Base Peak Chromatogram (BPC) spectra offered accurate ion molecular formulas ([M + H]⁺). The ion molecular formula was limited to a maximum numbers for 5 Nitrogen, 2 Sulfur, and 10 Oxygen. The identification of compounds was mainly based on the follow parameters: retention times, ion formula ([M + H]⁺), measured m/z (Meas. m/z), deviation between measured mass and theoretical mass of the selected peak (mDa) and mSigma. MSigma is a rate describing how well the theoretical isotopic peaks match to the sample isotopic peaks. Generally, the values were set as <5 mDa for deviation and <100 for mSigma, the lower was the better. Table 1 only showed the tentatively identified N-compounds of the minimum deviation and mSigma. The composition of compound is expressed by the class of chemical formula such as CₓHᵧNᵦOᵦSᵦ. Rdb is calculated from the number of atoms and their valency indicating the degree of unsaturation for molecules. The valences of C, N, O, S and H were assumed as 4, 3, 2, 2 and 1, respectively, as follow:

\[ R + \text{db} = \frac{2 + \sum n(\text{atom}) \times (\text{valency} - 2)}{2} \]

Each double bond or naphthene increases one rdb number and eliminates two hydrogen atoms, and every increment of three rdb units results in an additional aromatic ring fused to an aromatic core (Xia et al. 2016). Table 1 listed the rdb of [M + H]⁺, and rdb (M) = rdb ([M + H]⁺) + 0.5.

The rdb of compound was combined with its CWSFS to predict the structure. As nondestructive method, Fluorescence spectroscopy was used to compare the relative sizes of aromatic ring systems of the samples separated by HPLC. The conjugated π bonds of compounds resulted in a marked shift to longer wavelengths in their fluorescence spectra. Meanwhile, the fluorescence efficiency increases significantly with the increase of aromatic rings. In consideration of the “red shift” effect caused by alkylation and heteroatom, the numbers of aromatic rings of the compounds were summarized as follows: 270–300 nm for
single-ringed aromatics, 300–340 nm for double-ringed aromatics, 340–400 nm for three aromatic rings, 400–425 nm for four aromatic rings, larger than 425 nm for five- and above five-ringed aromatics (Michels et al. 1996).

In \( \text{N}_1\text{O}_1\text{S}_1 \) \((x + \gamma \leq 2)\) group, since the minimum rdb of \([\text{M} + \text{H}]^+\) for pyridines is 3.5, compounds with rdb < 3.5 are possible amines. The species with rdb = 3.5 may be pyridines or anilines. The ones with rdb = 4.5 may be pyridines/anilines/benzene linked an aliphatic ring or an unsaturated group. The ones with rdb = 5.5 may contain an aromatic ring and aliphatic rings and/or unsaturated groups. The compounds with rdb = 6.5 may be quinolones. Figure 2a showed the MS result of part of fraction a with lower polarity and ionized by APCI. Specifically, \([\text{C}_9\text{H}_8\text{N}]^+\) appeared at 10.3 min with rdb = 6.5 was presumed to be quinolone; \([\text{C}_{16}\text{H}_{34}\text{NO}]^+\) (at 14.4 min) with rdb = 0.5 and \([\text{C}_{25}\text{H}_{50}\text{NO}_2]^+\) (at 23.5 min) with rdb = 1.5 possibly contained an amino-group. Figure 2b presented the MS result of part of fraction b also with lower polarity and ionized by APCI. For example, \([\text{C}_{12}\text{H}_{26}\text{NO}]^+\) (at 8.0 min), \([\text{C}_7\text{H}_{16}\text{NS}_2]^+\) (at 19.1 min), \([\text{C}_9\text{H}_{18}\text{NS}_2]^+\) (at 20.0 min), \([\text{C}_{18}\text{H}_{36}\text{NO}]^+\) (at 23.5 min), of which rdb was smaller than 3.5, may be O- or S- aliphatic amines; \([\text{C}_{14}\text{H}_{22}\text{NO}_2]^+\) detected at 19.7 min with rdb = 4.5 may contain a pyridine/thiophene/phenyl ring with substituent group. Figure 3 showed the MS results of part of fraction a, b and c with polarity and ionized by ESI. More specifically, saturated amines were detected in Fig. 3a, as \([\text{C}_8\text{H}_{20}\text{NS}_2]^+\)
| No. | Time 2 (min) | Time 3 (min) | Meas. m/z | Ion formula [M + H]^+ | err | mSigma | rdb of [M + H]^+ |
|-----|--------------|--------------|-----------|------------------------|-----|--------|------------------|
| 1   | 10.3         | 130.0649     | C_9H_8N   | 0.2                    | 4.2 | 6.5    |
| 2   | 12.5         | 144.0822     | C_{10}H_{10}N | 1.4                | 10.1 | 6.5    |
| 3   | 12.7         | 156.0808     | C_{11}H_{10}N | 0.0                | 37.3 | 7.5    |
| 4   | 16.4         | 158.0972     | C_{12}H_{12}N | 0.8                | 14.3 | 6.5    |
| 5   | 17.3         | 164.1433     | C_{13}H_{14}N | 0.1                | 13.6 | 3.5    |
| 6   | 18.5         | 168.0801     | C_{13}H_{10}N | 0.7                | 19.2 | 8.5    |
| 7   | 14.0         | 170.0961     | C_{13}H_{12}N | 0.3                | 14.1 | 7.5    |
| 8   | 15.8         | 172.1122     | C_{13}H_{14}N | 0.1                | 16.3 | 6.5    |
| 9   | 19.7         | 180.0815     | C_{13}H_{10}N | 0.7                | 5.8  | 9.5    |
| 10  | 19.9         | 182.0955     | C_{13}H_{12}N | 1.0                | 5.9  | 8.5    |
| 11  | 16.7         | 184.1168     | C_{13}H_{14}N | 4.7                | 12.8 | 7.5    |
| 12  | 21.2         | 194.0966     | C_{13}H_{12}N | 0.1                | 29.3 | 9.5    |
| 13  | 20.9         | 196.1097     | C_{14}H_{14}N | 2.4                | 9.2  | 8.5    |
| 14  | 21.8         | 204.0791     | C_{14}H_{10}N | 1.6                | 5.2  | 11.5   |
| 15  | 16.4         | 206.0987     | C_{14}H_{12}N | 2.3                | 77.4 | 10.5   |
| 16  | 21.4         | 208.1134     | C_{14}H_{14}N | 1.4                | 66.0 | 9.5    |
| 17  | 24.4         | 218.0963     | C_{14}H_{12}N | 0.1                | 8.8  | 11.5   |
| 18  | 46.5         | 230.0975     | C_{15}H_{12}N | 1.1                | 12.1 | 12.5   |
| 19  | 26.3         | 232.1102     | C_{15}H_{14}N | 1.9                | 3.0  | 11.5   |
| 20  | 24.6         | 244.118      | C_{15}H_{14}N | 4.9                | 64.9 | 12.5   |
| 21  | 31.1         | 254.0979     | C_{15}H_{12}N | 1.5                | 19.9 | 14.5   |
| 22  | 9.8          | 138.092      | C_{16}H_{2}NO | 0.7                | 28.8 | 3.5    |
| 23  | 10.6         | 142.1229     | C_{16}H_{18}NO | 0.3               | 28.3 | 1.5    |
| 24  | 7.7          | 158.1544     | C_{16}H_{20}NO | 0.5               | 28.0 | 0.5    |
| 25  | 7.7          | 180.1341     | C_{17}H_{18}NO | 4.2               | 6.3  | 3.5    |
| 26  | 8.0          | 200.1996     | C_{17}H_{20}NO | 1.3               | 50.0 | 0.5    |
| 27  | 12.7         | 196.0758     | C_{17}H_{12}NO | 0.2               | 75.2 | 9.5    |
| 28  | 14.1         | 210.0913     | C_{18}H_{12}NO | 0.0               | 8.7  | 9.5    |
| 29  | 7.7          | 222.088      | C_{18}H_{12}NO | 3.3               | 81.8 | 10.5   |
| 30  | 11.6         | 232.0748     | C_{18}H_{10}NO | 0.9               | 57.9 | 12.5   |
| 31  | 14.4         | 256.2617     | C_{18}H_{20}NO | 1.8               | 1.5  | 0.5    |
| 32  | 14.3         | 246.0907     | C_{19}H_{20}NO | 0.6               | 29.1 | 12.5   |
| 33  | 19.4         | 252.139      | C_{19}H_{18}NO | 0.7               | 16.1 | 9.5    |
| 34  | 23.5         | 282.2777     | C_{19}H_{16}NO | 1.4               | 32.4 | 1.5    |
| 35  | 21.4         | 274.1245     | C_{19}H_{14}NO | 1.9               | 58.7 | 12.5   |
| 36  | 13.3         | 314.1588     | C_{20}H_{20}NO | 4.9               | 50.6 | 13.5   |
| 37  | 13.3         | 432.2366     | C_{21}H_{20}NO | 4.4               | 35.2 | 17.5   |
| 38  | 11.4         | 130.067      | C_{20}H_{2}NS | 1.5               | 41.3 | 1.5    |
| 39  | 14.1         | 144.0821     | C_{20}H_{4}NS | 2.0               | 18.0 | 1.5    |
| 40  | 12.7         | 156.0808     | C_{20}H_{6}NS | 3.4               | 58.3 | 2.5    |
| 41  | 11.7         | 158.0984     | C_{20}H_{2}NS | 1.4               | 15.1 | 1.5    |
| 42  | 14.0         | 170.0961     | C_{20}H_{4}NS | 3.7               | 29.1 | 2.5    |
| 43  | 16.4         | 172.1123     | C_{20}H_{6}NS | 3.1               | 29.1 | 1.5    |
| 44  | 14.9         | 180.082      | C_{20}H_{12}NS | 2.1               | 8.3  | 4.5    |
| 45  | 16.4         | 194.0985     | C_{20}H_{16}NS | 1.2               | 46.3 | 4.5    |
| 46  | 33.0         | 204.082      | C_{21}H_{14}NS | 4.9               | 24.9 | 6.5    |
Table 1 continued

