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# Ambient Analysis of Saturated Hydrocarbons Using Discharge-Induced Oxidation in Desorption Electrospray Ionization

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Saturated nonfunctionalized hydrocarbons can be oxidized in situ by initiating an electrical discharge during desorption electrospray ionization (DESI) to generate the corresponding alcohols and ketones. This form of reactive DESI experiment can be utilized as an in situ derivatization method for rapid and direct analysis of alkanes at atmospheric pressure without sample preparation. Betaine aldehyde was incorporated into the DESI spray solution to improve the sensitivity of detecting the long-chain alcohol oxidation products. The limit of detection for alkanes (C<sub>15</sub>H<sub>32</sub> to C<sub>30</sub>H<sub>62</sub>) from pure samples is ~20 ng. Multiple oxidations and dehydrogenations occurred during the DESI discharge, but no hydrocarbon fragmentation was observed, even for highly branched squalane. Using exact mass measurements, the technique was successfully implemented for analysis of petroleum distillates containing saturated hydrocarbons. (*J Am Soc Mass Spectrom* 2010, 21, 261–267) © 2010 American Society for Mass Spectrometry

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**N**on-polar hydrocarbons, the major constituent (90%) of petroleum distillates derived from crude oil [1], are difficult to analyze by mass spectrometry using atmospheric pressure ionization methods. Saturated hydrocarbons in particular, which lack functional groups and aromatic rings, can only be ionized by high voltage electron ionization (EI), chemical ionization (CI), field desorption (FD), or field ionization (FI). Among these methods, EI, and CI are not ideal for hydrocarbon mixture analysis due to significant fragmentation of molecular ions. As a result, FD and FI are the primary soft ionization methods used in petroleum analysis. However, heating the analytes during FD/FI can be problematic and may cause fragmentation of molecular ions, a problem that becomes acute for high boiling materials [2]. In addition, branched alkanes are easily fragmented in FD/FI, making quantitative measurement of isomeric paraffins very challenging [2, 3]. Atmospheric pressure photoionization (APPI) can be used to ionize nonpolar polycyclic aromatic hydrocarbons by producing a radical cation and/or a protonated molecule of the analyte, but it cannot be used to ionize saturated paraffins [4]. In spite of these difficulties, traditional hydrocarbon analysis in the petroleum industry continues to be an important subject. Recently, laser-induced acoustic desorption

(LIAD) coupled with gas-phase ion/molecule reactions under vacuum has shown great potential to achieve efficient ionization of saturated hydrocarbons with little [1] or no [5] fragmentation. Direct analysis of hydrocarbons under ambient conditions remains highly desirable however, because it allows easy implementation on both commercial and portable mass spectrometers of on-site analysis and has the potential for high throughput screening. This paper introduces a new method that addresses this problem.

Desorption electrospray ionization (DESI) is an ambient analysis method that shares some of the properties of the electrospray (ESI) technique [6]. In particular, oxidation artifacts of analytes have been reported in both DESI [7, 8] and ESI [9, 10]. In the recent report of Konermann et al. [10], it was noted that corona discharge-induced reactive oxygen species (ROS) are solely responsible for the multiple oxidations observed in ESI. Oxidative modifications during ionization adversely complicate spectral interpretation, especially for analytes prone to oxidative degradation, therefore, generally they should be avoided or suppressed [7–10]. Situations do exist, however, where the reactive species induced by electrical discharges can be used to advantage in chemical analysis (e.g., protein structural mapping [11]).

In this article, we report on direct hydrocarbon mixture analysis by reactive DESI-MS using in situ hydrocarbon oxidation (the result of electrical discharges deliberately made to accompany the DESI process by adjusting the DESI probe position). The initially

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formed alcohols are derivatized in situ to hemiacetals using betaine aldehyde, which is added to the spray solution as the reagent [12]. Reactive DESI, a variant on the basic DESI experiment, implements rapid chemical reactions occurring at the spot being sampled concurrently with acquisition of mass spectra to improve sensitivity and selectivity for target molecules [13], by simply doping the reagent into the spray solvent.

## Experimental

### Chemicals

Two petroleum distillates (vacuum gas oil saturates I and II having nominal boiling points between 343 and 540°C) were obtained from ExxonMobil Research and Engineering Co. (Annandale, NJ, USA). n-Alkane standards from C<sub>5</sub> to C<sub>40</sub> were purchased from Agilent Technologies (Santa Clara, CA, USA). All other chemicals were purchased from Sigma-Aldrich Inc. (Milwaukee, WI, USA). The solutions of hydrocarbon and petroleum samples were prepared by dissolving and diluting them in CHCl<sub>3</sub>. Microscope glass slides (75 × 25 mm) of 1 mm thickness (Gold Seal Products Inc., Portsmouth, NH, USA) were used as the substrate for DESI.

