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DART Fourier transform ion cyclotron resonance mass spectrometry for analysis of complex organic mixtures

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ABSTRACT

We report the first combination of a commercial direct analysis in real time (DART) source with FT-ICR MS and its application to analysis of complex organic mixtures. DART enables ionization of compounds with little or no sample preparation, and FT-ICR provides ultrahigh mass resolution and mass accuracy. The combination provides a rapid, robust, and reliable method for analysis of components spanning a wide range of chemical functionality. DART 9.4 T FT-ICR MS generates abundant molecular or quasimolecular ions from C_{60}, heavy petroleum, naphthenate deposits, and biotar, without fragmentation. Moreover, we demonstrate desorption/ionization of compounds with boiling points significantly higher than the DART source temperature. DART FT-ICR MS thus offers a new and useful atmospheric pressure ionization mass spectrometry technique for analysis of complex organic mixtures.

1. Introduction

Direct analysis in real time (DART) [1] is a relatively new atmospheric pressure ionization technique that has gained popularity for mass spectrometry-based analysis of compositionally complex organic mixtures [2], with applications in forensics [3], metabolomics [4,5], pharmacokinetics [6], petroleomics [7], homeland security [8,9], food and beverage analysis [10], etc. It offers rapid throughput for analysis of solid, liquid, and gaseous samples with minimal sample preparation requirement.

In DART, a glow discharge sustained by the continuous flow of He gas results in the generation of electronically excited (metastable) He atoms (2^3S_1, 19.82 eV) with lifetimes of up to 8000 s [11]. Positive ions can be formed when metastable atoms interact with ambient air upon exiting the source, resulting in the generation of protonated water clusters, which serve as proton transfer reagents for chemical ionization of analyte molecules desorbed from solid samples placed directly within the ionization region (Fig. 1). Under appropriate conditions, oxygen radical-cation ($O_2^{+\bullet}$) and nitric oxide cation (NO^+) can also be generated, resulting in analyte ionization by charge exchange, hydride abstraction, or/and oxidation reactions [1,12]. For analysis of samples dissolved in a solvent, the metastable helium atoms interact with the solvent molecules to generate primary ions in a transient microenvironment for subsequent chemical ionization of analytes [13]. Solvent molecular ions react with analyte molecules to generate both protonated analyte molecules by proton transfer and/or molecular ions by charge exchange. Negative ions can be produced by four main mechanisms: electron capture, dissociative electron capture, proton transfer, and anion attachment [13]. Recently it was reported that saturated hydrocarbons, alcohols, fatty acids, and esters form $[M+O_2]^{-\bullet}$ ions by anion attachment by means of negative ion DART [14].

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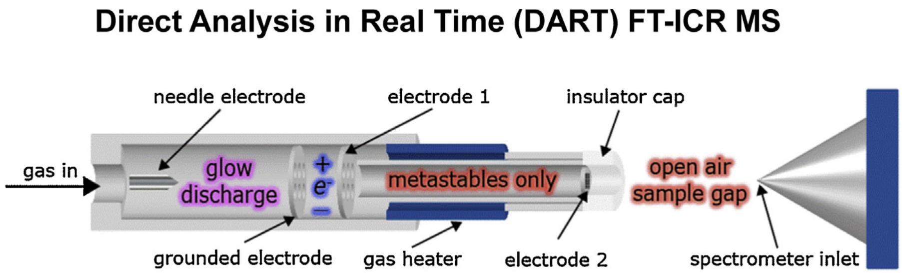

Adapted from www.jeolusa.com

$$He \rightarrow He^{*} \quad 19.8\ eV$$

$$He^{*} + M \rightarrow M^{+\bullet} + He + \bar{e} \tag{1}$$

$$He^{*} + nH_2O \rightarrow [(H_2O)_m + H]^{+} + [(H_2O)_k + OH]^{-} + He \tag{2}$$

$$M + [(H_2O)_m + H]^{+} \rightarrow [M + H]^{+} + mH_2O \tag{3}$$

$$M + [(H_2O)_k + OH]^{-} \rightarrow [M - H]^{-} + (k+1)H_2O \tag{4}$$

Fig. 1. Top: schematic diagram of the IonSense DART source (with permission from JEOL USA, Inc.). Bottom: reactions derived from metastable helium atoms, He* produced by glow discharge (see text).