| No. | Time 2 (min) | Time 3 (min) | Meas. m/z | Ion formula [M + H]^+ | lerrl [mDa] | mSigma | rdb of [M + H]^+ |
|-----|--------------|--------------|-----------|------------------------|-------------|---------|------------------|
| 47  | 16.4         | 206.0987     | C_{12}H_{16}NS | 1.1                    | 83.3        | 5.5     |
| 48  | 21.2         | 208.1115     | C_{13}H_{18}NS | 3.9                    | 16.9        | 4.5     |
| 49  | 21.4         | 218.0982     | C_{13}H_{16}NS | 1.5                    | 33.0        | 6.5     |
| 50  | 17.1         | 220.1108     | C_{14}H_{18}NS | 4.7                    | 90.8        | 5.5     |
| 51  | 21.4         | 230.099      | C_{14}H_{16}NS | 0.7                    | 29.1        | 7.5     |
| 52  | 31.1         | 254.0979     | C_{16}H_{16}NS | 1.9                    | 40.2        | 9.5     |
| 53  | 33.0         | 218.2134     | C_{22}H_{28}NO_{2} | 2.0                    | 17.3        | -0.5    |
| 54  | 12.5         | 368.1693     | C_{23}H_{32}NO_{2} | 4.8                    | 30.1        | 15.5    |
| 55  | 23.5         | 396.3811     | C_{25}H_{30}NO_{2} | 2.5                    | 72.7        | 1.5     |
| 56  | 19.1         | 382.185      | C_{25}H_{24}NO_{2} | 4.8                    | 66.6        | 15.5    |
| 57  | 16.4         | 178.0757     | C_{26}H_{28}NO_{2} | 3.9                    | 42.1        | 0.5     |
| 58  | 20.0         | 204.092      | C_{26}H_{18}NS | 4.5                    | 57.5        | 1.5     |
| 59  | 19.7         | 252.139      | C_{28}H_{34}NO_{2} | 2.7                    | 37.4        | 4.5     |
| 60  | 13.3         | 432.2366     | C_{28}H_{34}NO_{2} | 1.0                    | 52.7        | 12.5    |
| 61  | 12.5         | 368.1693     | C_{28}H_{26}NO_{2}S | 1.4                    | 8.0         | 10.5    |
| 62  | 11.7         | 368.1694     | C_{28}H_{26}NO_{2}S | 1.5                    | 49.5        | 10.5    |
| 63  | 13.3         | 382.185      | C_{28}H_{26}NO_{2}S | 1.4                    | 64.4        | 10.5    |
| 64  | 13.3         | 432.2366     | C_{28}H_{38}NO_{2}S | 2.4                    | 75.3        | 7.5     |
| 65  | 21.2         | 338.2355     | C_{18}H_{28}NO_{4} | 2.9                    | 40.9        | 4.5     |
| 66  | 12.5         | 440.1892     | C_{22}H_{32}NO_{4} | 3.6                    | 34.1        | 16.5    |
| 67  | 12.5         | 368.1693     | C_{22}H_{38}NO_{2}S | 1.9                    | 22.6        | 5.5     |
| 68  | 13.3         | 382.185      | C_{22}H_{32}NO_{2}S | 1.9                    | 71.1        | 5.5     |
| 69  | 7.9          | 195.0929     | C_{13}H_{11}N_{2} | 1.2                    | 34.8        | 9.5     |
| 70  | 13.3         | 219.0913     | C_{13}H_{11}N_{2} | 0.4                    | 59.3        | 11.5    |
| 71  | 8.7          | 231.0872     | C_{13}H_{11}N_{2} | 4.5                    | 37.9        | 12.5    |
| 72  | 25.2         | 259.1237     | C_{14}H_{15}N_{2} | 0.7                    | 14.3        | 12.5    |
| 73  | 15.6         | 261.1362     | C_{14}H_{17}N_{2} | 2.5                    | 11.6        | 11.5    |
| 74  | 21.6         | 303.2804     | C_{20}H_{38}N_{2} | 0.9                    | 15.9        | 4.5     |
| 75  | 10.3         | 313.26       | C_{20}H_{38}N_{2} | 3.8                    | 19.1        | 6.5     |
| 76  | 10.3         | 341.2924     | C_{20}H_{38}N_{2} | 2.7                    | 43.6        | 6.5     |
| 77  | 21.4         | 511.5016     | C_{20}H_{38}N_{2} | 3.0                    | 61.0        | 5.5     |
| 78  | 14.3         | 199.091      | C_{13}H_{11}N_{2}O | 4.4                    | 27.6        | 8.5     |
| 79  | 14.0         | 213.1065     | C_{13}H_{13}N_{2}O | 4.4                    | 7.7         | 8.5     |
| 80  | 14.0         | 305.1664     | C_{20}H_{22}N_{2}O | 1.5                    | 56.0        | 11.5    |
| 81  | 19.1         | 355.2782     | C_{20}H_{32}N_{2}O | 3.8                    | 20.5        | 7.5     |
| 82  | 10.3         | 359.303      | C_{20}H_{32}N_{2}O | 2.7                    | 75.9        | 5.5     |
| 83  | 8.7          | 143.0682     | C_{8}H_{13}N_{2}S | 4.5                    | 28.0        | 2.5     |
| 84  | 14.3         | 155.0678     | C_{8}H_{13}N_{2}S | 4.1                    | 31.2        | 3.5     |
| 85  | 11.4         | 181.0824     | C_{8}H_{13}N_{2}S | 3.0                    | 18.0        | 4.5     |
| 86  | 14.3         | 195.0929     | C_{8}H_{13}N_{2}S | 2.2                    | 56.8        | 4.5     |
| 87  | 7.9          | 355.1301     | C_{8}H_{19}N_{2}S | 3.8                    | 40.9        | 15.5    |
| 88  | 17.1         | 365.1074     | C_{8}H_{19}N_{2}S | 3.3                    | 79.6        | 17.5    |
| 89  | 15.8         | 409.1774     | C_{8}H_{23}N_{2}S | 4.1                    | 46.8        | 16.5    |
| 90  | 13.3         | 409.1774     | C_{8}H_{23}N_{2}S | 4.1                    | 46.8        | 16.5    |
| 91  | 13.3         | 155.0844     | C_{8}H_{19}N_{2}O_{2} | 2.9                    | 35.8        | 3.5     |
| 92  | 8.9          | 157.0966     | C_{8}H_{13}N_{2}O_{2} | 0.5                    | 41.3        | 2.5     |
| No. | Time 2 (min) | Time 3 (min) | Meas. m/z | Ion formula [M + H]^+ | lerr [mDa] | mSigma | rdb of [M + H]^+ |
