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Electrospray mass spectrometry of fossil fuels

Dongliang Zhan, John B. Fenn*

Department of Chemistry, Virginia Commonwealth University, Richmond, VA 23284-2006, USA

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Abstract

Exploratory experiments with electrospray ionization mass spectrometry have been carried out on crude oil, jet fuel, gasoline, and coal. The resulting mass spectra contain a remarkable amount of information on the composition and character of these sometimes very complex materials. They suggest that electrospray ionization may have found a new arena in which to exercise its powers. (Int J Mass Spectrom 194 (2000) 197–208) © 2000 Elsevier Science B.V.

Keywords: Electrospray ionization; Fossil fuels

1. Introduction

Ten years ago electrospray ionization mass spectrometry (ESIMS) was an intriguing novelty that had been tentatively probed by a few curious investigators [1–3]. Widespread interest in the technique was sparked by the demonstration in 1988 that it could produce intact ions of peptides and proteins [4]. Moreover, the larger the molecules, the more multiply charged were their ions (whose *m/z* values were thus almost always below 3000). Consequently, relatively modest mass analyzers could provide molecular weight (Mr) values for large biomolecules with unprecedented accuracy [5]. ESI now plays a rapidly growing role as a supplier of ions to thousands of mass spectrometers all over the world. Publications on the method and its results have gone from half a dozen per year in 1988 to 1000 or more since 1997. One of two principal reasons for this growth is ESI's ability to transform analyte species in solution to free ions in the gas phase on a continuous, as opposed to batch-wise, basis. The other is its ability to accomplish this transformation on large, complex, and fragile species that cannot possibly be vaporized for ionization by classical methods. These features have made ESI the interface of choice for coupling a liquid chromatograph to a mass spectrometer in the analysis of the polar species that play such a vital role in living systems.

It should be noted that the ions of "traditional" mass spectrometry usually comprise atoms or molecules that have lost or gained one or more electrons during a gas phase encounter with a photon, an ion, or another electron. An implicit requirement of such ionization is that the analyte must be volatile enough to produce useful concentrations of gaseous molecules as collision partners for the ionizing entities. Nonpolar molecules are generally much more easily vaporized than polar species of equivalent size. But even with nonpolar species thermal decomposition

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* Corresponding author. E-mail: jfenn@saturn.vcu.edu

Dedicated to Professor Jim Morrison on the occasion of his 75th birthday.

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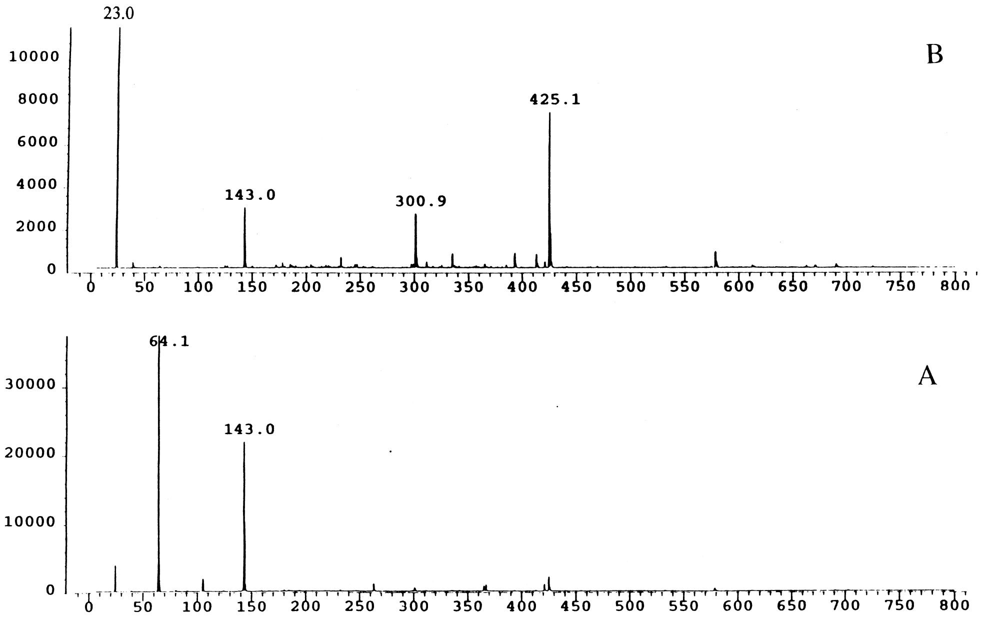

Fig. 1. ESI mass spectra for 1% Jet Fuel JP-8 in acetonitrile containing 0.1 mM NaBr infused at 2 uL/min. For panel A the nozzle-skimmer potential difference was 60 V, for panel B 120.

becomes a problem when Mr values get very high. Moreover, gas phase ionization methods usually cause some fragmentation of the parent molecule that can complicate the spectra. However, such fragmentation can also help to identify that parent.