### DESI-Mass Spectrometry

Reactive DESI analysis was performed using a ThermoFisher Scientific LTQ linear ion trap mass spectrometer (San Jose, CA, USA) coupled to an OmniSpray ion source from Prosofia, Inc. (Indianapolis, IN, USA). A sprayer-to-surface distance of less than 2 mm, a sprayer-to-inlet distance of less than 2 mm, and a spray impact angle of 52° were used. The spray voltage was set at a value in the range of 5 to 8 kV. The current in the DESI circuit is normally ~200 nA. When a visible electrical discharge was observed in the dark during the experiment, the current increased by a factor of 10 or more, but the highest current was still in the low  $\mu$ A range, so the mass spectrometer still operated normally. The nebulizing gas (N<sub>2</sub>) pressure was 150 psi and the solvent flow rate was 3  $\mu$ L/min. The spray solvent was acetonitrile (ACN)/chloroform (CHCl<sub>3</sub>) with 1:2 volume ratio, containing 50 ppm betaine aldehyde (BA). The same procedures were used with a Thermo Scientific Hybrid LTQ-Orbitrap mass spectrometer (Bremen, Germany). The betaine aldehyde ion at *m/z* 102.0913 was used as the lock-mass for accurate mass measurements. The Orbitrap resolution was set to 100,000.

### Oxidation Product Collection and GC-MS

To collect the DESI oxidation products, 3  $\mu$ L of 1000 ppm cyclopentadecane dissolved in CHCl<sub>3</sub> was deposited on a glass slide and subjected to DESI using MeOH:H<sub>2</sub>O (1:1, vol/vol) (without BA) as spray solvent. The residue of cyclopentadecane on the glass slide was collected after 5 min using 100  $\mu$ L CHCl<sub>3</sub> and

subsequently analyzed by GC/MS (Hewlett-Packard Engine; Hewlett-Packard Company, Wilmington, DE, USA). The same collection procedures were used to collect the oxidation products of *n*-octadecane. The capillary column (15 m DB-1) was heated from 40 °C (held for 0.3 min) to 320 °C at a rate of 10 °C per minute. The injector temperature was set at 250 °C. The products were detected by CI (reagent gas: methane) and EI (70 eV electrons).

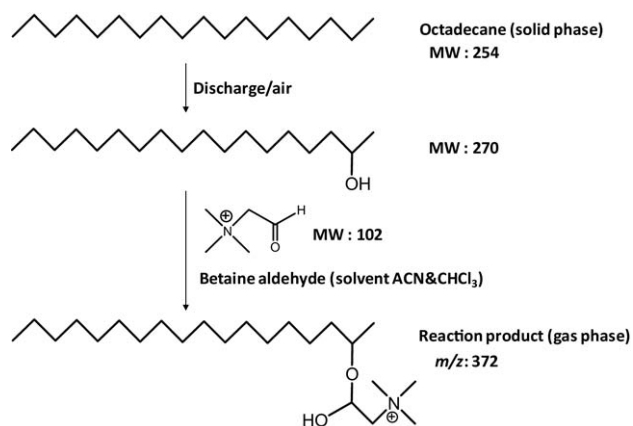
### GC-FI-TOF MS

Experiments were conducted using a Waters GCT (Manchester, UK) with a field ionization source. The details of the instrument, data analysis, and application can be found in previous publications [14]. Petroleum samples were diluted with methylene chloride to produce 1% solutions. About 1  $\mu$ L of the solution was injected using a 50:1 split ratio into the GC equipped with a non-polar 30 m DB-1 column. The GC oven temperature was ramped from 35 °C to 350 °C at 10 °C/min. The position of the FI emitter was carefully aligned with the end of the GC capillary column so that effluent molecules pass near the tips of the carbon dendrites. The pressure in the source was nominally 10<sup>-5</sup> torr. Ions formed in the FI source were transported into an acceleration region where packets of ions were ejected by an electric pulse (960 V) into the TOF MS (mass resolution ~ 7000) for mass analysis.