|-----|-------------|-------------|----------|------------------------|-----------|--------|-----------------|
| 93  | 10.3        | 163.1404    | C15H19N2O2 | 3.7                    | 81.5      | -0.5   |                 |
| 94  | 15.1        | 167.0843    | C15H19N2O2 | 2.8                    | 28.2      | 4.5    |                 |
| 95  | 12.8        | 175.1469    | C15H19N2O2 | 2.8                    | 28.7      | 0.5    |                 |
| 96  | 16.3        | 177.1577    | C16H21N2O2 | 2.1                    | 63.6      | -0.5   |                 |
| 97  | 19.1        | 179.0833    | C16H21N2O2 | 1.8                    | 74.7      | 5.5    |                 |
| 98  | 13.1        | 191.1732    | C16H23N2O2 | 2.2                    | 17.5      | -0.5   |                 |
| 99  | 17.8        | 191.0839    | C16H23N2O2 | 2.4                    | 35.6      | 6.5    |                 |
| 100 | 14.3        | 215.0846    | C16H23N2O2 | 3.1                    | 8.6       | 8.5    |                 |
| 101 | 22.0        | 217.0997    | C16H23N2O2 | 2.6                    | 12.4      | 7.5    |                 |
| 102 | 20.0        | 219.1136    | C16H23N2O2 | 0.8                    | 40.6      | 6.5    |                 |
| 103 | 21.9        | 221.1296    | C16H23N2O2 | 1.1                    | 49.5      | 5.5    |                 |
| 104 | 16.3        | 233.2186    | C17H29N2O2 | 3.8                    | 27.7      | -0.5   |                 |
| 105 | 23.4        | 233.1294    | C17H29N2O2 | 0.9                    | 64.9      | 6.5    |                 |
| 106 | 23.5        | 247.2352    | C17H29N2O2 | 1.1                    | 34.1      | -0.5   |                 |
| 107 | 14.6        | 246.0999    | C17H29N2O2 | 1.9                    | 21.5      | 9.5    |                 |
| 108 | 25.2        | 245.1268    | C17H29N2O2 | 1.7                    | 47.6      | 7.5    |                 |
| 109 | 25.2        | 247.1454    | C17H29N2O2 | 1.3                    | 40.0      | 6.5    |                 |
| 110 | 25.3        | 311.2659    | C18H35N2O2 | 3.4                    | 8.7       | 2.5    |                 |
| 111 | 23.7        | 399.2992    | C18H35N2O2 | 1.4                    | 49.8      | 7.5    |                 |
| 112 | 8.5         | 413.1283    | C19H35N2O2 | 0.2                    | 49.8      | 21.5   |                 |
| 113 | 14.9        | 579.2988    | C19H35N2O2 | 1.8                    | 35.9      | 22.5   |                 |
| 114 | 18.2        | 355.1308    | C19H35N2O2 | 1.1                    | 46.3      | 10.5   |                 |
| 115 | 27.1        | 361.1805    | C20H39N2O2 | 3.8                    | 97.8      | 7.5    |                 |
| 116 | 13.3        | 409.1774    | C20H39N2O2 | 0.7                    | 66.3      | 11.5   |                 |
| 117 | 21.4        | 413.2124    | C20H39N2O2 | 4.4                    | 72.4      | 9.5    |                 |
| 118 | 27.1        | 463.226     | C20H39N2O2 | 2.4                    | 20.6      | 12.5   |                 |
| 119 | 19.1        | 355.2782    | C20H39N2O2 | 0.4                    | 38.2      | 2.5    |                 |
| 120 | 23.7        | 391.2821    | C21H39N2O2 | 4.4                    | 42.2      | 5.5    |                 |
| 121 | 16.4        | 455.2201    | C21H39N2O2 | 4.9                    | 85.9      | 15.5   |                 |
| 122 | 13.6        | 161.0956    | C22H39N2O2 | 3.5                    | 32.5      | 1.5    |                 |
| 123 | 19.4        | 207.0793    | C23H39N2O2 | 2.9                    | 98.6      | 6.5    |                 |
| 124 | 21.6        | 333.315     | C23H39N2O2 | 3.8                    | 70.7      | -0.5   |                 |
| 125 | 23.5        | 375.356     | C23H47N2O3 | 2.1                    | 82.5      | -0.5   |                 |
| 126 | 23.7        | 365.1349    | C24H47N2O3 | 3.1                    | 39.5      | 12.5   |                 |
| 127 | 8.5         | 413.1283    | C24H47N2O3 | 3.6                    | 55.6      | 16.5   |                 |
| 128 | 16.4        | 445.1034    | C24H47N2O3 | 2.8                    | 78.2      | 21.5   |                 |
| 129 | 13.3        | 453.1678    | C24H47N2O3 | 4.7                    | 66.7      | 17.5   |                 |
| 130 | 18.7        | 465.1681    | C25H51N2O3 | 5.0                    | 63.8      | 18.5   |                 |
| 131 | 17.8        | 449.1734    | C25H51N2O3 | 1.9                    | 67.6      | 13.5   |                 |
| 132 | 16.4        | 455.2201    | C25H51N2O3 | 1.5                    | 99.1      | 10.5   |                 |
| 133 | 27.1        | 425.1746    | C26H51N2O3 | 3.0                    | 70.9      | 11.5   |                 |
| 134 | 31.1        | 659.2909    | C26H51N2O4 | 0.4                    | 37.4      | 26.5   |                 |
| 135 | 21.2        | 365.1348    | C26H51N2O4 | 0.4                    | 59.6      | 7.5    |                 |
| 136 | 13.3        | 453.1678    | C26H51N2O4 | 1.3                    | 42.9      | 12.5   |                 |
| 137 | 18.7        | 465.1681    | C26H51N2O4 | 1.6                    | 67.8      | 13.5   |                 |
| 138 | 23.7        | 365.1349    | C17H23N2O7 | 0.6                    | 34.8      | 8.5    |                 |
Table 1 continued