The nonpareil mass resolution and mass accuracy provided by Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) [15] are essential for analysis of complex organic mixtures [16–21]. Moreover, broadband phase correction [22] and “walking” calibration [23] significantly increase FT-ICR mass resolving power and mass accuracy without any modification or upgrade of instrument hardware. For example, absorption-mode FT-ICR MS can simultaneously resolve mass doublets separated by less than the mass of an electron (~0.0005 Da) in broadband mass spectra over a wide mass range [16]. By comparison, a DART source coupled to an orbitrap mass analyzer, at a mass resolving power ($m/\Delta m_{50\%}$) = 50,000 at m/z 200 demonstrated resolution of CH_4 vs. O (0.036 Da) at m/z 253 in a sparse mass spectrum [24]. However, the much higher resolving power of FT-ICR MS is needed for smaller mass splits in complex mixtures extending to much higher mass (e.g., C_4 vs. $^{13}CH_3S$, 0.0011 Da, requiring mass resolving power higher than 455,000 at m/z 500 – see below).

A custom-built DART source has previously been coupled with FT-ICR MS to characterize individual compounds and complex samples, including a petroleum crude oil [7]. However, the resulting DART mass spectrum of the crude oil differed from that obtained by electrospray ionization (ESI), and demonstrated preferential ionization of low molecular weight components, presumably due to inefficient desorption of larger molecules. Here, we combine a commercial DART source (IonSense, Inc.) with the same 9.4 T FT-ICR mass spectrometer to further explore the capabilities and limitations of the technique for analysis of complex organic mixtures.

2. Experimental methods

2.1. Samples and preparation

HPLC grade solvents (acetone and toluene) and fullerene C_{60} were purchased from Sigma–Aldrich (St. Louis, MO). The deasphalted oil sample, provided by an oil company, is the *n*-heptane soluble fraction (maltenes) from a high vacuum oil residue. Its atmospheric equivalent boiling point is 540 °C+ (ASTM method D7169) (in fact, the sample was never exposed to such a temperature – the maximum temperature in a refinery is limited to ~360–380 °C to prevent thermal cracking). The biotar sample is a product of fast pyrolysis of biomass (hardwood chips) under nitrogen and was obtained from Primus Green Energy, Inc. (Hillsborough, NJ). An emulsion formed in oil–water separators containing sodium naphthenates and solid deposit samples containing calcium naphthenates was received from Nalco Energy Services (Sugar Land, TX).

Fullerene C_{60} dissolved in toluene at a concentration of 5 mg mL^{-1} was introduced into the DART source through a melting point capillary. The deasphalted oil sample was diluted in toluene to a concentration of 1 mg mL^{-1} and continuously injected thorough a metal needle into a DART source (T_{source} = 370 °C) with a syringe pump at 5 μL min^{-1}. The biotar sample was dissolved in acetone at a concentration of 1 mg mL^{-1} and a melting point glass capillary was dipped into the solution and analyzed at a DART source temperature of 300 °C. Emulsion, deposit sample, and “ARN” extract were analyzed directly without dilution or other sample preparation. “ARN” acids isolated from a calcium naphthenate deposit as described elsewhere [25] were ionized at a DART source temperature of 470 °C. Specifically, a calcium naphthenate sample was washed repeatedly with toluene to remove entrapped crude oil until the color of the toluene phase was almost clear. After the toluene wash, calcium naphthenate was digested with 1 M hydrochloric acid, followed by toluene extraction. The organic extract containing ARN acids was then dried with a stream of nitrogen gas.

2.2. Instrumentation and mass analysis

A commercial DART ET source equipped with a DART 100-CE controller for source operation (IonSense, Saugus, MA) was coupled with a custom-built 9.4 T FT-ICR mass spectrometer [26,27] equipped with a Predator data station [28]. The outlet of DART source was axially aligned with the mass spectrometer inlet and the signal was optimized by varying the intervening distance from 4 to 20 mm. The DART source was operated at temperatures ranging from 250 to 500 °C, with helium gas (99.999% purity, Airgas) at ~6 L/min (i.e., 60% of the maximum) flow rate. High voltage (3500 V) was supplied to a needle to provide a glow discharge that generates primary ionizing species (ions, electrons, and electronically excited neutrals). The discharge electrode potential was set to +400 V for generation of positive ions and −400 V for negative ions. The grid electrode potential was set to 0 V to enable efficient transmission of both excited neutrals and charged species to maximize analyte ionization efficiency.