## Results and Discussion

### Oxidation Induced by Discharge in DESI

When a high voltage (5 to 8 kV) was applied to the spray in the DESI experiments (typical voltage used 4.5 kV), a visible discharge could be observed in the dark between the spray emitter and the mass spectrometer inlet capillary when these were positioned at distances of ~2 mm (Figure S1, Supporting Information, which can be found in the electronic version of this article). Discharges between the substrate (a glass slide) and the inlet capillary of the mass spectrometer were also observed when moving the substrate close to the emitter and hence to the inlet capillary (See Supporting Information for the video). Discharges in air produce reactive radicals including hydroxyl radical ( $\cdot$ OH), atomic oxygen (O), and nitric oxide (NO  $\cdot$ ), which can initiate a cascade of oxidation reactions in solution and in the gas phase [9, 15]. In the case of saturated hydrocarbons, possible oxidation products include alcohols and ketones. However, due to their low proton affinities and low acidities, long-chain alcohols and ketones are not efficiently ionized by conventional DESI (or by ESI). To enhance the detection sensitivity betaine aldehyde (BA), a reagent that efficiently reacts with nucleophiles and introduces a charge label, was incorporated in the DESI spray solvent [12]. BA reacts with alcohols to produce a hemiacetal salt which is readily

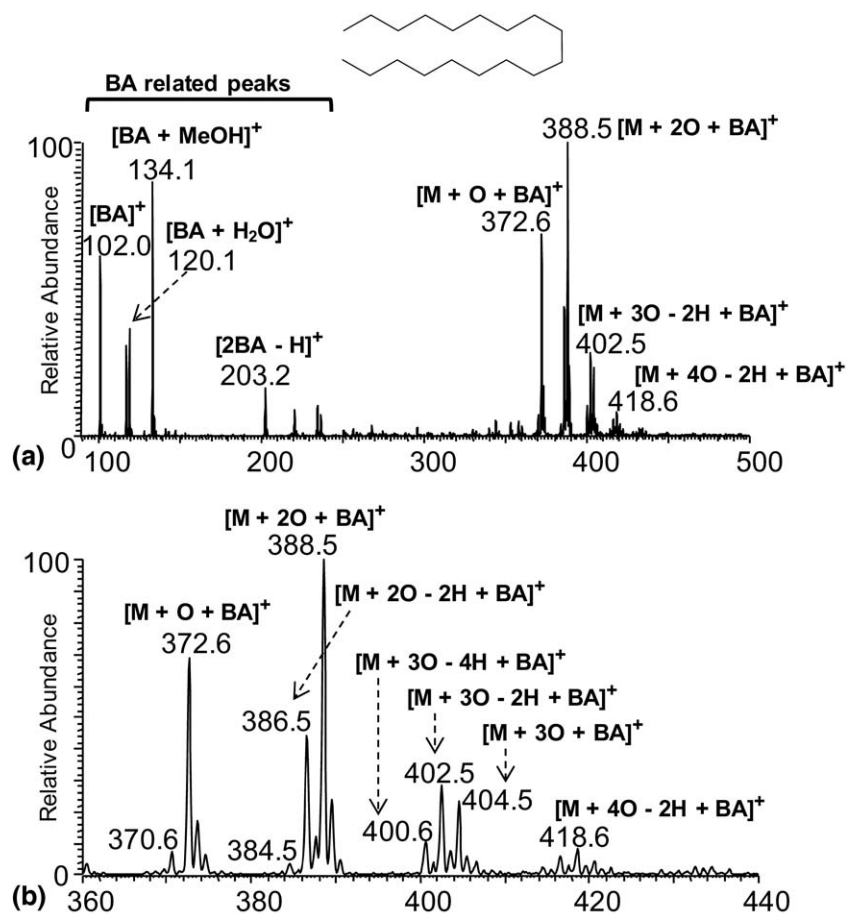


**Scheme 1.** In situ oxidation of hydrocarbons and reaction between the oxidation produced alcohol and betaine aldehyde.

ionized and detected in DESI (Scheme 1). For a target alkane of molecular weight  $M$ , the mono-oxidized product has a MW of  $(M + 16)$ , and the detected hemiacetal product  $[M + O + BA]^+$  gives a signal at  $m/z (M + 16 + 102)$ , where 102 corresponds to the molecular weight of BA. Note that the point of attachment of the hydroxyl

group is not known; it is not necessarily at the 2 position of  $n$ -octadecane as shown in the scheme. Multiple oxidations also occur during the discharge, but are not shown in the scheme for clarity.