| No. | Time 2 (min) | Time 3 (min) | Meas. m/z | Ion formula [M + H]$^+$ | err | mSigma | rdb of [M + H]$^+$ |
|-----|--------------|--------------|-----------|--------------------------|-----|--------|-------------------|
|     | 2-a          | 2-b          | 3a        | 3b                       | 3c  |        |                   |
| 139 | GC           | GC           | GC        | 13.3                     | 415.2117 | C$_{29}$H$_{31}$N$_2$O$_8$ | 4.2 | 31.7 | 5.5 |
| 140 | 13.3         | 437.1948     | C$_{29}$H$_{29}$N$_2$O$_8$ | 3.0 | 29.1 | 8.5 |
| 141 | 33.0         | 463.2266     | C$_{28}$H$_{33}$N$_2$O$_{10}$ | 2.0 | 41.3 | 4.5 |
| 142 | 13.3         | 409.1774     | C$_{29}$H$_{25}$N$_2$O$_{5}$ | 1.6 | 33.4 | 12.5 |
| 143 | 27.1         | 425.1746     | C$_{29}$H$_{25}$N$_2$O$_{6}$ | 3.9 | 28.6 | 12.5 |
| 144 | 13.3         | 453.1678     | C$_{29}$H$_{25}$N$_2$O$_{7}$ | 2.2 | 72.4 | 13.5 |
| 145 | 18.7         | 465.1681     | C$_{29}$H$_{25}$N$_2$O$_{7}$ | 2.5 | 29.3 | 14.5 |
| 146 | 16.4         | 455.2201     | C$_{29}$H$_{31}$N$_2$O$_{6}$ | 2.4 | 87.8 | 11.5 |
| 147 | 33.0         | 463.2266     | C$_{29}$H$_{31}$N$_2$O$_{5}$ | 3.9 | 27.9 | 13.5 |
| 148 | 18.3         | 579.2915     | C$_{29}$H$_{41}$N$_2$O$_{10}$ | 0.3 | 10.4 | 9.5 |
| 149 | 16.4         | 158.0972     | C$_{29}$H$_{21}$N$_2$O$_{2}$ | 4.8 | 13.4 | 2.5 |
| 150 | 23.4         | 210.0897     | C$_{29}$H$_{21}$N$_2$O$_{3}$ | 2.4 | 47.3 | 5.5 |
| 151 | 18.5         | 206.094      | C$_{29}$H$_{12}$N$_2$O$_{2}$ | 1.6 | 36.1 | 6.5 |
| 152 | 17.5         | 311.318      | C$_{29}$H$_{39}$N$_4$ | 1.1 | 16.0 | 1.5 |
| 153 | 15.1         | 301.1435     | C$_{29}$H$_{21}$N$_4$ | 1.1 | 6.1 | 13.5 |
| 154 | 20.5         | 353.3638     | C$_{29}$H$_{24}$N$_4$ | 0.0 | 17.1 | 1.5 |
| 155 | 27.1         | 345.2063     | C$_{29}$H$_{25}$N$_4$ | 1.1 | 9.4 | 12.5 |
| 156 | 16.1         | 365.3642     | C$_{29}$H$_{43}$N$_4$ | 0.3 | 24.0 | 2.5 |
| 157 | 17.5         | 377.3634     | C$_{29}$H$_{45}$N$_4$ | 0.5 | 20.4 | 3.5 |
| 158 | 18.7         | 375.16       | C$_{29}$H$_{10}$N$_4$ | 0.4 | 36.4 | 18.5 |
| 159 | 21.6         | 449.457      | C$_{29}$H$_{17}$N$_4$ | 0.7 | 23.5 | 2.5 |
| 160 | 27.1         | 425.1746     | C$_{29}$H$_{21}$N$_4$ | 1.5 | 60.4 | 21.5 |
| 161 | 17.8         | 449.1734     | C$_{29}$H$_{21}$N$_4$ | 2.6 | 16.2 | 23.5 |
| 162 | 16.4         | 455.2201     | C$_{29}$H$_{27}$N$_4$ | 3.0 | 35.0 | 20.5 |
| 163 | 12.5         | 337.1997     | C$_{29}$H$_{25}$N$_4$O | 2.6 | 39.5 | 10.5 |
| 164 | 16.1         | 351.3119     | C$_{29}$H$_{39}$N$_4$O | 0.1 | 90.6 | 3.5 |
| 165 | 21.6         | 353.3321     | C$_{29}$H$_{41}$N$_4$O | 4.6 | 9.9 | 2.5 |
| 166 | 23.5         | 381.3629     | C$_{29}$H$_{45}$N$_4$O | 4.1 | 24.3 | 2.5 |
| 167 | 23.7         | 365.1349     | C$_{29}$H$_{17}$N$_4$O | 4.8 | 23.5 | 17.5 |
| 168 | 23.5         | 395.3783     | C$_{29}$H$_{21}$N$_4$O | 3.9 | 10.6 | 2.5 |
| 169 | 20.5         | 421.3913     | C$_{29}$H$_{29}$N$_4$O | 1.2 | 13.4 | 3.5 |
| 170 | 18.7         | 465.1681     | C$_{29}$H$_{21}$N$_4$O | 2.9 | 56.2 | 23.5 |
| 171 | 18.7         | 375.16       | C$_{29}$H$_{23}$N$_4$S | 3.8 | 29.6 | 13.5 |
| 172 | 27.1         | 425.1746     | C$_{29}$H$_{23}$N$_4$S | 4.9 | 56.6 | 16.5 |
| 173 | 13.3         | 415.2117     | C$_{29}$H$_{27}$N$_4$O$_2$ | 1.1 | 22.0 | 14.5 |
| 174 | 13.3         | 437.1948     | C$_{29}$H$_{25}$N$_4$O$_2$ | 2.4 | 11.2 | 17.5 |
| 175 | 31.1         | 371.2049     | C$_{29}$H$_{25}$N$_4$O$_3$ | 2.8 | 54.7 | 9.5 |
| 176 | 23.7         | 467.1114     | C$_{29}$H$_{25}$N$_4$O$_3$ | 2.5 | 36.6 | 24.5 |
| 177 | 14.9         | 579.2988     | C$_{29}$H$_{39}$N$_4$O$_4$ | 2.2 | 18.6 | 18.5 |
| 178 | 31.1         | 659.2909     | C$_{29}$H$_{39}$N$_4$O$_6$ | 4.4 | 13.4 | 22.5 |
| 179 | 14.9         | 579.2988     | C$_{29}$H$_{41}$N$_4$O$_9$ | 3.7 | 33.1 | 9.5 |
| 180 | 12.5         | 440.1892     | C$_{29}$H$_{26}$N$_4$O$_3$ | 3.6 | 4.2 | 12.5 |
| 181 | 8.9          | 338.3281     | C$_{29}$H$_{40}$N$_5$ | 0.3 | 12.6 | 2.5 |
| 182 | 17.3         | 338.2364     | C$_{29}$H$_{26}$N$_5$ | 2.5 | 34.7 | 9.5 |
| 183 | 12.3         | 440.1887     | C$_{29}$H$_{21}$N$_5$ | 1.7 | 46.0 | 21.5 |
| 184 | 20.5         | 380.3409     | C$_{29}$H$_{42}$N$_4$O | 2.6 | 18.5 | 3.5 |
and $[\text{C}_{12}\text{H}_{28}\text{NO}_2]^+$ (at 16.4 and 33.0 min, respectively); amines with unsaturated chain (rdb = 3.5) also appeared, for example, $[\text{C}_8\text{H}_{16}\text{NS}]^+$ (at 11.7 min in Fig. 3a), $[\text{C}_8\text{H}_{16}\text{NO}]^+$ (at 10.6 min, in Fig. 3b) and $[\text{C}_9\text{H}_{20}\text{NO}]^+$ (at 7.7 min in Fig. 3c); Ions with rdb = 3.5, like $[\text{C}_{8}\text{H}_{12}\text{NO}]^+$, $[\text{C}_{11}\text{H}_{18}\text{N}]^+$ (at 9.8 min and 17.3 min in Fig. 3b, separately) and $[\text{C}_{12}\text{H}_{18}\text{NO}]^+$ (at 7.7 min in Fig. 3c), probably were alkoxylated-anilines/pyridines; $[\text{C}_9\text{H}_{16}\text{NS}]^+$ and $[\text{C}_{12}\text{H}_{16}\text{NS}]^+$ (at 16.4 and 21.2 min in Fig. 3a, b separately), with rdb = 4.5, may contain an aromatic ring with substituent group; $[\text{C}_{12}\text{H}_{16}\text{NS}]^+$ (at 16.4 min in Fig. 3a) with rdb = 5.5 may consist of an

