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Characterization of Sulfides in Atmospheric Residue Fractions Using Selective Oxidation Followed by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

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Abstract: An improved analytical method was developed for identifying sulfide compounds from aromatic fractions in Lungu atmospheric residue (LGAR). Sulfides in residue aromatics were selectively oxidized into sulfoxides using tetrabutyl ammonium periodate (TBAP) and identified by positive-ion Electrospray Ionization Source (ESI) Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). Results showed that sulfides with lower polarity in LGAR aromatics could effectively ionize in ESI using this approach. Additionally, the oxidized sulfides were mainly S1 and S2 class species. The most abundant oxidation-generated sulfoxides O1S1 and O1S2 in LGAR aromatics had DBE values of 3~10 and 8~12, respectively. The S2 class species, whose condensation degree was higher than that of S1, were likely in the form of containing both cyclic sulfides and thiophenic compounds.

Keywords: residue fraction; sulfide; selective oxidation; ESI FT-ICR MS

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1. Introduction

The types and distribution of sulfur compounds in residue are the focus of petrochemical research. However, due to the complexity of composition and the structure of residue system, the related research is largely restricted by chemical separation and analysis. An in-depth study of the structural composition and the distribution of sulfur compounds provides a theoretical basis for improving the processing of residue, which has important guiding significance.

In recent years, the development of Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR MS) technology has provided a more effective analytical method for 'Petroleomics' research. FT-ICR MS has ultra-high mass resolution and can really study the composition of petroleum from the level of molecular element composition [1–3]. Qian et al. [4,5] revealed the oil composition at the molecular level and carried out a series of researches on the application of FT-ICR MS taking advantage of the Exxon Mobil. Previous researches revealed the advantages of FT-ICR MS in analyzing the structure and composition of petroleum, and provided reference for subsequent researchers. Kim et al. [6,7] used FT-ICR MS to analyze the structural composition of petroleum samples, such as petroleum acids, N, S, O-containing heteroatom compounds, and did a lot of pioneering work. Tian [8], Shi [9], and others also achieved important breakthrough in the field of FT-ICR MS analysis of petroleum structure composition. Advances in mass spectrometry resolution, ionization technology, and data processing methods, are important factors for the wide application of FT-ICR MS in the field of petroleum analysis. FT-ICR MS has greatly promoted the development of the concept and method of 'Petroleomics' [10].

The Atmospheric Pressure Photoionization (APPI) and Electrospray Ionization Source (ESI) were currently more suitable ionization methods for the analysis of sulfur-containing compounds [11]. Sulfur-containing compounds were ionized directly by the APPI source [12–14], while the derivatization with methyl iodide or silver cation was necessary for the ESI source [15]. The combination of Electrospray Ionization Source (ESI) and FT-ICR MS has been widely used in the analysis of non-hydrocarbon compounds in heavy oil. As ESI is a selective ionization source, the sulfur compounds with non-polarity and weak polarity in residue cannot be analyzed directly. The sulfur compounds can be converted into corresponding salts by methyl derivatization, and ionized in the ESI source for analysis after improving the polarity of the sulfur compounds [16–19]. The methylation method was frequently used in petroleum fractions analysis through ESI FT-ICR MS [20–23]. However, the method of methyl derivatization combined with ESI analysis also has some shortcomings, such as differences in selectivity and the conversion of different types sulfur compounds in the process of methylation, and a defect in detecting sulfur compounds with high degrees of condensation [18,24]. Liu et al. [25] used a selective oxidation method combined with ESI FT-ICR MS to detect sulfur compounds in diesel fractions and oil sand bitumen saturates, which provided a new idea for high resolution mass spectrometry analysis of sulfur compounds. Cai et al. [26] studied the structure differences of sulfur compounds in heavy oils by tandem mass spectra of FT-ICR MS coupled with collision-induced dissociation. Chen et al. [27] introduced a novel method for direct sulfur compounds characterization in petroleum samples by ESI FT-ICR MS using fluoroboric acid as a new ionization promoter. Rowland et al. [28] presented an analytical method of crude oil composition combination with the ultrahigh mass resolving power of FT-ICR MS at 21 T, which provides the highest mass resolving power and mass measurement accuracy for detailed characterization.