The mass spectrometer was operated as follows: tube lens, 50 V; inlet metal capillary, 70 V and heated with 12 W; and skimmer, 12 V [29]. The generated ions were accumulated in an external linear octopole ion trap [30], ejected by applying a dc voltage to angled wires, and then transferred by rf-only octopoles [31] (operated at 2.0 MHz and 240 V_{p-p}) to an open cylindrical Penning ion trap [32]. Ions were subjected to broadband frequency-sweep (chirp) dipolar excitation (at a sweep rate of 50 Hz/μs and amplitude, 450 V_{p-p}) followed by direct broadband image current detection to yield 8 Mword time-domain data. 20 time-domain acquisitions were summed, Hanning-apodized, and zero-filled once before fast Fourier transformation and magnitude calculation. ICR frequency to mass-to-charge conversion was based on the quadrupolar electrostatic trapping potential approximation [33,34].

2.3. Data analysis

Prior to mounting of the DART source, the mass spectrometer was calibrated by use of electrospray-ionized Agilent HP mix No. G2421A (Agilent Technologies, Santa Clara, CA) under ESI. FT-ICR mass spectra of complex mixtures (i.e, petroleum and bio-tar samples) were internally calibrated with respect to a highly abundant homologous series of ions spanning a wide mass range. Singly charged ions with mass spectral peak magnitude greater than 6 times the standard deviation of the baseline noise were Kendrick-sorted and imported into Microsoft Excel for identification with a formula calculator as per a previously reported procedure [35]. Kendrick mass defect was used to identify homologous series for peak assignment [36]. The most abundant homologous series of ions used for internal calibration can differ from sample to sample. For example, for (−) DART FT-ICR MS for sodium naphthenates, it was the O_2 class (DBE = 1). Relative isoabundance-contoured plots of double bond equivalents (DBE = number of rings plus double bonds to carbon) [37] vs. carbon number serve to visualize data for all members of a given heteroatom class ($N_nO_oS_s$) simultaneously.

3. Results and discussion

3.1. Need for high mass resolving power

In general, DART can generate both even- and odd-electron positive ions, and very narrow mass splits must be resolved for organic compounds containing C, H, N, O, and S atoms. Examples of mass splits that require ultrahigh resolving power are shown in Table 1. Resolution of those splits over a wide mass range is achievable only with FT-ICR MS, because the mass resolving power ($m/\Delta m_{50\%}$) entries in the right column in Table 1 represent the minimum required to barely resolve two peaks of equal magnitude; much higher resolving power is needed to resolve peaks of significantly different magnitude [38].

3.2. DART source temperature and fractionation

DART FT-ICR mass spectra of complex mixtures (e.g., petroleum or environmental samples) may exhibit a truncated molecular weight distribution if the components span a wide range of boiling temperature. The above phenomenon is known as "fractionation" and results from faster evaporation of more volatile molecules, resulting in underestimation of the higher-boiling components. The fractionation effect can be minimized by use of direct sample injection and signal averaging.

To investigate the DART temperature limitation, we analyzed fullerene C_{60} at a DART source temperature (370 °C) well below the C_{60} sublimation temperature (500 °C) [39]. (Note that the temperature reported by the DART software is from a thermocouple embedded in the ceramic heater, not in the gas stream. Therefore, the actual gas temperature is lower, and is a function of the heater core temperature, gas flow rate, and heat capacity of the gas [40].) Fig. 2 shows a positive ion DART FT-ICR mass spectrum of the fullerene, C_{60}. The highest magnitude peak corresponds to $[M+H]^+$ ions, and is produced in the source by ion-molecule reactions that result in proton transfer from H_3O^+. The proton affinity (PA) is 167 kcal/mol [41] for H_2O and 190 kcal/mol [42] for

Table 1
Common mass "splits" observed by DART MS analysis of complex organic mixtures.