| No. | Time 2 (min) | Time 3 (min) | Meas. $m/z$ | Ion formula [M + H]$^+$ | err$|$ [mDa] | mSigma | rdb of [M + H]$^+$ |
|-----|-------------|-------------|-------------|------------------------|-----------|--------|------------------|
| 185 | 12.5        | 440.1892    | C$_{26}$H$_{26}$N$_5$S | 1.1 | 40.2 | 16.5 |
| 186 | 12.5        | 440.1892    | C$_{23}$H$_{30}$N$_5$S$_2$ | 4.5 | 66.7 | 11.5 |
| 187 | 13.3        | 432.2366    | C$_{26}$H$_{30}$N$_5$O$_2$ | 2.8 | 45.8 | 13.5 |
| 188 | 23.7        | 365.1349    | C$_{24}$H$_{17}$N$_5$O$_3$ | 0.8 | 23.0 | 13.5 |
| 189 | 13.3        | 437.1948    | C$_{26}$H$_{25}$N$_5$O$_4$ | 1.6 | 15.9 | 13.5 |
| 190 | 27.1        | 425.1746    | C$_{26}$H$_{17}$N$_5$O$_2$ | 2.5 | 35.6 | 17.5 |
| 191 | 23.5        | 396.3811    | C$_{26}$H$_{16}$N$^+$ | 0.2 | 58.8 | 2.5 |
| 192 | 13.3        | 415.2117    | C$_{26}$H$_{15}$N$_5$O$_3$ | 3.4 | 28.0 | 4.5 |
| 193 | 13.3        | 409.1774    | C$_{26}$H$_{24}$N$_5$O$_3$ | 1.8 | 52.1 | 7.5 |
| 194 | 27.1        | 425.1746    | C$_{26}$H$_{20}$N$_5$O$_2$ | 0.5 | 42.7 | 7.5 |
| 195 | 23.7        | 467.1114    | C$_{26}$H$_{22}$N$_5$O$_2$ | 0.5 | 52.6 | 10.5 |
| 196 | 13.3        | 453.1678    | C$_{26}$H$_{15}$N$_3$O$_2$ | 4.6 | 30.0 | 3.5 |
| 197 | 18.7        | 465.1681    | C$_{26}$H$_{15}$N$_3$O$_2$ | 4.2 | 67.5 | 4.5 |
| 198 | 13.3        | 453.1678    | C$_{26}$H$_{20}$N$_5$O$_2$ | 1.2 | 49.8 | 8.5 |
| 199 | 18.7        | 465.1681    | C$_{26}$H$_{20}$N$_5$O$_2$ | 0.9 | 46.5 | 9.5 |
| 200 | 12.3        | 440.1887    | C$_{26}$H$_{20}$N$_5$O$_2$ | 0.3 | 31.1 | 2.5 |
| 201 | 12.3        | 440.1887    | C$_{26}$H$_{20}$N$_5$O$_2$ | 3.7 | 13.7 | 7.5 |
| 202 | 13.3        | 453.1678    | C$_{26}$H$_{20}$N$_5$O$_2$ | 2.8 | 51.2 | 4.5 |
| 203 | 18.7        | 465.1681    | C$_{26}$H$_{20}$N$_5$O$_2$ | 3.2 | 48.9 | 5.5 |
| 204 | 15.8        | 365.1074    | C$_{26}$H$_{17}$N$_5$O$_2$ | 0.7 | 56.4 | 13.5 |
| 205 | 33.0        | 365.1427    | C$_{26}$H$_{21}$N$_5$O$_2$ | 0.4 | 60.0 | 12.5 |
| 206 | 8.7         | 407.1887    | C$_{26}$H$_{21}$N$_5$O$_2$ | 4.7 | 87.0 | 7.5 |
| 207 | 13.3        | 415.2117    | C$_{26}$H$_{17}$N$_5$O$_2$ | 4.5 | 5.1 | 9.5 |
| 208 | 13.3        | 437.1948    | C$_{26}$H$_{17}$N$_5$O$_2$ | 2.1 | 43.0 | 7.5 |
| 209 | 12.3        | 440.1887    | C$_{26}$H$_{17}$N$_5$O$_2$ | 3.7 | 24.9 | 6.5 |
| 210 | 8.7         | 407.1887    | C$_{26}$H$_{17}$N$_5$O$_2$ | 1.3 | 84.4 | 12.5 |
| 211 | 23.7        | 467.1114    | C$_{26}$H$_{22}$N$_5$O$_2$ | 2.0 | 63.0 | 14.5 |
| 212 | 33.0        | 463.2266    | C$_{26}$H$_{17}$N$_5$O$_2$ | 0.5 | 48.3 | 8.5 |
| 213 | 12.3        | 440.1887    | C$_{26}$H$_{17}$N$_5$O$_2$ | 0.3 | 15.1 | 11.5 |
| 214 | 19.1        | 579.2923    | C$_{26}$H$_{17}$N$_5$O$_2$ | 4.2 | 32.3 | 4.5 |
| 215 | 19.1        | 579.2923    | C$_{26}$H$_{17}$N$_5$O$_2$ | 0.2 | 38.4 | 8.5 |
| 216 | 19.1        | 579.2923    | C$_{26}$H$_{17}$N$_5$O$_2$ | 3.6 | 33.6 | 13.5 |
| 217 | 31.1        | 659.2909    | C$_{26}$H$_{17}$N$_5$O$_2$ | 2.3 | 46.7 | 12.5 |
| 218 | 31.1        | 659.2909    | C$_{26}$H$_{17}$N$_5$O$_2$ | 1.1 | 28.1 | 17.5 |
| 219 | 31.1        | 659.2909    | C$_{26}$H$_{17}$N$_5$O$_2$ | 3.6 | 58.7 | 21.5 |
| 220 | 31.1        | 659.2909    | C$_{26}$H$_{17}$N$_5$O$_2$ | 3.0 | 37.6 | 21.5 |
| 221 | 13.3        | 453.1678    | C$_{26}$H$_{17}$N$_5$O$_2$ | 2.6 | 55.2 | 13.5 |
| 222 | 12.5        | 440.1892    | C$_{26}$H$_{17}$N$_5$O$_2$ | 0.5 | 61.9 | 7.5 |
Identification of nitrogen-polyaromatic compounds in asphaltene from co-processing of coal...