The objective of the present work is to characterize the sulfides present in Lungu atmospheric residue (LGAR) aromatics. Sulfur-containing aromatics were isolated from the LGAR by the saturates/aromatics/resins/asphaltenes (SARA) chromatography method. Tetrabutyl ammonium periodate (TBAP) was used to selectively oxidize sulfides in LGAR aromatics to sulfoxide compounds. Then, the composition and distribution of sulfides were investigated by ESI FT-ICR MS analysis after polarity enhancement, and the method for characterizing sulfides in residue fractions was explored. Insights into the chemical composition of residue were further obtained via analyzing the data coupled with results.

2. Materials and Methods

2.1. Sulfur-Containing Fractions Separation

A representative high-sulfur LGAR was employed as the feedstock (>360 °C, supplied by Tarim Petrochemical Ltd., Sinkiang, China). LGAR was separated into four subfractions by SARA fractionation using the standard SH/T 0509-92 method (Chinese Standards for Petroleum and Natural Gas Industry). All subfractions were weighed after the complete removal of the corresponding solvents. The sulfur analysis of LGAR and subfractions was conducted by Elements Analyzer (Vario EL III, Germany Elementar Company, Langenselbold, Germany).

2.2. Selective Oxidation and Sample Preparation

Aromatics of LGAR were separated with reference to the SHT0509-92. About 1.0 g of aromatics were extracted, dissolved in 5 mL methanol and 25 mL toluene, added TBAP (excess oxidant was added at 1:1 according to the total sulfur molar ratio of each component), stirred, refluxed, and cooled to room temperature for 30 min. The reaction solution was transferred to the separator funnel with toluene, and the organic phase was extracted with 40 mL water for 4 times, then extracted with 20 mL toluene. The organic phase was collected, evaporated, and dried. Aromatic oxidation products were transferred to an alumina chromatographic column with 1% water by 20 mL toluene. The column was first wetted with 30 mL petroleum ether, then washed with 80 mL toluene to remove the unoxidized components after adding oil samples, and then washed with 40 mL toluene-ethanol to obtain the oxidized components containing sulfoxides.

2.3. Mass Spectrometric Analysis

The aromatics or sulfoxides samples were dissolved in 1 mL toluene about 10 mg, of which 15 µL was diluted to 1 mL with a mixed solution of toluene-methanol (volume ratio 3:7), 5 µL formic acid was added. The mixture was gently oscillated and mixed, and then analyzed with FT-ICR MS (Bruker, Billerica, MA, USA). The magnetic field intensity of FT-ICR MS is 9.4 T; ESI ionization source, positive ion mode; polarization voltage, −4000 V; injection speed, 180 µL/h; sampling frequency, 1 s; mass range, 200~1000 Da, spectra superimposed 128 times. Data processing methods References [9,18].

3. Results

3.1. Determination of Sulfides in LGAR Aromatics

The yield and sulfur distribution in LGAR aromatics are shown in Table 1. The sulfur content of LGAR is 3.31%, 40.79% of which is concentrated in aromatics, indicating that the aromatic fractions separated by liquid-solid chromatography contain a considerable number of sulfur compounds, which are not pure aromatic hydrocarbons. Because the separation of liquid-solid adsorption chromatography is based on polarity differences between different residue components, the polarity of these sulfur compounds is close to the polarity of aromatic hydrocarbons, they were washed off the chromatographic column together with aromatic hydrocarbons. Sulfur in aromatics is an important component of sulfur compounds in LGAR.

Table 1. The yield and sulfur distribution in LGAR aromatics.

Sample	Yield/%	w(S)/%	K [1]/%	Sulfide Sulfur/%	Thiophenic Sulfur/%
Aromatics	33.75	4.00	40.79	9.35	31.44
LGAR	100.00	3.31	100.00	16.01	83.99

[1] K—the mass fraction ratio of aromatic sulfur to LGAR total sulfur.

Sulfides in the fraction were selectively oxidized to sulfoxides with high polarity after oxidant, then, the oxidation products were separated by washing with appropriate polarity solvent. The contents of sulfoxides and unoxidized thiophenic sulfurs in the oxidation product were determined quantitatively, and the contents of sulfide and thiophenic sulfur in the fraction before oxidation could be obtained indirectly. After the oxidation of aromatics, the average yield of chromatographic separation products was over 98%, and the total yield of sulfur can reach 95%, indicating that the method of TBAP selective oxidation combined with chromatographic separation has a good separation and enrichment effect on sulfides in LGAR [29]. It was determined that about 22.92% sulfur of the aromatics were oxidizable sulfides and about 77.08% were thiophenic sulfur. The sulfides in aromatics accounted for 58.40% of the total sulfides in LGAR.

