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Structure characterization of polyaromatic hydrocarbons in Arabian mix vacuum residue by electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry

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Abstract

Molecular formulas of constituents in vacuum residue were characterized by Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). Evaluation of electrospray ionization (ESI) ability for hydrocarbons by using model compounds indicates that aromatic compounds having more than two fused rings without functional group are detectable as molecular ions, while that basic nitrogen-containing compounds produce protonated ions in the ESI solvent of methanol/chloroform. Thus, even peaks appear for both hydrocarbons and nitrogen-containing compounds in methanol/chloroform. Although basic nitrogen compound detected selectively in mixture of equal molar concentration of hydrocarbons, hydrocarbon could be observed almost the same intensity when the concentration of nitrogen compounds was adjusted as low as that of Arabian mix vacuum residue (AM-VR: N 0.4 wt.%). When ESI solvent of methanol/chloroform/trifluoroacetic acid (TFA) was used, protonated hydrocarbons produced predominantly as odd peaks. Thus, it was revealed that peaks originating from nitrogen-containing compounds and hydrocarbons can be clearly distinguished by changing composition of ESI solvents. In application to AM-VR, protonated nitrogen-containing compounds ($[C_nH_{2n+Z}N + H]^+$ and $[C_nH_{2n+Z}NS + H]^+$; even masses) were observed selectively in methanol/chloroform, and both protonated nitrogen-containing compounds and protonated or sodium-cationized hydrocarbons ($[M + H]^+$ or $[M + Na]^+$; odd masses) were observed simultaneously in the solvent composition of methanol/chloroform/TFA.

Keywords: FT-ICR; Electrospray; Complex mixture analysis; Vacuum residue; Hydrocarbon detection

1. Introduction

Heavy oil, such as vacuum residue, obtained from crude oil as a by-product becomes increasingly heavy with development of the refinery technology. Use of heavy oil causes serious problems such as deactivation of catalyst due to formation of coke and sludge when heavy oil is converted into more valuable products (e.g., gasoline). In order to establish the best processing conditions for effective conversion of heavy oil, it is essential to elucidate the structural characteristics of feed heavy oil. However, heavy oil is an extremely complex mixture of variety of compounds [1] and its constituents have a significant variation depending on the production places and the refinery conditions.

The structural characteristics of heavy oil have been investigated by means of several analytical techniques, such as $^1H/^{13}C$ NMR, [2] IR, [3] X-ray and the gel permeation chromatography (GPC) [4]. Bulk properties, such as the average linearity of paraffin and the average degree of aromatization, have been estimated by those techniques. Although the elucidation of the average chemical properties is very important to understand the structural characteristics of heavy oil, minor constituents undetectable from those averaged structural information may seriously affect the processing of heavy oil, for example catalyst deactivation [5].

Mass spectrometry (MS) is a viable tool to solve the problem lying on the heavy oil analysis, because it is able to provide a compositional inventory of vacuum residue that is made up of thousands of compounds. Several ionization techniques have been examined for the petrochemical mass spectrometry, such as low-voltage electron ionization

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(LVEI), [6–8] field ionization mass spectrometry (FIMS), [9] thermospray-interface (TSP) MS, [8] and matrix assisted laser desorption/ionization (MALDI) [10,11]. However, prior to characterize the chemical structure of each constituent molecule in heavy oil with these ionization methods, vacuum residue samples must be separated into several fractions by chromatography because of insufficient resolution of conventional mass spectrometers.

Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) has an ultra-high resolving power and achieves a high accuracy, i.e., mass errors less than 1 ppm. Molecular formulas of compounds contained in complex mixtures can be estimated with FT-ICR MS, when singly-charged molecular ions are preferentially produced without fragmentation [12]. Several research groups have recently applied FT-ICR MS to petrochemical composition analyses. FT-ICR MS equipped with 3 T magnet and LVEI was applied to determine the molecular formulas of aromatic compounds in petroleum distillates including hetero-atoms, such as sulfur, nitrogen and oxygen [13,14]. Rodgers et al. developed 5.6 T FT-ICR MS connected to an all-glass heated inlet system with LVEI, and applied it to diesel fuels and identified 500 aromatic compounds either with or without sulfur atoms [15]. Our group carried out measurements by using 7 T FT-ICR MS equipped with an in-beam EI source for *n*-heptane soluble fraction separated from Arabian heavy vacuum residue and characterized hydrocarbons and sulfur-containing species with *m*/*z* less than 700 [16]. Although these studies have demonstrated the viability of FT-ICR MS to determine chemical formulas of constituent molecules in petroleum-related materials, the conventional LVEI is basically applicable to only volatile materials and may generate fragmentation of constituent molecules.