As shown in Figure 1a,  $n$ -octadecane was sensitively detected by reactive DESI using in situ oxidation as a first derivatization step, a nonpolar solvent [ACN/CHCl<sub>3</sub> (1:2)] to desorb the nonpolar analyte and/or its reaction products from the glass slide, and using BA as a dopant in the spray solution to produce charge labeling (the second derivatization step). The signals seen in the low mass range ( $m/z$  102, 120, 134, 203) are BA but not analyte related. For example, the peaks at  $m/z$  120 and 134 are due to the reaction products between BA and traces of water and methanol in the solvent spray. The peaks in the higher mass range (between  $m/z$  370 and 420) are  $n$ -octadecane related and correspond to addition of one molecule of BA (102 Da, the molecular weight of BA, see Scheme 1) and one or more (up to 5) additions of 16 Da (corresponding to one or more O atoms). Peaks two mass units below those just assigned were also observed and they are due to alcohol dehydrogenation (Figure 1b). Oxidation products other than alcohols to which BA is highly selective,



**Figure 1.** (a) Reactive DESI of  $n$ -octadecane. (b) Same spectrum showing mass range  $m/z$  360 to 440. An aliquot of 1  $\mu$ L of  $n$ -octadecane solution (200 ppm) dissolved in CHCl<sub>3</sub> was spotted on a microscope glass slide for analysis after drying in air.

were not detected. Besides *n*-octadecane, other saturated alkanes (C15 to C30) can also be oxidized and detected at levels as low as 20 ng in pure samples. Cyclopentadecane, squalane (a branched alkane), cholesterol, and octadecylbenzene display the same oxidation and dehydrogenation pattern without evidence of fragmentation (Figure S2, Supporting Information). As opposed to FI/FD, no hydride abstraction [16] was observed in these spectra. In addition, fragmentation of branched alkanes, which occurs in FI/FD, was not observed in reactive DESI.

The factors affecting the extent of oxidation during the discharge include the spray voltage, the distance between the spray emitter and the MS inlet capillary, the distance between the substrate and the inlet capillary, and the conductivity of the solvent. The extent of oxidation can be reduced by using a lower spray voltage or longer distances between the spray emitter and the inlet capillary of the mass spectrometer. Under these conditions, the discharge phenomenon becomes weaker (no longer visible in the dark) and/or intermittent. The result of reducing the discharge intensity is a general decrease in intensity of all oxidation-related peaks. However, the number of oxygen additions to each molecule remains largely the same. Attempts to increase the selectivity of the process to produce solely mono-oxidized products by changing the operating conditions were not successful. Non-alkylated aromatic compounds such as benzene and naphthalene can also be oxidized in low power plasmas [17], but they give very weak signals in the reactive DESI experiments. This is due to the decreased reactivity of aromatic alcohols toward BA, as the nucleophilicity of the hydroxyl groups in the aromatic alcohols is reduced through electron delocalization on the aromatic ring. For example, when analyzing a mixture of 2-naphthol ( $1 \times 10^{-8}$  mol) and cyclopentadecanol ( $1 \times 10^{-8}$  mol), the signal of the reaction product of 2-naphthol with BA is  $\sim 100$  times less than that of cyclopentadecanol (Figure S3, Supporting Information).

To determine the oxidation products induced by electrical discharges accompanying DESI, the hydrocarbon residue on the glass slide was collected (see Experimental section, note BA was not used for these experiments) for GC analysis. The results show that cyclic alcohols and ketones were generated as oxidation products of cyclopentadecane and that there is no evidence for ring opening or fragmentation (Figure S4 and S5, Supporting Information). No isomers are possible for the mono-oxidized products cyclopentadecanol and cyclopentadecanone. However, mono-oxidation of a straight-chain alkane like *n*-octadecane, can lead to a variety of isomers. The GC-MS data show that positions at or near the end of the chain are preferred (Figure S6 and S7, Supporting Information). The detailed mechanism for this observation is not clear at this stage, but presumably this is because radicals, such as hydroxyl radicals, show some selectivity in terms of the types of bonds with which they react, although this selectivity is

in the context of a highly reactive and therefore relatively indiscriminate reactivity [18]. The oxidation products of hydrocarbons in DESI are consistent with those obtained using a discharge reactor [19], which also generates isomeric alcohols and ketones from short alkanes like hexane.