3.2. FT-ICR Mass Spectrum of Aromatics and Oxidation Sulfides

The composition of residue and its oxidized derivatives are very complex. There are a lot of mass spectra peaks in the mass spectrum, but there are not many elements (such as C, H, N, O, S) that make up these compounds. FT-ICR MS can classify different molecules based on their elemental composition. The mass spectra peaks of the same compounds homologues show continuous normal distribution (the mass difference between adjacent mass spectra peaks is 14.0156 Da). The difference between adjacent stronger mass spectra peaks is 2.0156 Da, and the corresponding Equivalent Double Bond ((DBE), which is the sum of the double bonds and naphthenes number) differs by 1. That is, there is a double bond or a saturated naphthene ring in the molecule. The molecular formula corresponding to one or several mass spectra peaks in the mass spectrum can be determined according to these characteristics, and the identification of other mass spectra peaks can be realized quickly. Figure 1 shows the FT-ICR MS spectra of aromatics and sulfides oxides in LGAR. The relative mass distribution of aromatics before oxidation is in the range of m/z 200–800, and the relative mass distribution of oxides after selective oxidation is similar to that before treatment.

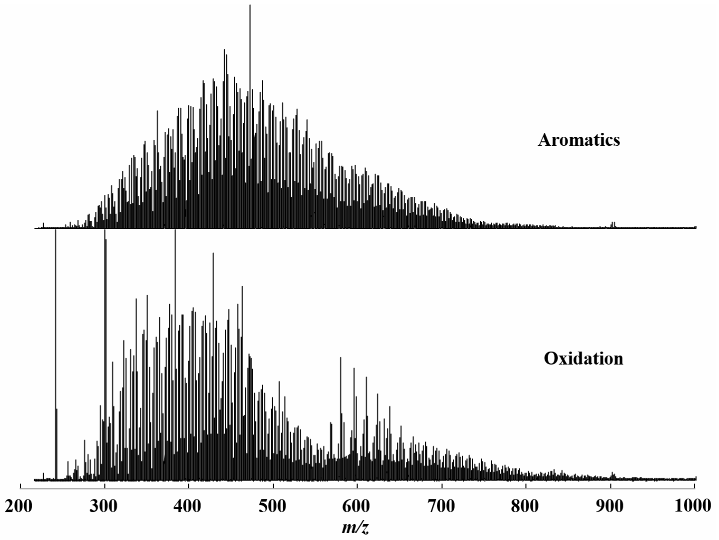
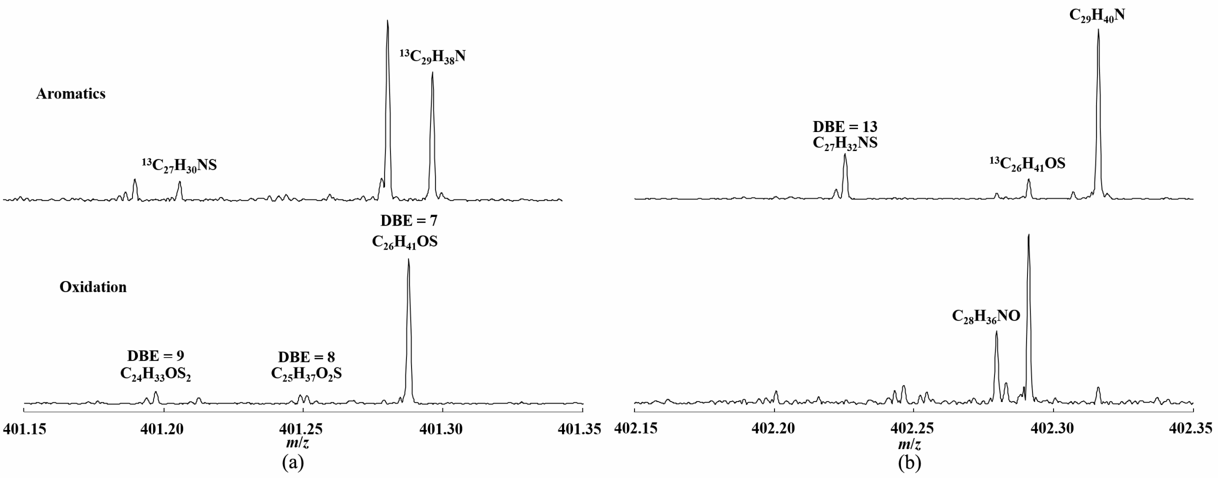


Figure 1. The mass spectrum of LGAR aromatics before and after selective oxidation.