In contrast to LVEI, electrospray ionization (ESI) [17] is known to be a softer ionization method avoiding fragmentation especially for vacuum residues which have had thermal experience(over 350 °C). ESI is able to ionize non-volatile materials on the basis of the adduct formation at polar functional groups (e.g., –OH, $–NH_2$) with protons or metal cations contained in a solvent. ESI has been developed to mainly analyze polar compounds. Non-polar compounds, which are major constituents of heavy oil, are difficult to be analyzed by ESI. There are many approaches to over come this difficulty, such as electrochemistry-MS [18] and APPI [19]. Those techniques have succeeded in observing non-polar compounds; however, they need additional apparatus attached to the standard ESI source. For these reasons, very few applications of ESI MS have been performed in the characterization of petroleum-related materials. Zhan and Fenn applied ESI quadrupole MS to analyze polar constituents of fossil fuel [20]. The resolving power, however, was insufficient to identify the obtained peaks. Roussis and Praulx examined Ag^+ ESI for ionizing hydrocarbons in a petroleum sample [21]. Ag coordination ionspray-MS is a useful technique to ionize non-polar polycyclic aromatic compound, peroxide, or α-tocopherol [22]. In a particular application for a petroleum sample, however, the formation of complex with Ag^+ makes the spectrum too complicated to be recorded by a tandem double focusing magnet sector mass spectrometry, since isotopic mass doublets (^{107}Ag and ^{109}Ag) are detected for every observed constituent.

One of the challenges of ESI MS, concerning mass resolution in the application to a very complex mixture, can be overcome by employing FT-ICR MS. At present, ESI FT-ICR MS is earning a great success for the structural analysis of bio-related materials, such as peptides and digested proteins [23]. Several researchers have applied ESI FT-ICR MS for the aqueous solution of humic substances, which are also very complex mixtures but are more polar than vacuum residues [24,25]. FT-ICR MS is a viable tool to directly determine molecular formulas from accurate masses with a high resolving power. Application of FT-ICR MS to a petroleum sample is expected to provide high throughput for the characterization of constituents in the very complex mixture. Moreover, FT-ICR MS coupled with ESI can analyze a large set of constituents in vacuum residue without an influence of fragmentation. We have demonstrated briefly that ESI FT-ICR MS is a potential tool to characterize Arabian mix vacuum residue (AM-VR) [26]. Qian et al. characterized nitrogen-containing aromatic compounds selectively in heavy petroleum crude oil [27]. Constituents containing neither nitrogen nor sulfur atoms were not observed under their ESI condition. A highly selective detection of hetero-atom containing trace constituents is one of the useful aspects of ESI; however, the exhaustive and sensitive analysis of hydrocarbons is essentially in great demand, because they are the primary parts of petroleum sample.

In the present study, we applied ESI FT-ICR MS to the molecular formula determination of several kinds of selected constituent in AM-VR without any pre-separation procedures such as chromatography. Since hydrocarbons are major part of vacuum residues, we will particularly focus our discussion on the detection of hydrocarbon constituents, which is another challenge of ESI. In order to evaluate ESI conditions for ionizing hydrocarbons, we examined a range of model compounds in various ESI solvent. On the basis of knowledge obtained by the model compound analysis, high-field (7 T) ESI FT-ICR mass spectra of AM-VR were recorded by using methanol/chloroform as well as methanol/chloroform/TFA. We demonstrate that the tune of acidity of ESI solvent enables the selective detection of hydrocarbons and compounds with basic nitrogen-functional groups in heavy oil. The peaks observed in each spectrum were attributed to the molecular formulas based on the accurate mass values and the mass spectrometric pattern analyses, and the constituents in AM-VR were characterized by means of the hydrogen deficiency index (Z value defined as $C_nH_{2n+Z}N_mS_s$) and carbon number.

2. Experimental methods

2.1. Sample preparation

AM-VR, with elemental composition (wt.%) of C 84.3, H 9.9, S 5.2, N 0.4 and O 0.2 (diff.), was used as a heavy oil sample [26]. Model compounds and all solvents were obtained from Wako Pure Chemical Industries, Ltd. HPLC grade methanol, chloroform and trifluoroacetic acid (TFA) were used without further purification. Acetic acid was distilled in advance. The other chemicals with guaranteed reagent were used as received. A series of aromatic compounds with or without nitrogen, such as carbazole, acridine, pyrene, and coronene, were dissolved individually or as a mixture into methanol/chloroform (80:20, v/v) to assess the detectability of ESI, i.e., ionizable ring size and difference in peak intensity between hydrocarbons and heteroatom-containing compounds. In order to examine the effect of solvent acidity on the peak ratio of molecular ion to protonated (or sodium-cationized) ion, coronene and AM-VR were dissolved individually in methanol/chloroform (80:20), methanol/chloroform/acetic acid (100:20:1), and methanol/chloroform/TFA (100:10:0.1).

2.2. Mass spectrometer

All experiments were carried out on a BioAPEX 70e FT-ICR mass spectrometer (Bruker Daltonics Inc., Billerica, MA) and an external ESI source (Analytica of Branford Inc.). The sample solutions were infused into the ESI source in a positive ion mode by a syringe pump at a rate of $60\,\mu l\,h^{-1}$ and were desolvated by countercurrent nitrogen gas heated to 250 °C. Nitrogen needle-gas flowed out through the grounded coaxial needle to metal-capped glass capillary (~-3.5 kV). FT-ICR MS experimental event sequences and parameters were adjusted to optimize sensitivity by the Bruker's XMASS software running on a Silicon Graphics INDY (R5000) computer system. Accumulating ions in the external ion reservoir hexapole for 3 s were followed by transporting to the analyzer cell (trapping voltage 1.1 and 1.3 V on the front and rear plates, respectively) through the electrostatic lens system. A broad band chirp excitation was used for all the experiments. The experimental FT-ICR time domain data (sampling frequency 1.25 MHz, size 256 kilo points) were acquired using the commercially available Bruker XMASS acquisition soft ware. Absolute peak intensity was obtained by using the *peak pick* module available in the Bruker's XMASS package. Each molecular formula (a possible combination of atomic masses which give the least deviation from the measured mass) was obtained by using *mass analysis* module. All FT-ICR spectra were internally calibrated by using poly(ethylene glycol) with the average molecular weights of 300 and 600.