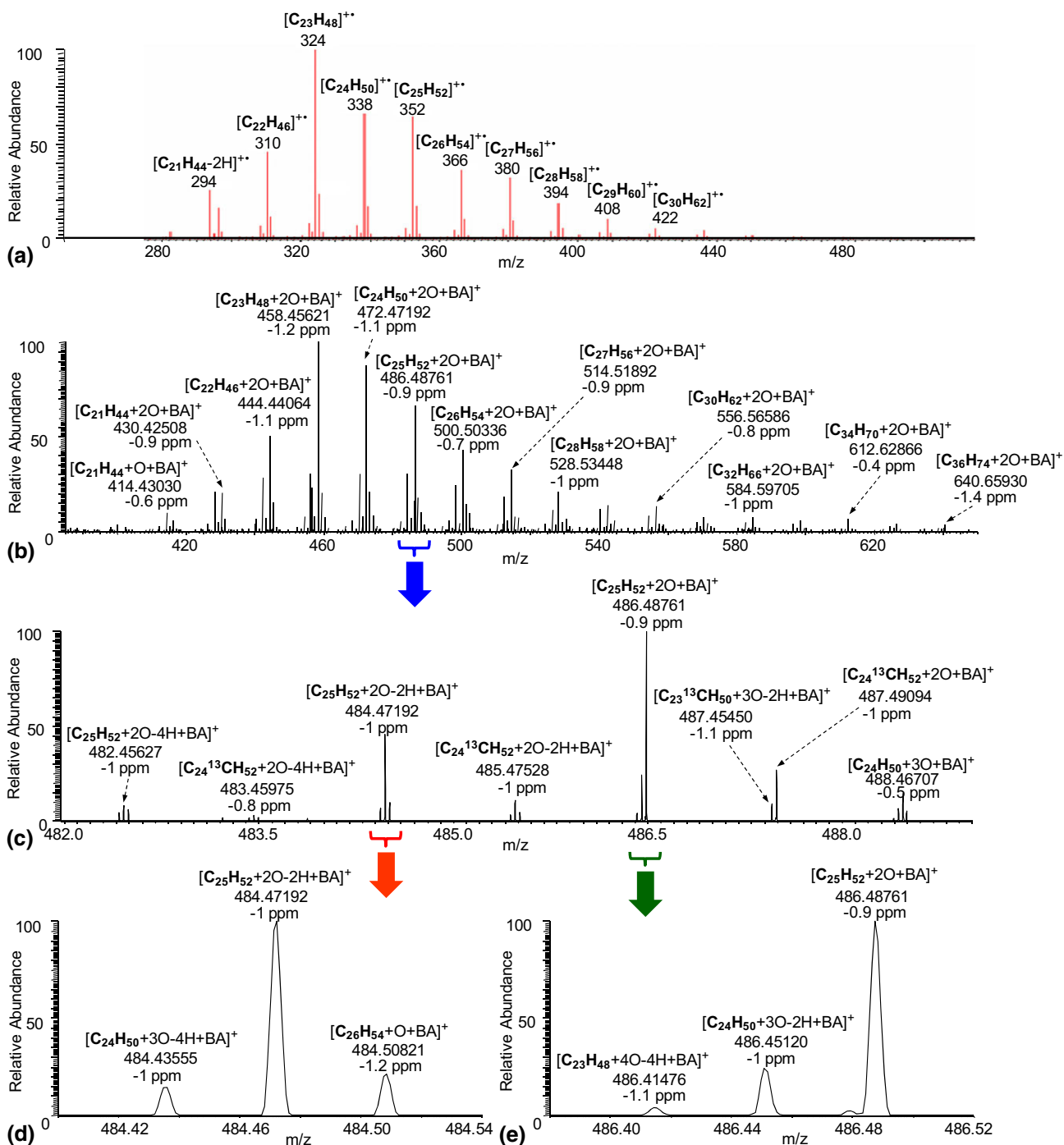
### *Petroleum Sample Analysis Using High Resolution Orbitrap*

Since dehydrogenation accompanies oxidation and the nominal masses of the units [O – 2H] and [CH<sub>2</sub>] is the same, the oxidation plus dehydrogenation peaks of shorter alkanes overlap with the lower oxygenation products of the longer alkanes. Mixtures of alkanes with continuous carbon numbers give products that generally cannot be resolved using a linear ion trap with mass resolution of  $\sim 2000$ . This problem can be addressed by high-resolution mass spectrometry [20], e.g., by using reactive DESI on a high-resolution Orbitrap mass spectrometer. The exact mass of each peak was measured and chemical formulas were automatically assigned in the XCalibur 2.0 software. The original alkane, the number of oxygen atoms added and the extent of dehydrogenation was derived by subtracting the formula of BA (C<sub>5</sub>H<sub>12</sub>ON) from the automatically assigned formula.