The main compounds at m/z = 401, 402 were identified. From the local enlarged map, Figure 2, it can be seen that 5–6 different types of compounds were identified in a very narrow m/z window, and this high mass resolution can run through the mass range of the whole component. The compounds of aromatics ionized under ESI conditions are mainly nitrogen-containing compounds before oxidation. The corresponding compounds changed obviously in the mass spectra of the oxidized fractions after oxidation, and the mass spectra peaks with higher relative abundance are sulfoxides.



(a) (b)

Figure 2. The local enlarged map of LGAR aromatics mass spectrum: (**a**) m/z = 401; (**b**) m/z = 402.

Since the types of sulfur-containing compounds are extremely complex, the type of compound is represented by the type and number of heteroatoms contained in the molecule during data processing. As shown in Figure 3, compared with the main heteroatom types of aromatics and oxidized samples, the compounds ionized by unselectively oxidized aromatics under ESI conditions were mainly nitrogen-containing compounds, and many sulfur-containing compounds such as N1S1, O1S1, and O2S1 were also identified in aromatics. It can be seen that the elemental composition of petroleum is very complex. Sulfur-containing compound molecules contain not only sulfur atoms, but also other heteroatoms (N, O), forming compounds such as NxSy, OxSy, or NxOySz (x, y, z is the number of different atoms). These types of sulfur-containing compounds were ionized easily under positive ion ESI condition because of containing N, O heteroatoms, and having stronger polarity than ordinary sulfur compounds (Sx).

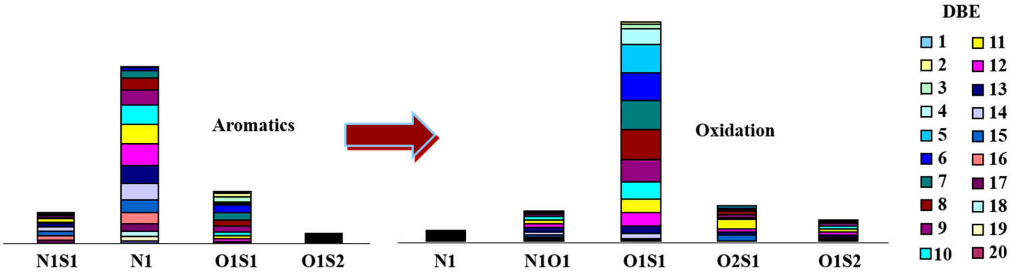


Figure 3. Broadband and mass scale expanded ESI FT-ICR mass spectrum of aromatics and oxidation sulfides.

3.3. Changes of Sulfur Types in LGAR Aromatics before and after Selective Oxidation

As the positive ion ESI produces $[M + H]^+$, the peaks of odd mass units correspond to compounds containing S and O atoms. As shown in Figure 2 $m/z = 401$, even numbers correspond to compounds containing an odd number of N1 atoms or ^{13}C isotopes. At $m/z = 402$, the isotope peak of $C_{26}H_{41}OS$ was found, and there was a ^{13}C isotope in the molecule, which further verified the existence of O1S1 in the components. From Figure 3 we could summarize that the DBE of O1S1 sulfur-containing compounds are distributed in multiple intervals, indicating that there may be multiple parent nuclear structures of O1S1. Among them, the O1S1 class with DBE equal to 2 may be a dicyclic sulfide or sulfoxide with a hydroxyl group, and the possible structure with DBE equal to 11 may be a side of dibenzofuran and a thiophene ring [30,31]. In addition, the existence forms of two sulfur atoms in O1S2 and S2 in the same sample are not the same. Sulfoxide sulfur may exist in O1S2, while N1S1 compounds may exist mainly in the form of indole thiophene and carbazole thiophene [19].