Fig. 4  Fluorescence spectra of fraction a (a), fraction b (b) and fraction c (c) (Time in labels referred to the moment when the FL spectrometer began to scan at 240 nm at a rate of 240 nm/min. Furthermore, it took the compound 0.75 min from FL detector to MS detector. Besides, the ph referred to phenyl)
Table 2 Isomeric compounds detected in Fig. 2 and Fig. 3

| No. | Ion formula [M + H]⁺ | Meas. m/z | Experimental m/z | | Meas. m/z | Experimental m/z | | errl [mDa] | Msigma | rdb | Retention time (min) | Detected in figures |
|-----|----------------------|-----------|------------------||-----------|------------------||-----|--------|-----|------------------|------------------|
| 1   | C₆H₁₃N₂O₂            | 191.1733  | 191.1754         | | 2.1      | 14.9            | | -0.5 | 13.1 | 2a               |
| 2   | C₇H₁₃N₂O₂            | 191.1739  | 191.1754         | | 1.6      | 16.0            | | -0.5 | 13.2 | 2a               |
| 3   | C₇H₁₃N₂O₂            | 191.1732  | 191.1754         | | 2.3      | 35.9            | | -0.5 | 13.5 | 2a               |
| 4   | C₁₁H₁₇N₂O₂           | 213.1068  | 213.1022         | | 4.5      | 7.4             | | 8.5   | 14.6 | 2a               |
| 5   | C₁₁H₁₇N₂O₂           | 213.1066  | 213.1022         | | 4.4      | 4.5             | | 8.5   | 15.7 | 2a               |
| 6   | C₁₀H₁₆N₄             | 311.3185  | 311.3169         | | 1.6      | 13.0            | | 1.5   | 17.5 | 2a               |
| 7   | C₁₀H₁₆N₄             | 311.3165  | 311.3169         | | 0.5      | 24.7            | | 1.5   | 18.0 | 2a               |
| 8   | C₁₀H₁₆N₄             | 311.3178  | 311.3169         | | 0.9      | 15.2            | | 1.5   | 18.2 | 2a               |
| 9   | C₁₁H₁₇N₄             | 311.3170  | 311.3169         | | 0.1      | 15.5            | | 1.5   | 18.6 | 2a               |
| 10  | C₂₅H₅₀NO₂             | 396.3811  | 396.3836         | | 2.5      | 72.7            | | 1.5   | 23.5 | 2a               |
| 11  | C₂₅H₅₀NO₂             | 396.3813  | 396.3836         | | 2.3      | 79.0            | | 1.5   | 24.0 | 2a               |
| 12  | C₂₅H₅₀NO₂             | 396.3810  | 396.3836         | | 0.9      | 13.1            | | 3.5   | 20.9 | 2a               |
| 13  | C₂₅H₅₀NO₂             | 396.3804  | 396.3836         | | 0.3      | 17.2            | | 3.5   | 21.1 | 2a               |
| 14  | C₂₅H₅₀NO₂             | 396.3815  | 396.3836         | | 1.4      | 12.0            | | 3.5   | 21.2 | 2a               |
| 15  | C₁₁H₁₂N              | 182.0947  | 182.0964         | | 1.8      | 7.8             | | 8.5   | 19.3 | 2b               |
| 16  | C₁₁H₁₂N              | 182.0948  | 182.0964         | | 1.7      | 10.0            | | 8.5   | 19.7 | 2b               |
| 17  | C₁₁H₁₂N              | 182.0954  | 182.0964         | | 1.0      | 2.3             | | 8.5   | 19.9 | 2b               |
| 18  | C₁₁H₁₂N₂O₂           | 245.1265  | 245.1285         | | 2.0      | 32.2            | | 7.5   | 24.6 | 2b               |
| 19  | C₁₁H₁₂N₂O₂           | 245.1296  | 245.1285         | | 1.2      | 41.0            | | 7.5   | 24.8 | 2b               |
| 20  | C₁₄H₁₇N₂O₂           | 245.1298  | 245.1285         | | 1.4      | 54.4            | | 7.5   | 24.9 | 2b               |
| 21  | C₁₆H₂₅NO              | 144.0819  | 144.0808         | | 1.2      | 29.3            | | 6.5   | 12.3 | 3a               |
| 22  | C₁₆H₂₅NO              | 144.0822  | 144.0808         | | 1.4      | 10.1            | | 6.5   | 12.5 | 3a               |
| 23  | C₁₆H₂₅NO              | 144.0826  | 144.0808         | | 1.8      | 19.9            | | 6.5   | 13.3 | 3a               |
| 24  | C₁₆H₂₅NO              | 158.0984  | 158.0964         | | 2.0      | 16.6            | | 6.5   | 11.7 | 3a               |
| 25  | C₁₁H₁₂N              | 158.0977  | 158.0964         | | 1.3      | 19.5            | | 6.5   | 14.0 | 3a               |
| 26  | C₁₁H₁₂N              | 158.0972  | 158.0964         | | 0.8      | 14.3            | | 6.5   | 16.4 | 3a               |
| 27  | C₈H₁₈NS              | 355.1301  | 355.1263         | | 3.8      | 40.9            | | 15.5  | 17.1 | 3a               |
| 28  | C₈H₁₈NS              | 355.1308  | 355.1263         | | 4.4      | 42.8            | | 15.5  | 18.2 | 3a               |
| 29  | C₇H₁₄NS              | 130.0670  | 130.0685         | | 1.5      | 41.3            | | 1.5   | 11.4 | 3b               |
| 30  | C₇H₁₄NS              | 130.0666  | 130.0685         | | 1.9      | 38.4            | | 1.5   | 12.2 | 3b               |
| 31  | C₈H₁₄NS              | 144.0826  | 144.0841         | | 1.6      | 28.4            | | 1.5   | 12.2 | 3b               |
| 32  | C₈H₁₄NS              | 144.0829  | 144.0841         | | 1.3      | 32.8            | | 1.5   | 12.7 | 3b               |
| 33  | C₈H₁₄NS              | 144.0821  | 144.0841         | | 2.0      | 18.0            | | 1.5   | 14.1 | 3b               |
| 34  | C₁₂H₁₄N              | 172.1120  | 172.1121         | | 0.1      | 16.3            | | 6.5   | 15.8 | 3b               |
aromatic ring and unsaturated groups and/or aliphatic rings. Ions with \( \text{rdb} = 6.5 \), like \([C_{10}H_{10}N]^+\), \([C_{11}H_{12}N]^+\) (at 12.5 and 16.4 min in Fig. 3a, respectively) and \([C_{12}H_{14}N]^+\) (at 15.8 min in Fig. 3b), contained quinolone rings possibly.