Figure 2a shows the mass spectrum of a petroleum distillate containing vacuum gas oil saturates (boiling point > 316 °C) obtained using FI on a time-of-flight (TOF) mass spectrometer. Figure 2b shows the mass spectrum of the same petroleum distillate using reactive DESI on a high-resolution Orbitrap mass spectrometer. The nominal masses of the assigned alkanes are consistent with the results obtained using FI (Figure 2a). From the exact masses of the major peaks which in this case are due to two oxygen additions, alkanes from C<sub>21</sub>H<sub>44</sub> to C<sub>36</sub>H<sub>74</sub> were assigned with an error of less than 1.5 ppm in Figure 2b. Reactive DESI shows a similar relative signal response but a slightly higher sensitivity to larger alkanes (C<sub>30</sub>H<sub>62</sub> to C<sub>36</sub>H<sub>74</sub>) compared with FI. The minor peaks in Figure 2b correspond to multiple dehydrogenations and to <sup>13</sup>C isotopes, as shown in the expanded mass spectrum (Figure 2c). Further expansions (Figure 2d and e) show that the peaks of alkane oxidation products with a mass difference of 0.03 Da are easily resolved and accurately assigned. Another vacuum gas oil sample, containing alkanes in a slightly different mass range, was also analyzed (Figure S8, Supporting Information). However, the relative signal response is different in this case for the smaller alkanes (C<sub>17</sub>H<sub>36</sub> to C<sub>20</sub>H<sub>42</sub>) when comparing reactive DESI and FI.

To further study the signal response of alkanes as a function of molecular mass, experiments were done using a standard solution of alkanes containing discontinuous carbon number alkanes between C<sub>5</sub>H<sub>12</sub> to C<sub>40</sub>H<sub>82</sub>, each of known wt%. Figure 3a shows the amounts of each of the alkane constituents relative to

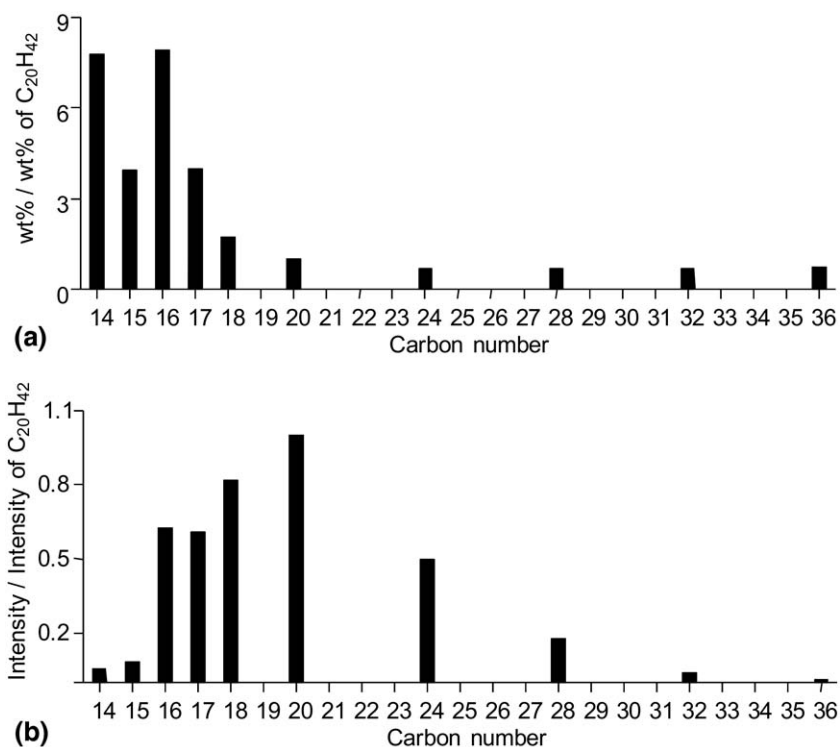




**Figure 2.** (a) FI-TOF mass spectrum of vacuum gas oil saturates I (b); reactive DESI-Orbitrap mass spectrum of the same vacuum gas oil saturates and the expanded mass ranges (c), (d), and (e). The original petroleum distillate sample was diluted 100 times with  $CHCl_3$  and 2  $\mu L$  aliquots of the diluted solution were spotted onto a microscope glass slide.

*n*-eicosane. Figure 3b shows the signal responses of the alkanes represented relative to *n*-eicosane (corresponded to the highest peak), calculated from the mass spectrum obtained using reactive DESI (Figure S9, Supporting Information). Alkanes smaller than  $C_{14}H_{30}$  were not observed. The response increases with carbon number up to 20, and then decreases. Further confirmation of the response was obtained using another

alkane mixture containing the same amount of each alkane from  $C_{21}H_{44}$  to  $C_{30}H_{62}$ , and the results show a continuous signal decrease as carbon number increases (Figure S10, Supporting Information). The low responses for the smaller alkanes are likely due to their volatility in open air. Alkanes smaller than heptadecane are liquids, which form liquid hydrophobic films on the glass slide and can be easily removed by the spray plume during



**Figure 3.** (a) Wt% of alkanes relative to wt% *n*-eicosane in an alkane standard. (b) Signal response of different alkanes relative to *n*-eicosane, derived from the mass spectrum. The signal response of each alkane was calculated as the sum of all the oxidation and dehydrogenation peaks. Signals were not observed for C<sub>5</sub>H<sub>12</sub> to C<sub>13</sub>H<sub>28</sub>.