Doublet	m_2–m_1, Da	Minimum resolving power ($m/\Delta m_{50\%}$) at m/z 500
C_2H_4 vs. N_2	0.0252	20,000
H_2N vs. O	0.0238[a]	22,000
H_4O_2 vs. C_3	0.0211	24,000
O_2 vs. S	0.0178	29,000
C_2H_3 vs. ^{13}CN	0.0170	30,000
H_6S vs. C_2N	0.0159[a]	32,000
HN_2 vs. ^{13}CO	0.0157[a]	32,000
C4 vs. O_3	0.0153	33,000
CH_2 vs. N	0.0126[a]	40,000
$^{13}CH_5S$ vs. C_3N	0.0115	44,000
N_2 vs. CO	0.0112	45,000
H_4O_3 vs. C_2N_2	0.0099	51,000
C_2H_2 vs. $^{13}C_2$	0.0089	57,000
^{13}CH vs. N	0.0081	62,000
H_3NS vs. $C_3{}^{13}C$	0.0047	107,000
CH vs. ^{13}C	0.0045[a]	112,000
C_2N vs. $^{34}SH_4$	0.0039[a]	129,000
$^{13}C_2$ vs. CN	0.0036[a]	139,000
H_4S vs. C_3	0.0034	148,000
$C_2H^{34}S$ vs. $NS^{13}C$	0.0028	179,000
C_4 vs. $^{13}CH_3S$	0.0011[a]	455,000

[a] Mass split due to simultaneous presence of even- and odd-electron ions.

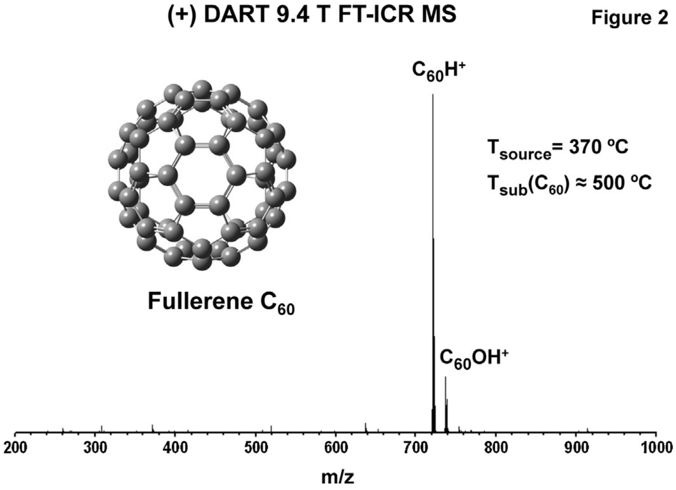

Fig. 2. Positive ion DART 9.4 T FT-ICR mass spectrum of fullerene C_{60} at a DART source temperature (T_{source} = 370 °C) well below the sublimation point (T_{sub} = 500 °C) of C_{60}.

$(H_2O)_2$, compared to 204 kcal/mol [43] for C_{60}. The peak at *m*/*z* 737 ($[M+O+H]^+$) is due to oxidation of fullerene during atmospheric pressure ionization. Thus, DART enables ionization of high-boiling compounds due to desorption/ionization of analyte molecules by highly energetic reagents (ions and electronically excited neutrals) [1], formed in the source region.

3.3. DART FT-ICR MS for petroleum analysis

To evaluate the suitability of DART for analysis of compositionally complex mixtures of high-boiling compounds spanning a wide molecular weight range, we examined a deasphalted oil containing compounds boiling at ≥540 °C. Fig. 3 shows a DART FT-ICR mass spectrum with signals from 400 to 1600 Da and a number-average molecular weight of ~1100 Da. Note that the molecular weight distribution was the same as obtained by ESI and atmospheric pressure photoionization [44], validating the applicability of DART for petroleum analysis.

3.4. Sodium naphthenates

Another potential application of DART is direct analysis of rock samples, geological and production deposits, and natural objects of organic origin. We therefore applied (−) DART FT-ICR MS to analyze industrial naphthenate deposits formed by the interaction of naphthenic acids with monovalent (Na^+, K^+) and divalent (Ca^{2+}, Mg^{2+}) ions from produced waters that cause severe problems during petroleum production [45,46]. Naphthenic acids are encountered in all crude oils and their abundance depends on petroleum maturity and degree of biodegradation. The correlation between concentration of naphthenic acids detected by negative ion (ESI) mass spectrometry and total acid number has been established recently [47]. In the petroleum industry the term "naphthenic acids" encompasses all carboxylic acids, including acyclic, cyclic (truly naphthenic), and aromatic. Naphthenates can occur as stable emulsions, soap, sludge, and deposits. Sodium naphthenates predominantly form emulsions and soaps, and consist of monoprotic carboxylic acids with carbon number from C_{15} to C_{35}.