3. Results and discussion

3.1. ESI mass spectra of model aromatic compounds

3.1.1. Ionizable aromatic ring size

The viability of ESI MS for the analysis of polycyclic aromatic hydrocarbons was investigated by Barkel and Asano [28]. In order to establish ESI FT-ICR MS detection of hydrocarbon components, a series of model compounds having various aromatic ring numbers from 2 to 7 were individually measured (Table 1). These compounds have been reported to be detected in AM-VR [29]. Peaks were detected for phenanthrene (three ring) at *m*/*z* 178.077, pyrene (four ring) at *m*/*z* 202.078, benzo[a]pyrene (five ring) at *m*/*z* 252.091, and coronene (seven ring) at *m*/*z* 300.093 by using methanol/chloroform as the ESI solvent. No peak was detected for naphthalene (two ring). The detected peaks of model compounds were attributed to molecular ions $[M]^+$, indicating no adduct formation under the present ESI conditions. The observerd results are the same as that reported by Barkel, where anthracene, pyrene, and perylene were observed as molecular ions and naphthalene was not detected [30]. For an aromatic hydrocarbon compound without any functional groups, the stability of molecular ions depends on the size of fused rings [30] due to the delocalization effect on their conjugated π-electron systems. Ionization energy of each model compound is listed in Table 1. The results using model compounds indicate that molecular ions of pure aromatic compounds having equal to or more than three fused rings or having lower ionization energy than 7.86 eV

Table 1
Experimental mass and ionization energy of model compounds

Compound	Experimental mass (Da)	Theoretical mass (Da)	Ionization energy[a] (eV)	Molecular formula (number of aromatic rings)
Naphthalene	–	128.0621	8.14	$[C_{10}H_8]^+$ (2)
Phenanthrene	178.0776	178.0777	7.86	$[C_{14}H_{10}]^+$ (3)
Pyrene	202.0778	202.0777	7.41	$[C_{16}H_{10}]^+$ (4)
Benzo[a]pyrene	252.0931	252.0934	7.12	$[C_{20}H_{12}]^+$ (5)
Coronene	300.0930	300.0934	7.29	$[C_{24}H_{12}]^+$ (7)
Acridine[b]	180.0802	180.0808	7.80	$[C_{13}H_9N+H]^+$ (3)
Carbazole	167.0731	167.0730	7.57	$[C_{12}H_9N]^+$ (3)

[a] Ref. [37].

[b] Acridine was detected as protonated molecular ion $[M + H]^+$.

are detectable under this ESI conditions. Calemma et al. have estimated the average size of the polyaromatic core of constituents in vacuum residues to be about seven aromatic rings [31,32]. Hence it was expected to detect mostly PAH constituents in AM-VR under the present ESI conditions.

3.1.2. Ionization efficiency of nitrogen-containing compounds versus polyaromatic hydrocarbon by ESI

Pure hydrocarbons or apolar compounds without functional groups are less suitable to be ionized by ESI than nitrogen-containing hydrocarbons or polar compounds [27]. A mixture of representative model compounds was examined to evaluate the ability of ESI FT-ICR MS for analyzing aromatic hydrocarbons and nitrogen containing compounds in parallel. The test mixture consisted of pyrene, coronene, carbazole, and acridine with the same concentration in methanol/chloroform. As shown in Fig. 1, the peaks were detected as molecular ions for pyrene, coronene and carbazole, whereas acridine was detected as being protonated and as predominant peak. A similar tendency, i.e., basic nitrogen compounds were ionized preferentially by ESI, was observed by Marshall's and co-workers [27,33]. AM-VR, however, consists of mostly hydrocarbons and nitrogen content is only 0.4% in the elemental composition. By taking such lower concentration of nitrogen-containing constituents in AM-VR into consideration, ESI FT-ICR mass spectrum was measured for the test mixture with biased concentrations. Although the peak intensities of pyrene and carbazole were weak due to a suppression effect on the aromatic ring size, the peak intensity of coronene was almost the same as that of acridine when hydrocarbons to nitrogen containing compounds molar ratio of 10 was used (Fig. 2). The peak with *m*/*z* 301 observed in Fig. 2 was attributable to dibutyl phthalate sodium salt. The peak with *m*/*z* 179 was a foldover peak from out of the lower mass range, since the peak position shifted when the sampling frequency was changed.