DESI and before reaction. The decreased response for larger alkanes could be due to a decreased solubility in the chosen solvent or a lower desorption efficiency.

## Conclusion

We have demonstrated that saturated hydrocarbon molecules can be ionized in DESI at atmospheric pressure by taking advantage of oxidation during deliberately produced electrical discharges in conjunction with in situ alcohol derivatization using BA as the reactive DESI reagent. Similarly, the ketones formed as oxidation products probably could be detected using hydroxylamine [21] or long-chain amines [22] as derivatizing agents. This was judged unnecessary given that the needed information was obtained from the alcohols. Unlike ESI electrochemical reactions in solution, in which redox is dictated by the reduction potentials of analytes [23], redox chemistry occurring in the gas phase is often related to electron capture or charge exchange in desorption ionization techniques [24, 25]. Discharge induced oxidation in ESI and DESI is mainly caused by radicals generated at atmospheric pressure. The reactive DESI method may be implemented either on commercial or on portable mass spectrometers for rapid analysis of petroleum saturates. As opposed to FI/FD, heating is not needed in reactive DESI experiments. Consequently, no fragmentation of the studied hydrocarbons is observed in reactive DESI, even in the case of the branched alkane, squalane. The signal

response in reactive DESI falls at both high and low carbon numbers and may be related to volatility, desorption efficiency, and oxidation efficiency of alkanes. Although the extent of unsaturation may be difficult to determine due to accompanying dehydrogenation, the results of ambient analysis of petroleum distillates indicate that this method is capable of rapid and accurate determination of carbon distributions in saturated hydrocarbon samples. A detailed modeling of dehydrogenation may be needed to apply the technique to quantitative analysis of petroleum products. Another potential application of the technique may be in the combination with ion mobility mass spectrometry to differentiate dehydrogenation products from cyclic paraffins.

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## Appendix A Supplementary Material

Supplementary material associated with this article may be found in the online version at [doi:10.1016/j.jasms.2009.10.006](https://doi.org/10.1016/j.jasms.2009.10.006).