The relative abundance of O1S1 in the oxidized fractions after oxidation was much higher than that of other oxidized fractions, indicating that the ionization of weakly polar sulfide sulfur in ESI source was realized effectively by increasing the polarity of sulfide after selective oxidation. However, the mass spectra peaks of N1 and N1S1 with higher abundance in the aromatic spectrum before reaction were reduced or disappeared after separation. In addition, O2S1 sulfides were identified in the oxidized sample, which were not acid. Because the acid can only be ionized in the negative ion mode, and the mass spectra peak does not appear in the positive ion mode. Moreover, TBAP is unable to oxidize thiophene, and sulfur oxide ether stays in the sulfoxide stage [32,33], and sulfoxide O2S1 appears in the product. It can be confirmed that these compounds are generated by the further oxidation of a small amount of O1S1 in the aromatics, indicating that some sulfoxide sulfur does exist in O1S1.

In addition, the relatively low abundance of N1O1 indicates that a small amount of nitride compound was oxidized at the same time. However, the unreacted components with unchanged polarity in the sample, such as O1S1 and O1S2, were washed to the unoxidized components after oxidation, which did not affect the analysis of the oxidized components. O1S1 and O1S2 in the oxidized fraction were derived from the oxidation of S1 and S2 sulfides. In this study, O1S1 and O1S2 sulfides were used to represent oxidizable sulfides, and the distribution characteristics of sulfides in LGAR aromatics were analyzed.

3.4. Oxidized Fraction Analysis by ESI FT-ICR MS

Compounds can be divided into different groups according to the DBE value. For example, the molecular formula of tetrahydrothiophene is C_4H_8S (corresponding sulfoxide is C_4H_8OS), that is, DBE = 1, the DBE value of tetrahydrothiophene and its homologues is 1, while the DBE values of thiophene and benzothiophene compounds are 3 and 6, respectively. The identified compounds were analyzed statistically by DBE, and the DBE and carbon number distribution of O1S1 and O1S2 were made. The size of the scattered points in the figure represents the relative abundance.

The compound containing one sulfur atom in the molecule is a major component of oxidized sulfide sulfur. As shown in Figure 4, the DBE values of O1S1 compounds were continuously distributed from 1 and 13, and the carbon number distribution was from 15 and 50. The relative abundance of O1S1 compounds with DBE equal to 3–10 and carbon number in the range of 20–35 was higher. Theoretically, the sulfides containing 1–4 rings in the parent structure correspond to DBE = 1–4, while the DBE of thiophene compounds is 3. TBAP cannot oxidize thiophene, so it can be concluded that there are 1–4 ring thioethers. The parent structure of DBE = 5 may be a cyclic sulfide with one benzene ring, while that of DBE = 6 may be a two rings sulfide with benzene rings. The parent structure of DBE = 7 may be benzotetrahydrobenzothiophene (one aromatic ring and one naphthenic ring), and DBE = 9, 10 are DBE = 6, 7 structures with a benzene ring, respectively.