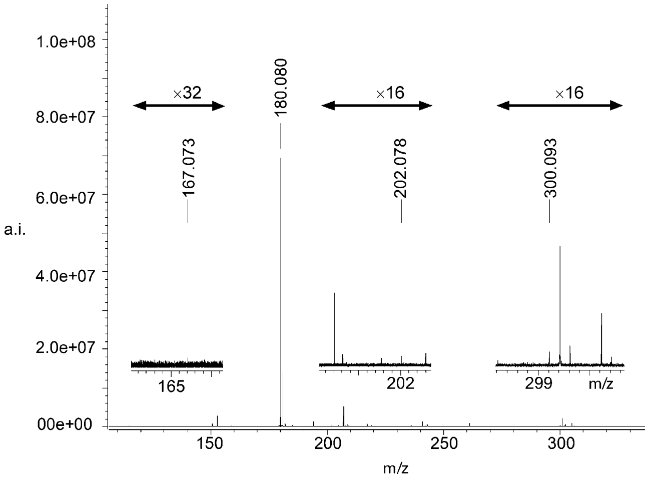


Fig. 1. ESI FT-ICR mass spectrum of test mixture; carbazole (*m*/*z* 167.073), pyrene (*m*/*z* 202.078), coronene (*m*/*z* 300.093), and acridine (*m*/*z* 180.080) in methanol/chloroform (80:20 vol.%). The concentration of every compound was set to the same (5 pmol/μL).

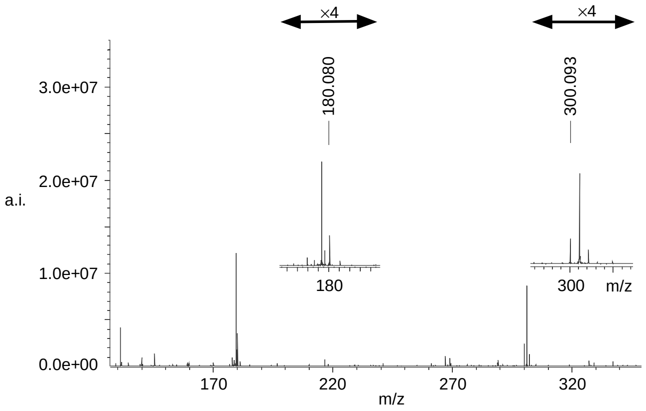


Fig. 2. ESI FT-ICR mass spectrum of test mixture in methanol/chloroform (80:20 vol.%), insets show the expanded view of acridine ($[M + H]^+$: *m*/*z* 180.080) and coronene ($[M]^+$: *m*/*z* 300.093). The concentrations of acridine and carbazole were 0.5 pmol/μL each and pyrene and coronene were 5 pmol/μL each. Thus, the final nitrogen content of the model mixture was adjusted to 0.4%.

Our objective is detection of hydrocarbons in vacuum residues since hydrocarbons are major constituents in petroleum. Ueda et al. have observed PAHs in AM-VR by FI-MS [29]. Hence we assessed a series of PAHs as an index of the ESI capability for hydrocarbons. Although the arrangement of aromatic rings may influence on the ionization efficiency of PAH because of a different extent of the conjugation system, the ion formation of PAH without hetero atom in ESI is thought to mainly depend on the aromatic ring size considering the ionization energy. Present result obtained for the model PAH compounds of different ring sizes is consistent with previous reports of PAH [30] measurement by ESI and can be an indicator of the ionization efficiencies of PAHs in AM-VR. Consequently, the model compound analysis ensures that hydrocarbons with highly conjugated aromatic rings, which must be a large part of vacuum residue but have not been thought to be amenable of ESI MS, can be analyzed by ESI FT-ICR MS.

3.2. Characterization of AM-VR by ESI FT-ICR MS

3.2.1. ESI FT-ICR mass spectrum of AM-VR and characterization of peak pattern

On the basis of knowledge obtained by the above model compound analysis, AM-VR was subjected to ESI FT-ICR MS by using methanol/chloroform as solvent. The mass spectrum is shown in Fig. 3. Several prominent peaks over a range of *m*/*z* scale may originate from impurities contained in the solvents, such as plasticizers. The AM-VR spectrum showed single-mode distribution which has been usually observed in petroleum samples. A pattern analysis for the observed peaks was conducted as below in detail. A mass scale expanded segment of Fig. 3 is shown in Fig. 4. Even-mass ions are obviously more abundant than odd-mass ions. The peaks with odd mass are higher in mass by 1.003 Da than the adjacent peaks with even masses. This

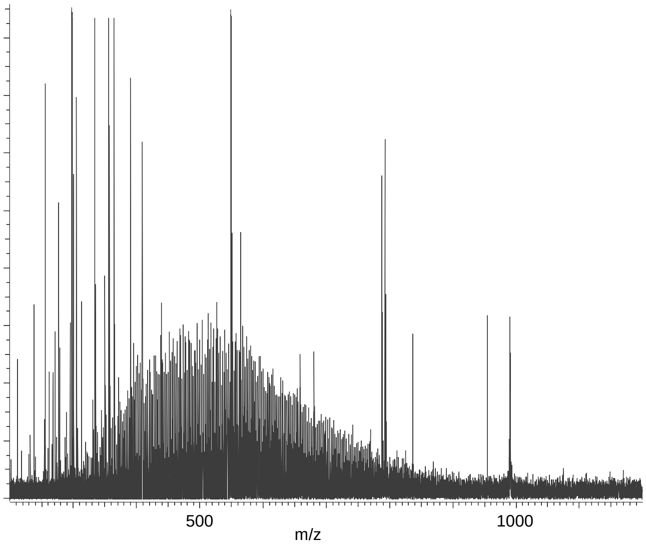


Fig. 3. ESI FT-ICR mass spectrum of AM-VR in methanol/chloroform.