## References

1. Crawford, K. E.; Campbell, J. L.; Fiddler, M. N.; Duan, P.; Qian, K.; Gorbaty, M. L.; Kenttamaa, H. I. Laser-Induced Acoustic Desorption/Fourier Transform Ion Cyclotron Resonance Mass Spectrometry for Petroleum Distillate Analysis. *Anal. Chem.* **2005**, *77*, 7916–7923.
2. Liang, Z.; Hsu, C. S. Molecular Speciation of Saturates by On-Line Liquid Chromatography-Field Ionization Mass Spectrometry. *Energy Fuels* **1998**, *12*, 637–643.
3. Gross, J. H.; Vékey, K.; Dallos, A. Field Desorption Mass Spectrometry of Large Multiply Branched Saturated Hydrocarbons. *J. Mass Spectrom.* **2001**, *36*, 522–528.
4. Purcell, J. M.; Hendrickson, C. L.; Rodgers, R. P.; Marshall, A. G. Atmospheric Pressure Photoionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry for Complex Mixture Analysis. *Anal. Chem.* **2006**, *78*, 5906–5912.
5. Duan, P. G.; Fu, M. K.; Pinkston, D. S.; Habicht, S. C.; Kenttamaa, H. I. Gas-Phase Reactions of  $\text{ClMn}(\text{H}_2\text{O})^+$  with Polar and Nonpolar Hydrocarbons in a Mass Spectrometer. *JACS* **2007**, *129*, 9266–9267.
6. Nefliu, M.; Smith, J. N.; Venter, A.; Cooks, R. G. Internal Energy Distributions in Desorption Electrospray Ionization (DESI). *J. Am. Soc. Mass Spectrom.* **2008**, *19*, 420–427.
7. Benassi, M.; Wu, C.; Nefliu, M.; Ifa, D. R.; Volný, M.; Cooks, R. G. Redox Transformations in Desorption Electrospray Ionization. *Int. J. Mass Spectrom.* **2009**, *280*, 235–240.
8. Pasilis, S. P.; Kertesz, V.; Van Berkel, G. J. Unexpected Analyte Oxidation During Desorption Electrospray Ionization-Mass Spectrometry. *Anal. Chem.* **2008**, *80*, 1208–1214.
9. Chen, M. L.; Cook, K. D. Oxidation Artifacts in the Electrospray Mass Spectrometry of a  $\beta$  Peptide. *Anal. Chem.* **2007**, *79*, 2031–2036.
10. Boys, B. L.; Kuprowski, M. C.; Noel, J. J.; Konermann, L. Protein Oxidative Modifications During Electrospray Ionization: Solution Phase Electrochemistry or Corona Discharge-Induced Radical Attack? *Anal. Chem.* **2009**, *81*, 4027–4034.
11. Wong, J. W. H.; Maleknia, S. D.; Downard, K. M. Study of the Ribonuclease-S-Protein-Peptide Complex Using a Radical Probe and Electrospray Ionization Mass Spectrometry. *Anal. Chem.* **2003**, *75*, 1557–1563.
12. Wu, C.; Ifa, D. R.; Manicke, N. E.; Cooks, R. G. Rapid, Direct Analysis of Cholesterol by Charge Labeling in Reactive Desorption Electrospray Ionization. *Anal. Chem.* **2009**, *81*, 7618–7624.
13. Nyadong, L.; Hohenstein, E. G.; Galhena, A.; Lane, A. L.; Kubanek, J.; Sherrill, C. D.; Fernandez, F. M. Reactive Desorption Electrospray Ionization Mass Spectrometry (DESI-MS) of Natural Products of a Marine Alga. *Anal. Bioanal. Chem.* **2009**, *394*, 245–254.
14. Qian, K. N.; Dechert, G. J. Recent Advances in Petroleum Characterization by GC Field Ionization Time-of-Flight High-Resolution Mass Spectrometry. *Anal. Chem.* **2002**, *74*, 3977–3983.
15. Morand, K.; Talbo, G.; Mann, M. Oxidation of Peptides During Electrospray Ionization. *Rapid Commun. Mass Spectrom.* **1993**, *7*, 738–743.
16. Klesper, G.; Rollgen, F. W. Field-Induced Ion Chemistry Leading to the Formation of  $(M - 2n\text{H})^{+}$  and  $(2M - 2m\text{H})^{+}$  Ions in Field Desorption Mass Spectrometry of Saturated Hydrocarbons. *J. Mass Spectrom.* **1996**, *31*, 383–388.
17. Ascenzi, D.; Franceschi, P.; Guella, G.; Tosi, P. Phenol Production in Benzene/Air Plasmas at Atmospheric Pressure. Role of Radical and Ionic Routes. *J. Phys. Chem. A* **2006**, *110*, 7841–7847.
18. Xu, G.; Chance, M. R. Hydroxyl Radical-Mediated Modification of Proteins as Probes for Structural Proteomics. *Chem. Rev.* **2007**, *107*, 3514–3543.
19. Kudryashov, S. V.; Shchegoleva, G. S.; Sirotkina, E. E.; Ryabov, A. Y. Oxidation of Hydrocarbons in a Barrier Discharge Reactor. *High Energy Chem.* **2000**, *34*, 112–115.
20. Marshall, A. G.; Rodgers, R. P. Petroleomics: Chemistry of the Underworld. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 18090–18095.
21. Huang, G.; Chen, H.; Zhang, X.; Cooks, R. G.; Ouyang, Z. Rapid Screening of Anabolic Steroids in Urine by Reactive Desorption Electrospray Ionization. *Anal. Chem.* **2007**, *79*, 8327–8332.
22. Nyadong, L.; Late, S.; Green, M. D.; Banga, A.; Fernandez, F. M. Direct Quantitation of Active Ingredients in Solid Artesunate Antimalarials by Noncovalent Complex Forming Reactive Desorption Electrospray Ionization Mass Spectrometry. *J. Am. Soc. Mass Spectrom.* **2008**, *19*, 380–388.
23. Vanberkel, G. J.; McLuckey, S. A.; Glish, G. L. Electrochemical Origin of Radical Cations Observed in Electrospray Ionization Mass Spectra. *Anal. Chem.* **1992**, *64*, 1586–1593.
24. Zhang, J.; Frankevich, V.; Knochenmuss, R.; Friess, S. D.; Zenobi, R. Reduction of Cu(II) in Matrix-Assisted Laser Desorption/Ionization Mass Spectrometry. *J. Am. Soc. Mass Spectrom.* **2003**, *14*, 42–50.
25. Pelzer, G.; Depauw, E.; Dung, D. V.; Marien, J. Oxidation-Reduction Processes Occurring in Secondary Ion Mass Spectrometry and Fast Atom Bombardment of Glycerol Solutions. *J. Phys. Chem.* **1984**, *88*, 5065–5068.