Naphthenates have traditionally been isolated by a time-consuming purification protocol for subsequent analysis by negative ion ESI MS [25]. Fig. 4 shows the broadband negative ion DART FT-ICR mass spectrum of sodium naphthenates obtained

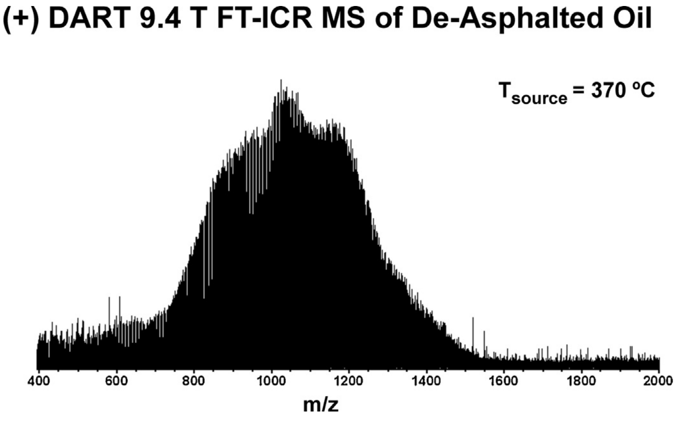

Fig. 3. Positive ion DART 9.4 T FT-ICR mass spectrum of a de-asphaltened high vacuum gas oil.

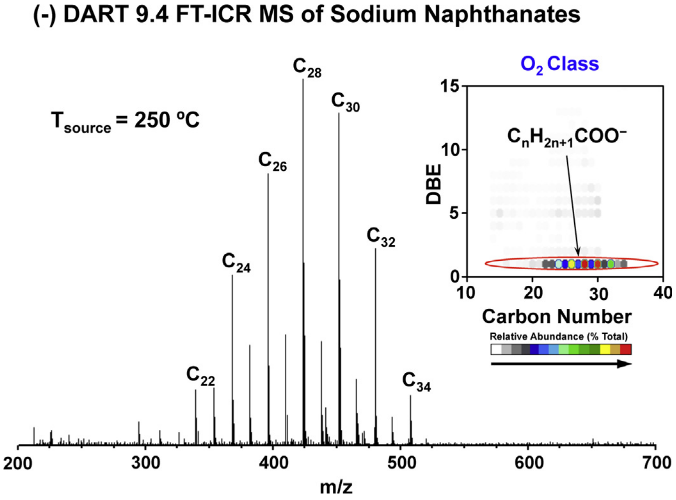

Fig. 4. Negative ion DART 9.4 T FT-ICR mass spectrum of a sodium naphthenate emulsion. Inset: isoabundance-contoured plot of double bond equivalents (DBE) vs. carbon number for O_2 class ions.

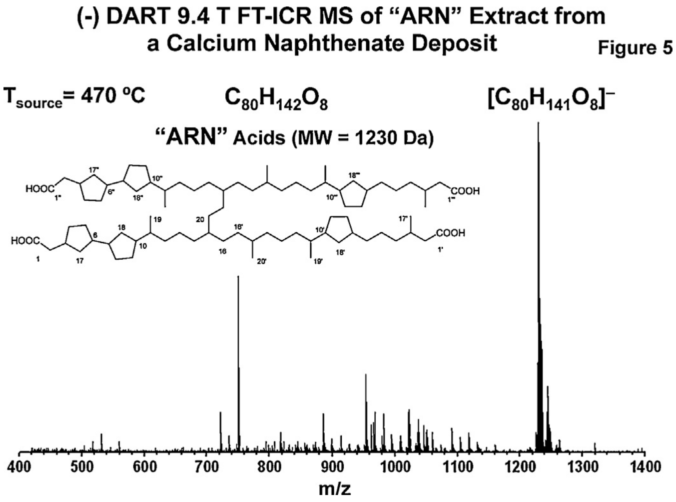

Fig. 5. Negative ion DART 9.4 T FT-ICR mass spectrum of an "ARN" extract from a calcium naphthenate deposit, clearly showing singly charged $[M-H]^-$ ions from ARN acids. The accompanying ARN acid structure was suggested by Lutnaes et al. [45].