In \( \text{N}1\text{O}_{a}\text{S}_c(a \pm c \leq 2) \) group, the molecular structure became more complex with \( \text{rdb} \) bigger than 7.5, it may contain a phenylpyridine ring/quinoline ring/amine ring/an indole ring plus an unsaturated alkyl/aliphatic ring/ester/carbonyl group. For instance, ions with \( \text{rdb} = 7.5 \), like \([C_{13}H_{14}N]^+\) (at 16.7 min, in Fig. 2b), \([C_{12}H_{14}N]^+\) (at 14.0 min in Fig. 3a) and \([C_{11}H_{10}N]^+\) (at 12.5 min in Fig. 3b), contained quinolone rings possibly.

In \( \text{N}1\text{O}_{a}\text{S}_c(a \pm c \leq 2) \) group, the molecular structure became more complex with \( \text{rdb} \) bigger than 7.5, it may contain a phenylpyridine ring/quinoline ring/amine ring/an indole ring plus an unsaturated alkyl/aliphatic ring/ester/carbonyl group. For instance, ions with \( \text{rdb} = 7.5 \), like \([C_{13}H_{14}N]^+\) (at 16.7 min, in Fig. 2b), \([C_{12}H_{14}N]^+\) (at 14.0 min in Fig. 3a) and \([C_{11}H_{10}N]^+\) (at 12.5 min in Fig. 3b), contained quinolone rings possibly.

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In \( \text{N}1\text{O}_{a}\text{S}_c(a \pm c \leq 2) \) group, the molecular structure became more complex with \( \text{rdb} \) bigger than 7.5, it may contain a phenylpyridine ring/quinoline ring/amine ring/an indole ring plus an unsaturated alkyl/aliphatic ring/ester/carbonyl group. For instance, ions with \( \text{rdb} = 7.5 \), like \([C_{13}H_{14}N]^+\) (at 16.7 min, in Fig. 2b), \([C_{12}H_{14}N]^+\) (at 14.0 min in Fig. 3a) and \([C_{11}H_{10}N]^+\) (at 12.5 min in Fig. 3b), contained quinolone rings possibly.

CWSFS could confirm partial conjecture by \( \text{rdb} \). Figure 4a presented the fluorescence spectra of fraction a separated by HPLC. There was moderate intensity fluorescence at 330 nm and 360 nm respectively due to \([C_{10}H_{9}N]^+\) and \([C_{15}H_{11}N]^+\), indicating they had a double-ringed aromatic and three aromatic structures. The weak intensity fluorescence was around 410 nm caused by \([C_{25}H_{21}NO_2]^+\) because of its four aromatic rings. All of their ions sturctures \([C_{10}H_{10}N]^+\) (with \( \text{rdb} = 6.5 \)), \([C_{12}H_{14}N]^+\) (with \( \text{rdb} = 11.5 \)) and \([C_{25}H_{22}NO_2]^+\) (with \( \text{rdb} = 15.5 \)) were supposed above shown in Fig. 4a, proving that CWSFS result was consist with \( \text{rdb} \) conjecture. Figure 4b showed the fluorescence spectra of fraction b separated by HPLC. \([C_{8}H_{11}NO]^+\), \([C_{11}H_{9}N]^+\), \([C_{13}H_{9}NO]^+\) had obvious fluorescence at 298 nm, 331 nm, 379 nm, due to structures of a single-
ringed aromatic, double-ringed aromatic, and three aromatic rings, respectively. These were also corresponding to the conjecture by rdb mentioned before. Besides that, C_{11}H_{17}NO, C_{13}H_{9}N had strong fluorescence around 280 nm and 370 nm in Fig. 4c, separately, corresponding to single aromatic ring and three aromatic rings. These verified the alkoxylated-aniline/pyridine structures inferred by rdb = 3.5 of [C_{11}H_{18}NO]^{+} and benzoquinoline/acridine/cycloheptaindole structures with rdb = 9.5 of [C_{13}H_{10}N]^{+}.