peak pattern suggests that the peaks with even masses come from compounds whose all carbons are ^{12}C. Further, intensity of the peaks with odd masses (ca. 35%) suggests that the peaks with odd masses originate from the same compounds as the adjacent even mass ones but containing one ^{13}C instead of ^{12}C, since constituents detected in this region have around 35 carbons. Molecular formulas for the even m/z peaks can be determined by the calculation of formula mass with the least deviation. For the formula mass calculation, it was assumed that molecules were composed of ^{1}H, ^{12}C, ^{16}O (less than 2), ^{14}N (less than 2), and ^{32}S (less than 2). The error tolerance for the estimated formula mass was set at less than ±100 mDa. Table 2 gives an example of the candidate molecular formulas for the peak observed at m/z 466.3460 in Fig. 4. Deviations in mass values between measured peaks and calculated molecular formulas are less than 5 mDa. The molecular formula $C_{34}H_{44}N$ (formula mass 466.3468 Da) is the most probable one because it has the least deviation (0.8 mDa) from the measured m/z 466.3460 in Fig. 4. In positive-ion mode, electrospray often yields quasi-molecular ions, i.e., even electron species consisting of intact molecules with protons or other cation adducts. The most probable estimated molecular formula satisfies with the “nitrogen rule”; even mass ions contain an odd number of nitrogens. Qian’s group has also detected nitrogen-containing molecules as protonated ions in crude oil by micro ESI FT-ICR MS with the solvent system of methanol/methylene chloride/acetic acid [27]. Sulfur and/or oxygen containing compounds were observed in their spectrum. In contrast to this, those compounds have not been detected in the spectrum of AM-VR except for a minor peaks of $C_nH_{2n+Z}NS$. The incongruity of the observed compounds may be elucidated by two reasons: (1) the elemental compositions of AM-VR differs compared to that of the sample used by Qian et al. in; the former has a lower oxygen: 0.2 (diff.) (wt.%) than the latter. (2) A suppression effect on sulfur compounds may occur in the source region. Since we have reported the detection of sulfur compounds in Arabian vacuum residue, which is closely related to AM-VR, by means of in-beam EI FT-ICR MS, [16] peaks of sulfur compounds are presumably suppressed by the peaks of basic nitrogen compounds which are preferentially ionized by ESI. Another series of periodic pattern, an interval of 2.016 Da, at even mass was observed in Fig. 4. It corresponds to the atomic weight of 2H (2.016 Da). Considering the constituents in AM-VR and the result of previous in-beam EI measurements, [16] there is a series of compounds having the same carbon number with various Z values ($[C_nH_{2n+Z}N_m + H]^+$). Another mass scale-expanded segment of Fig. 3 is shown in Fig. 5. The peaks are present with intervals of 14.014–14.017 Da, which correspond to the formula weight of methylene group (CH_2 = 14.015 Da). This peak pattern insists the existence of the constituents with a similar aromatic structure and different alkyl side-chain lengths. Vacuum residues contain thousands of compounds. Some of them have the same molecular formulas and yet different structures. Although FT-ICR MS can determine the molecular formulas of constituents in complex mixture, those constitutional isomers cannot be identified by simple mass measurement at present

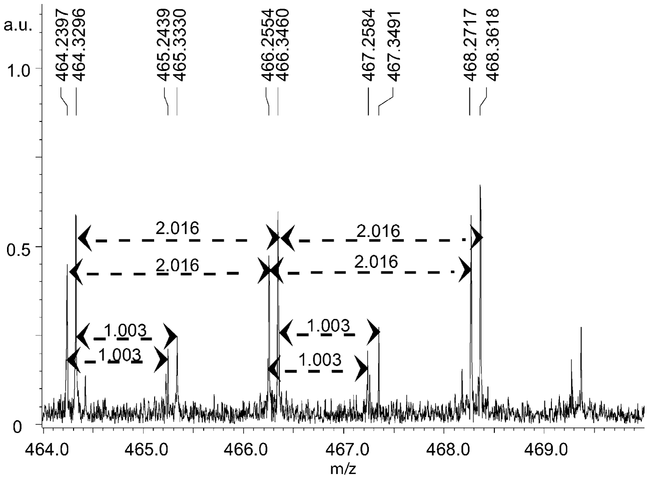


Fig. 4. An expanded view of the full mass range AM-VR mass spectrum of Fig. 3; showing periodic peak patterns induced by ^{13}C and 2H.

Table 2
Candidate molecular formulas having close masses to a peak with m/z 466.3460

Formula mass (Da)	Difference (mDa)	Z[a]	Molecular formula				
			^{12}C	^{1}H	^{14}N	^{32}S	^{16}O
466.3468	0.8	−25	34	44	1	–	–
466.3502	4.2	−15	31	48	1	1	–
466.3410	−5.0	−3	27	52	2	2	–
466.3536	7.6	−3	28	54	1	2	–
466.3376	−8.4	−15	30	46	2	1	–
466.3554	9.4	−15	30	46	2	–	2
466.3342	−11.8	−25	33	42	2	–	–

[a] Hydrogen deficiency index: $[C_nH_{2n+Z}N_mS_sO_o + H]^+$.