from a stable emulsion interfacial layer in oil/water separation units. Although the analysis does not require any sample preparation, and takes only several seconds, it nevertheless provides rich compositional detail about the naphthenic acids. Specifically, the detected acids exhibit DBE = 1, corresponding to saturated acyclic carboxylic acids (fatty acids). Saturated fatty acids form an emulsion in the sodium naphthenate deposit, in accord with their structurally determined surfactant properties (polar carboxylic head and nonpolar aliphatic tail). The acid composition derived from (−) DART FT-ICR MS closely matches that from (−) ESI FT-ICR MS for similar extracts [25]. Notably, the absence of dimers in the (−) DART mass spectrum, in addition to much shorter analysis time, is another advantage of DART over ESI. Concentration-dependent naphthenic acid multimer formation (e.g., $[2M-H]^-$ ions) is usually observed with (−) ESI and requires additional ion activation (either collision-induced dissociation or infrared multiphoton dissociation) [48]. Finally, DART mass spectra are less subject to matrix effects than ESI, resulting in wider applicability of DART for screening of targeted compounds in complex matrices.

3.5. Calcium naphthenates

In petroleum production, calcium naphthenates are formed from high molecular weight tetraprotic carboxylic acids (so-called "ARN" acids) with ~80 carbons, and produce sludge and solid