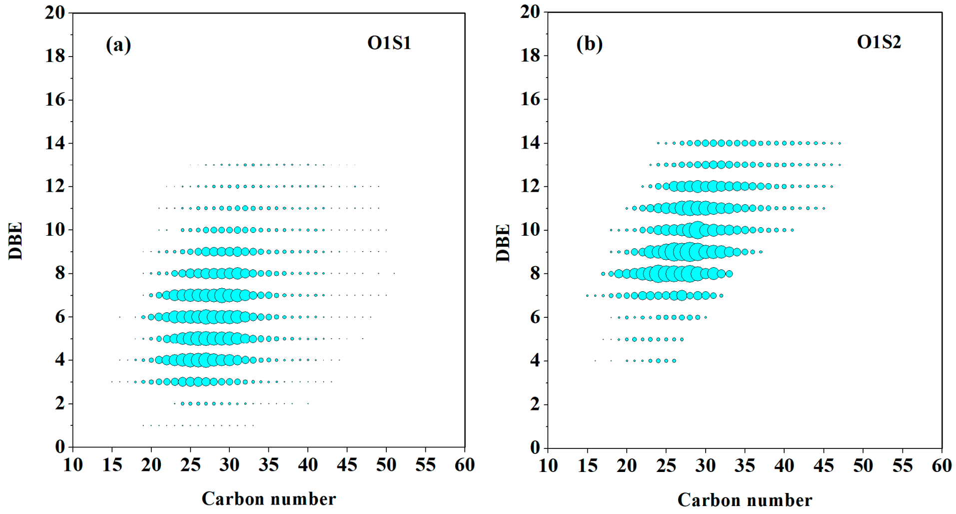


Figure 4. Isoabundance pattern for DBE versus the carbon number of the sulfides species for the LGAR aromatics: (**a**) O1S1; (**b**) O1S2. Note: The size of dot corresponds to the abundant of sulfides species in the sample. The largest dot correspond to the most abundant O1S1 and O1S2 species.

The DBE upper and lower limits of O1S2 compounds are higher than those of O1S1, indicating that the degree of condensation increases with the increase of the sulfur atoms number. Sulfides with DBE equal to 8–12 have high relative abundance. The presence of these compounds indicates that sulfur compounds in petroleum do not contain only one sulfur atom, and heavy crude oil and heavy fractions may also contain multiple sulfur atoms (S2, S3, etc.). S2 may be a compound containing both cyclic sulfide and thiophene ring structure [19], in which thiophene sulfur has good stability because its sulfur atoms participate in the conjugated effect of aromatic system and form stable large π bonds, and is difficult to oxidize for the small electron cloud density on sulfur atom and the low degree of activation. However, the sulfide sulfur in the molecule exhibits the properties of general cyclic sulfide, which is easy to oxidize to sulfoxide, thus changing the polarity of the entire S2 molecule and being ionized and analyzed in ESI easily.

4. Discussion

FT-ICR MS combined with ESI ionization source can analyze the composition of residue components to research the composition of residue under the molecular element composition level. However, the sample needs to be pretreated by enhanced polarity before analysis in order to realize the ionization of sulfur-containing compounds, which can be solved effectively by oxidation. The ionization products of aromatics without selective oxidation are mainly N1 compounds under ESI conditions. The relative mass distribution range of oxidized fractions after selective oxidation was similar to that, and the types of compounds changed significantly. The relative abundance of O1S1 produced by oxidation was much higher than that of other types. It indicates that the ionization of weak polarity sulfide in ESI source is effectively realized by increasing the polarity of sulfides after selective oxidation.

However, it was also found that the sulfide sulfurs contained in the oxidizable sulfur fraction and separated by TBAP were not simple alkyl (alkyl, naphthenic, or aromatic) sulfide sulfur-containing compound. Traditionally, the compound in which the oxygen atom in the ether molecule is replaced by a sulfur atom is sulfide, and its structure R-S-R′ is two identical or different alkyl groups connected by sulfur atoms. Among the different polar residue components, there may be a variety of sulfur-containing types in the sulfide sulfurs that can be oxidized by TBAP. R and R′ may be a mixed structure of alkyl, heterocyclic and various alkyl groups containing N and O heteroatoms. It can be oxidized to sulfoxide by TBAP because of containing a C-S bond sulfide structure or the properties of sulfide. Conversely, heteroatomic compounds with this C-S bond sulfide structure may not necessarily be oxidized by TBAP. The oxidizable sulfide sulfur in the aromatics of LGAR are mainly S1 and S2 classes. The DBE values of the oxidized O1S1 class compounds are continuously distributed from 1 and 13, and the carbon number distribution is from 15 and 50. O1S1 compounds with DBE values 3–10 have higher relative abundance. The condensation degree of O1S2 compounds was higher than that of O1S1, and the relative abundance of DBE values 8–12 was higher. S2 may be compounds containing both cyclic sulfide and thiophene rings structures.

5. Conclusions

This study investigates a method for the characterization of sulfides in atmospheric residue fractions using selective oxidation followed by FT-ICR MS. The advantage of this method is that sulfides can be analyzed from the complex components of residue, which contains thiophenic compounds, polycyclic aromatic hydrocarbons, and other compounds. TBAP can selectively oxidize the weak polarity sulfides into sulfoxides, which can be effectively further realized in ESI source. In this study, the aromatic of atmospheric residue is used to illustrate this method. Similar performance is expected for vacuum residue or other fractions of residue, such as resin and asphaltene.

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