However, most of arylamines and 2-hydroxyquinoline (C_{9}H_{7}NO) cannot be effectively ionized and detected under the positive ion mode because of its relative weak basicity caused by hyperconjugation or the presence and position of the hydroxy group (Hughey et al. 2001; da Silva et al. 2014).

In N_{1}O_{2}S_{2} (x + y = 3–4) group, it became complex, structures could not be proposed just by rdb, and CWSFS could be informative sometimes. For example, [C_{20}H_{32}. NO_{2}S_{2}]^{+} (peak 5 at 13.3 min in Fig. 3a), with rdb = 5.5, may be unsaturated ketones, but it fluoresced at 290 nm indicated that it was aromatic structure.

In N_{2} group, the species with rdb = 4.5, like [C_{20}H_{35}N_{2}]^{+} appeared at 21.6 min in Fig. 2a, may be a pyridine or an aniline with an amino group, unsaturated amine was also possible. The proposed structure of compound with rdb = 5.5 ([C_{35}H_{63}N_{2}]^{+} at 21.4 min in Fig. 2a,) was indole or a pyridine or an aniline with an amino group as well as alkylated-benzimidazole. With rdb from 6.5 (as [C_{23}H_{37}N_{2}]^{+} at 10.3 min in Fig. 2a) to 12.5 (as [C_{18}H_{15}N_{2}]^{+} at 25.2 min in Fig. 2b), pyrrolic and pyridine rings may exist.

Fig. 5 EIC (a) and mass spectra (b and c) of isomers of [C_{11}H_{11}N_{2}O_{2}]^{+} (m/z = 203.0849) detected by GC-APCI-MS.
Moreover, in N2O-S (α + γ ≤ 3) group, series of species with \( rdb < 4.5 \) may have two amino groups, for example, \([C_7H_{19}N_2O_2]^+\), \([C_9H_{23}N_2O_2]^+\) and \([C_{18}H_{41}N_2O_3]^+\) (at 10.3, 13.1 and 21.6 min in Fig. 2a, separately), all with \( rdb = -0.5 \), may be saturated aliphatic amines. Species with \( rdb > 8.5 \) may contain a benzoquinoline or acridine ring.

Fig. 6 EIC (a) and mass spectra (b and c) of isomers of \([C_{13}H_{12}N]\)^+ (\(m/z = 182.0955\)) detected by GC-APCI-MS.
with an amino group besides quinoline and indole rings connected by a bridged bond, for example, \([C_{25}H_{22}NO_2]^+\) (at 12.5 min in Fig. 3a) with \(rdb = 15.5\) may consists of phenyls-pyridines or ester-quinoline and so on, estimating \(C_{25}H_{21}NO_2\) fluoresced at longer than 400 nm shown in Fig. 4a.

As shown in Table 1, \(N_\beta O_\gamma S_\delta\) (\(\beta = 3–5, \alpha + \gamma = 0–10\)) had \(rdb\) values from 1.5 to 21.5. Since the minimal \(rdb\) number for \([M + H]^+\) of an aromatic ring is 3.5, aliphatic amine compounds existed, like \([C_{18}H_{39}N_4]^+\) (\(rdb = 1.5\), at 17.5 min in Fig. 2a).

Possible structures of partial compounds comprehensively analyzed by \(rdb\) and fluorescence spectra were exhibited in Fig. 4. In addition, lower fluorescence intensity was observed when the wavelength was longer than 420 nm in Fig. 4. Since the intensity area was proportional to the concentration of the sample in diluted solution, this indicated that the compounds mainly had less than four aromatic rings. This is applied to compare among similar compounds (as is the case on N-compounds) in the same conditions.

### 4.2 Isomers

This work combined chromatography with MS to separate and analyze isomers since TOF-MS could not distinguish isomers. The existence of isomers was confirmed by the apparent difference in retention time shown in Table 2 and several clean mass spectra of isomers were presented in Fig. 5. Retention times of isomers are dependent on the
strength of reversible intermolecular forces of functional groups, molecular spatial structures, partition coefficient between stationary phase and mobile phase. Moreover, volatilities and polarities of isomers also played a major role in GC and HPLC separation, respectively (da Silva et al. 2014).

Identification of the target peaks of isomers can be simplified by using of extracted ion chromatograms (EIC). Figure 5 shown two chromatographic peaks of \([C_{11}H_{11}N_{2}O_{2}]^+\) \((m/z = 203.0849)\) detected by GC-APCI MS, indicating the existence of isomers at 20.9 min and 21.4 min. Since the rdb number of \(C_{11}H_{10}N_{2}O_{2}\) is 8, one of the possible chemical structures may be a quinoline plus various alkyl groups. Such alkyl groups with various structures induced the difference in volatilities and retention time. For another instance, Fig. 6 presented three isomers of \(C_{13}H_{11}N\) separated by GC.

Methanol, as the mobile phase, has high adsorption effects on the NPAC due to the interactions induced by hydrogen bonds O–H…N and O–H…π. Thus compounds with low polarity have long retention times in HPLC (Xia et al. 2016). For example, Fig. 7 presented two chromatographic peaks of \([C_{19}H_{17}N_{4}]^+\) \((m/z = 301.1447)\) detected by HPLC–ESI–MS, the isomers appearing at 14.2 min and 15.1 min. The possible structures of \([C_{19}H_{17}N_{4}]^+\) (rdb = 13.5) may contain carbazole/phenylalanine/phenylpyrimidine and so on. Thus isomeric compounds with different polarities led to flow out in HPLC in turn. \(C_{13}H_{9}N\) also had two isomers shown in Fig. 8.
However, specific isomer structural assignment is not obtained here. We could not get the exact position of functional groups in the aromatic chain by mass spectra. For example, it is not sure that C13H9N is benzoquinoline or acridine or phenanthridine, and so on. It proposes target for following work.

5 Conclusion

N-containing compounds were extracted from asphaltene that was produced by co-processing coal tar and oil residue and purified by Soxhlet extraction. It is proven to be an effective approach for separation and detailed characterization of three distillates of N-containing compounds by GC-APCI-Q-TOF MS and HPLC-FL-ESI-Q-TOF-MS analysis. More than two hundred N-compounds were tentatively identified, most of them contain N-polyaromatic aromatic rings, including pyridines, pyrroles, anilines, quinolones, carbazoles and indoles for N0O2Sb (b = 1–2) class. In N6SbO2Sb (b = 3–5) class, aliphatic amine may exist. CWSFS indicated structures of two or three aromatic rings were the majority of NPAC. Possible structures of partial compounds were proposed by comprehensive analysis of rdb and fluorescence spectra. Some isomers were separated. Characterization of the chemical compositions of NPAC in asphaltene should be beneficial to nitrogen removal and the effectively application.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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