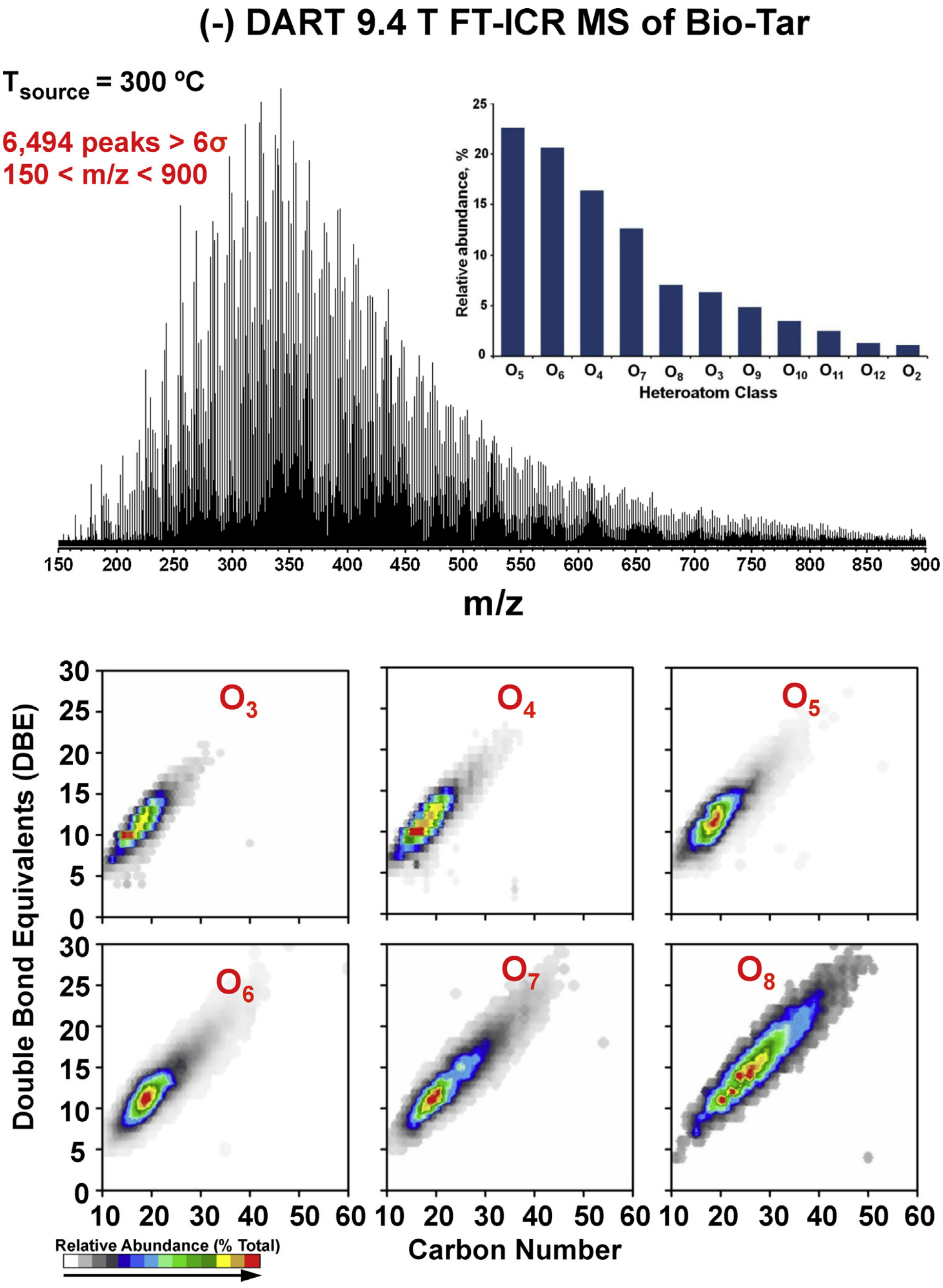

Fig. 6. Top: negative ion DART 9.4 T FT-ICR mass spectrum of a biotar sample. Inset: summed relative abundances for each member of the O_x (x = 2–12) heteroatom class. Bottom: isoabundance-contoured plots of DBE vs. carbon number for each of the most abundant heteroatom classes.

deposits [25,49]. C_{80} ARN acid molecular weights range from 1228 to 1236 Da, and their elemental compositions have been determined by FT-ICR accurate mass measurement [50]. ARN acids were first found in deposits from an offshore Norwegian Sea oil field. The term "ARN" ("eagle" in Norwegian) derives from their talon-like structure determined by NMR [51]. The structure of ARN acids (a head-to-head linked isoprenoid 20-bis-16,16′-biphytane carbon skeleton with four to six cyclopentane rings) is believed to closely resemble the tetraethers in lipid membranes from Archaea bacteria [52,53], a family of microorganisms found in most petroleum reservoirs.

The (−) DART FT-ICR mass spectrum of the "ARN" extract from a solid calcium naphthenate deposit (Fig. 5) clearly shows abundant $[M-H]^-$ ions from "ARN" acids (confirmed by high resolution mass measurement). In contrast to (−) ESI, which produces both singly and doubly-charged ions [49], DART generates exclusively singly-charged $[M-H]^-$ ions. Prior low resolution mass spectra for naphthenate extracts derived from atmospheric pressure chemical ionization also yielded preferential (if not exclusive) formation of singly-charged ions for ARN acids [54]. DART ionization (like atmospheric pressure chemical ionization (APCI)) takes place in the gas phase, and formation of doubly-charged ions from singly-charged small molecules is energetically unfavorable. In contrast, with ESI, analytes are typically pre-ionized in solution (and thus can be multiply-charged) as ions are transferred from liquid to gas phase.

3.6. Bio-tar

Finally, we apply DART FT-ICR MS for characterization of biotar produced from hardwood chips during fast pyrolysis under nitrogen. The primary components of wood include bio-polymers (cellulose, hemi-cellulose, lignin) that decompose on heating in the absence of oxygen. In general, pyrolysis of biomass results in the formation of gas, liquid (biotar), and solid (charcoal) phases. Fast pyrolysis is used to maximize the yield of liquid products that can be further upgraded to produce transportation fuels [55]. The application of DART time-of-flight MS for analysis of mainly volatile, low molecular weight compounds formed during wood pyrolysis has been reported [56].

Compositional characterization of biotar is crucial for the development and optimization of technology in manufacturing of bio-fuels. The negative ion DART FT-ICR mass spectrum of biotar (Fig. 6, top) reveals more than 6400 different elemental compositions spanning a wide mass range $150 < m/z < 900$. The most abundant heteroatom ion classes (Fig. 6, top inset) are O_n ($n = 3$–8). Fig. 6, bottom demonstrates the distribution of components within each heteroatom class, graphically sorted according to DBE and carbon number. All of the biotar O_n classes are highly aromatic (i.e., high DBE for a given carbon number). The diagonal distribution in DBE vs. carbon number is characteristic of polymers: i.e., composition and molecular weight increase proportionally with addition of each successive monomer unit. Here again, (−) DART determination of the most abundant heteroatom classes and the distribution of components in the DBE vs. carbon number plots are similar to those from (−) ESI [57], except for small differences in relative abundances.

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