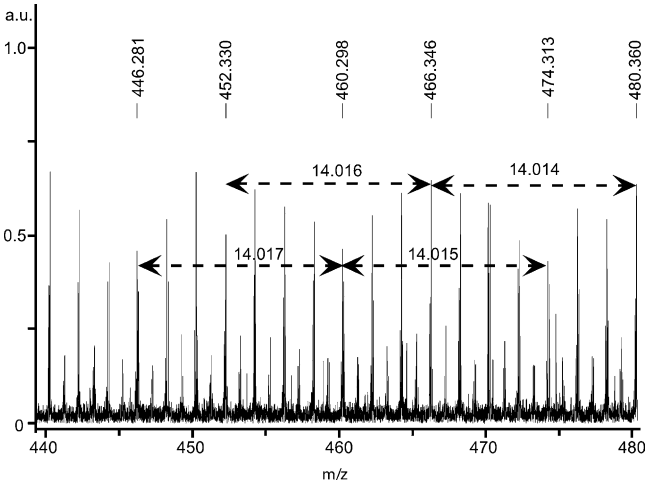


Fig. 5. An expanded view of the full mass range AM-VR mass spectrum of Fig. 3; a periodic peak pattern induced by CH_2.

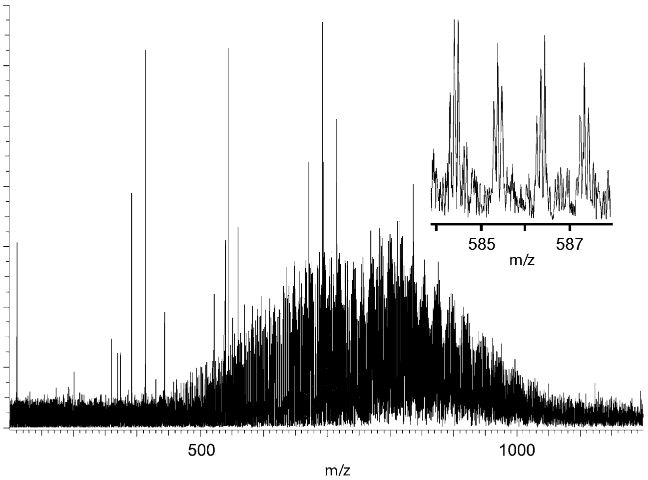


Fig. 6. ESI FT-ICR mass spectrum of AM-VR in methanol/chloroform/TFA. Inset shows the expanded view of around *m/z* 585.

state. These characteristic patterns were observed over the whole range of the spectrum. In a similar way, the molecular formulas were determined for all even peaks observed in the whole range. The estimated molecules for the peaks with even masses consist of one-nitrogen containing hydrocarbons as major constituents, and of one-nitrogen and one-sulfur containing hydrocarbons as minor ones. Unexpectedly, hydrocarbons contained in AM-VR were not detected under this ESI conditions. There are several reasons not to be observed molecular ions of hydrocarbons in AM-VR; experimental time scale was too long, or sample high concentration lead to a subsequent reaction with other neutral species, or aromatic ring size was too small. Although our in-beam EI measurement [16] detected small PAHs in a light fraction of AM-VR, the chromatography separation insisted AM-VR must contain species whose aromatic ring size are three and more [29]. The exclusion of small ring size PAH may partially originate from ionization suppression effect on the basis of molecular size.

3.2.2. ESI FT-ICR mass spectrum of AM-VR in methanol/chloroform/TFA

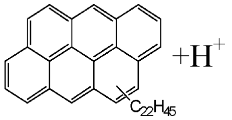
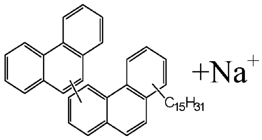
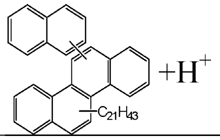
In order to extend molecular ion lifetime, TFA was added to the solvent. TFA may stabilize molecular ions by interactions between the non-nucleophilic CF_3 and radical cations. ESI FT-ICR mass spectrum of AM-VR by using methanol/chloroform/TFA is shown in Fig. 6. Although the mass spectrum showed single-mode distribution, the mode value of the distribution in methanol/chloroform/TFA shifts toward higher *m*/*z* of 800 than that in methanol/chloroform. TFA is a strong acid which may promote protonation of analyte, especially of highly developed aromatic compounds. Therefore compounds with relatively low proton affinity and with high molecular weights are considered to be ionized more effectively in methanol/chloroform/TFA than in methanol/chloroform. The effect of addition of TFA may be discussed by using a model compound in latter part of this paper. Forming non-covalent complexes, such as dimmer, is another possibility of the observed mode shift. This possibility can be excluded because infrared multi-photon dissociation (25 W CO_2 laser irradiation for 50 ms) had a little effect on the mass distribution of the AM-VR. Low molecular weight compounds disappear in Fig. 6, presumably due to external accumulation of a lot of ions, which may eject some unstable small ions in a low mass region from the hexapole [34]. Although the detected peak range changed relying on solvent composition in the present ESI experiments, the ranges were extended toward a higher mass region than that of our previous EI application for Arabian heavy vacuum residues [16]. This insists that ESI may ionize the compounds which cannot be detected in EI experiments.

Being different from the methanol/chloroform spectrum (Fig. 4), peaks with odd and even masses have similar intensities in case of methanol/chloroform/TFA (Fig. 6 inset). This peak pattern insists that the peaks with odd masses also originate from compounds whose all carbons are ^{12}C. Addition of TFA induced the detection of new species which cannot be detected by using methanol/chloroform as a solvent. Another possibility for strong peak intensity of the odd mass peak in methanol/chloroform/TFA is signal suppression caused by strong ion pairing between the TFA anion and the protonated sample cation of basic compound [35,36]. Increasing of peak intensity of odd mass was synergized by protonation of hydrocarbons and suppression effect of basic nitrogen compounds. The mass spectrometric pattern and the molecular formula determination may be discussed below in detail.

3.2.3. Characterization of AM-VR constituents observed in methanol/chloroform/TFA

In Fig. 6 inset, the peak interval between an even mass and the adjacent odd one changes randomly. Molecular formulas for $m/z = 585.4427$, 587.3635, and 649.4743 were determined in a similar way for the peaks with even masses

Table 3
Estimated molecular formulas and probable structures for observed peaks with *m/z* 585.4427, 587.3633, and 649.4743 in Fig. 6

Measured mass (Da)	Molecular formula	Formula mass (Da) (difference (mDa))	Z^a	Probable structure
585.4427	$C_{44}H_{57}$	585.4455 (−2.8)	−32	
587.3633	$C_{43}H_{48}Na$	587.3648 (−1.5)	−38	
649.4743	$C_{49}H_{61}$	649.4767 (−2.4)	−38	

[a] Hydrogen deficiency index: $[C_nH_{2n+Z}N_mS_sO_o + H \text{ (or } + Na)]^+$.

(Table 3). These peaks with odd masses are assigned to protonated or sodium-cationized hydrocarbons without heteroatoms, such as nitrogen and sulfur, with less than 3 mDa deviation. The result suggests that the solvent composition of methanol/chloroform/TFA may enable one to detect hydrocarbon constituents in vacuum residue by ESI FT-ICR MS. This is sensitive issue, i.e., protonation of apolar species in ESI process is not generally accepted view by MS community. Hence we conducted the verification of our insistence by using a model compound.

3.3. Mass spectra of coronene in ESI solvent with different acidity

In order to confirm the generation of protonated hydrocarbons, coronene was measured as a model compound. Fig. 7 shows the ESI FT-ICR mass spectra of coronene in three different solvents: (a) methanol/chloroform, (b) methanol/chloroform/acetic acid, and (c) methanol/chloroform/TFA. Ratio of peak intensities of the molecular ion to the protonated ion decreased in the order: (a) > (b) > (c). Only the molecular ion was observed in the spectrum without acid (a), while the protonated ion was principally detected in the spectrum with TFA (c). Judging from the coronene measurement, selection of solvent composition is very essential to observe protonated molecular ions of aromatic hydrocarbons. Berkel and co-workers have reported that those aromatic hydrocarbons were ionized as radical cations in the ESI solvent (methylene chloride) containing TFA, DDQ, or antimony pentafluoride [30]. One of the possible reasons for detecting protonated form of coronene in the presence of acetic acid or TFA at the present study is role of methanol as a proton donor to assist protonation of polycyclic aromatic hydrocarbons in the acidic solvent system. Different from TFA in methylenechloride solution, acetic acid and TFA work as Bronsted acid in protic solution and donate proton to solvent. Therefore, the peak intensity of protonated ion in methanol/chloroform/TFA was more abundant since TFA is stronger acid than acetic acid. Although further study is needed to elucidate the precise mechanisms, distinction between protonated hydrocarbons and protonated nitrogen-containing compounds as odd and even peaks, respectively, should be expedient for the application to complex analysis, such as vacuum residue, as shown above.

3.4. Distribution of detected compound in AM-VR

Fig. 8 summarizes results of the molecular formula analyses for the all peaks with even masses observed in the range of 570 < *m/z* < 670 in Fig. 3. The peak intensities

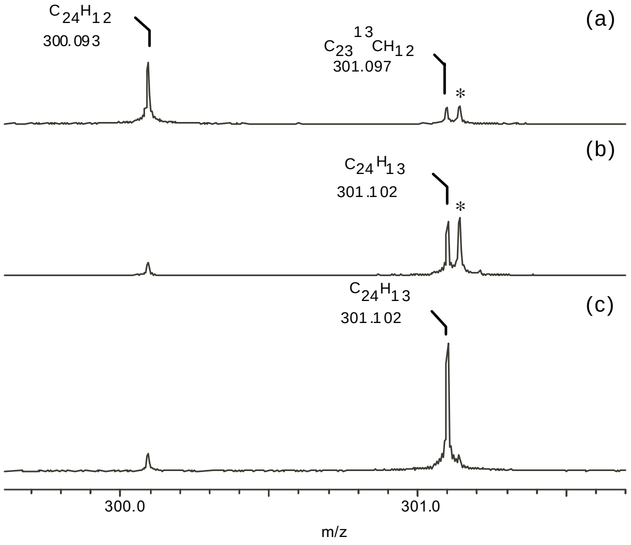


Fig. 7. ESI FT-ICR mass spectra of coronene ($C_{24}H_{12}$) in different solvent compositions; (a) methanol/chloroform, (b) methanol/chloroform/acetic acid, (c) methanol/chloroform/TFA. Starred peak (∗) originates from a plasticizer contained in the solvent.

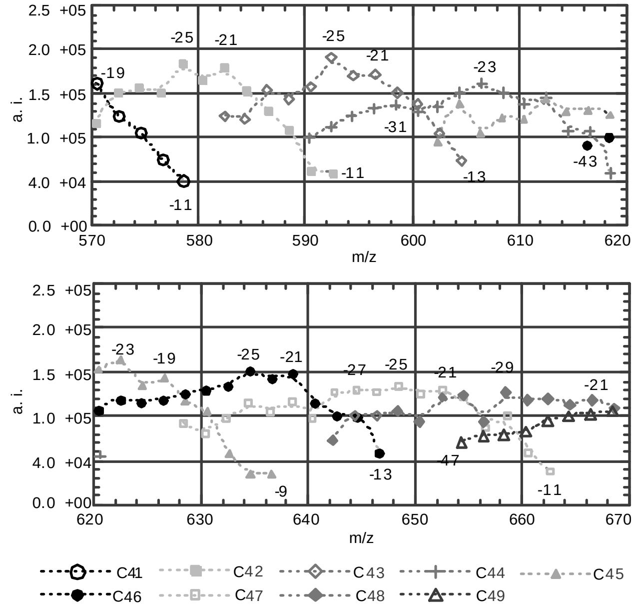


Fig. 8. Relation of peak intensity against Z value of $[C_nH_{2n+Z}N + H]^+$. Molecules having the same carbon number, which was determined by the molecular formulas, are linked with a dashed line; C_{41} (○), C_{42} (■), C_{43} (◇), C_{44} (+), C_{45} (▲), C_{46} (●), C_{47} (□), C_{48} (◆), and C_{49} (△).

are plotted against m/z and molecules having the same carbon number are linked with a dashed-line. Z values ($[C_nH_{2n+Z}N_mS_s + H]^+$) are denoted in the diagram. In Fig. 8, nitrogen-containing compounds with carbon numbers from 41 to 49 were detected, where the Z values varied from −47 to −9. Interestingly, the maximum intensity is observed at the Z value of around −25, irrespective of either the carbon numbers or the m/z values. This result suggests that a series of detected molecules in AM-VR may have a similar aromatic ring condensation with different lengths of alkyl side chains.

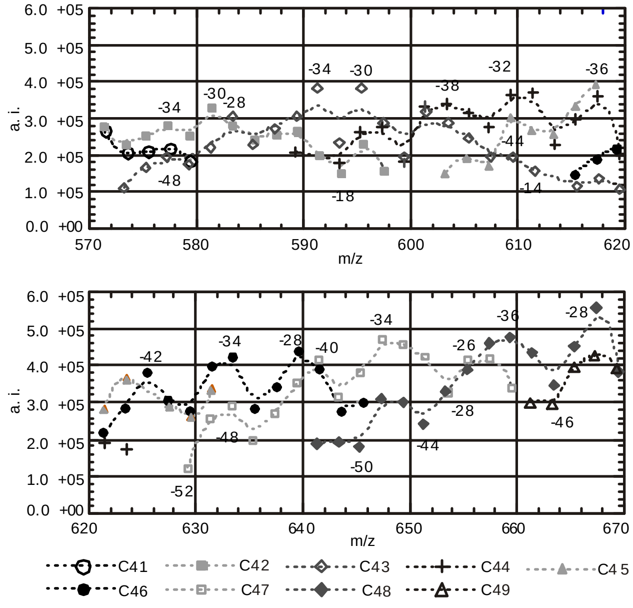


Fig. 9. Relation of peak intensity against Z value of $[C_nH_{2n+Z} + Na]^+$. Molecules having the same carbon number, which was determined by the molecular formulas, are linked with a dashed line; C_{41} (○), C_{42} (■), C_{43} (◇), C_{44} (+), C_{45} (▲), C_{46} (●), C_{47} (□), C_{48} (◆), and C_{49} (▲).

The results of the peak analysis of all the odd masses observed in the range of $570 < m/z < 670$ in Fig. 6 are summarized in Fig. 9. The adducted hydrocarbons with carbon numbers from 41 to 49 are detected, while the Z values range from −54 to −8, which correspond to 1–10 aromatic rings. In contrast to nitrogen-containing compounds profile shown in Fig. 8, several maxima with different Z values were observed for each carbon number in Fig. 9; i.e., the distribution of Z value of hydrocarbons was broader than that of nitrogen-containing compounds. The profile also suggests that compounds with wide variety of aromatic structures are present, although more detailed structural analysis, such as MS/MS, may be required to elucidate those structures.

4. Conclusion

We have demonstrated that aromatic hydrocarbons with equal to or more than three condensed rings and without any polar functional groups are ionized by ESI. Furthermore, tunable effect of detected compounds has been also demonstrated as even and odd peaks for nitrogen-containing compounds and aromatic hydrocarbons, respectively, by changing ESI solvent composition, such as methanol/chloroform and methanol/chloroform/TFA. All the nitrogen-containing compounds and hydrocarbons in AM-VR detected in the range of $570 < m/z < 670$ were characterized by ESI FT-ICR MS and structures estimated based on accurate mass measurements were discussed in relation to hydrogen deficiency index and carbon number. The maximum intensity for nitrogen-containing compounds is observed at the Z value of around −25 irrespective of m/z values, while no such maximum is observed for hydrocarbons. Further improvement in ionization efficiency of hydrocarbons is required to obtain a spectrum which reflects the whole constituents in vacuum residues.

In the combination of the tuning effect of ESI solvent composition and FT-ICR MS for the selective analysis of constituents in a very complex mixture, the proposed method is expected to extend analytical application of ESI FT-ICR MS with its distinguished performance.

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