ES ions, on the other hand, depending on the polarity of the dispersing field, generally comprise excess anions or cations from sample solution that is dispersed into tiny charged droplets by the intense electric field that gives "electrospray" its name. These excess anions or cations are on the surface of those droplets and constitute their charge. By a process that remains the subject of much debate, evaporation of solvent from the droplets releases those surface ions into the ambient gas. The released ions can comprise not only the species normally considered to be solute cations or anions as such, but also adducts of those species with neutral polar molecules. The existence of such charged adducts is not always obvious and is frequently ignored in the chemistry of electrolyte solutions. Held together by ion–dipole interaction, hydrogen bonding, or some combination of such forces, these adducts of solute ions with solute neutrals are sometimes known as "quasimolecular ions" to distinguish them from ions comprising a neutral molecule that has gained or lost one or more electrons. Their existence and identity are much more apparent when they are in the gas phase than when they are in the liquid phase. Indeed, one of the major contributions of ESIMS to science may well turn out to be the new window that it opens on the chemistry and physics of liquid solutions.

It has been much lamented that ESI cannot produce ions from nonpolar compounds such as hydrocarbons. Consequently, attempts have been made to form complexes of polar and nonpolar compounds in the hope that ES would ionize the polar component of such a complex, thus making the hydrocarbon component of the resulting ion identifiable by mass analysis. For example, Van Berkel et al. were able to carry out ESIMS analysis on complexes of crown ethers with some polyaromatic hydrocarbons [6]. However, there is little evidence so far that this approach can provide a convenient and general cure

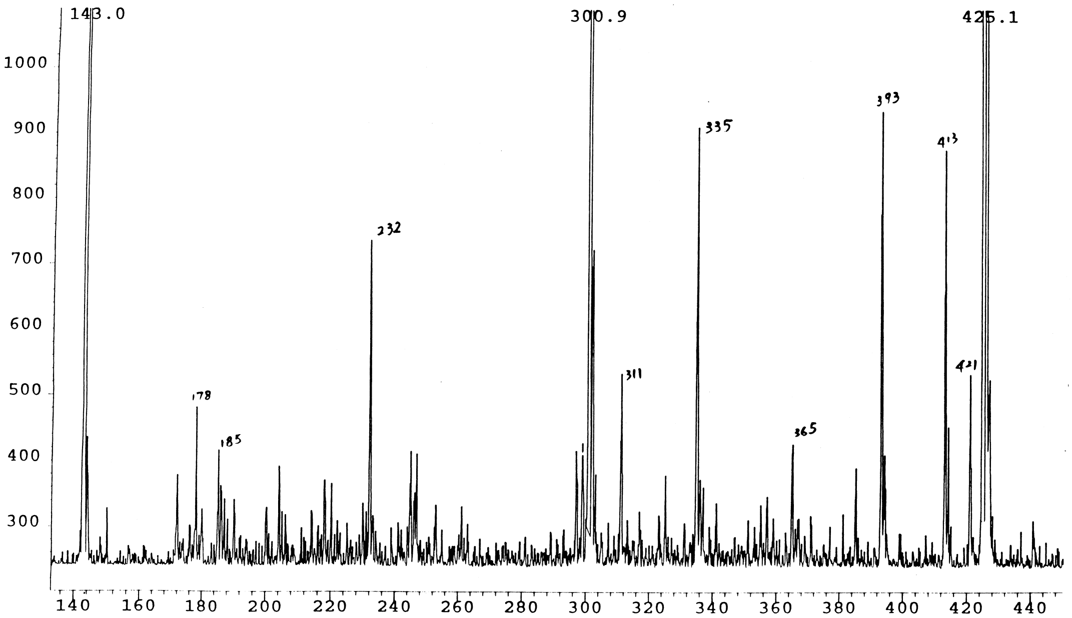

Fig. 2. Magnification of a portion of the spectrum in Fig. 1B obtained by expanding the ordinate scale.

for ESI's inability to ionize molecules that do not contain atoms or groups with a permanent dipole or in which a strong dipole can be induced by a nearby charge. The net result is that ESIMS has found very little application in the characterization and analysis of materials such as fossil fuels that consist mainly of nonpolar hydrocarbons. Thus, we found no references to this use of ESIMS in a recent review on methods for analysis of petroleum and its products [7], in one on applications of mass spectrometry [8], or in any of the abstracts of papers presented in the last several ASMS Conferences on Mass Spectrometry and Allied Topics. What we have found recently in the laboratory is that in at least some of these materials the content of polar species is high enough for ESIMS to provide interesting and informative mass spectra. This report summarizes some of the results from some exploratory experiments.

2. Apparatus and procedures

All mass analyses were carried out with a triple quadrupole instrument (Delsi-Nermag 30-10) fitted with an electrospray source (Analytica, Branford, CT). Sample solutions were infused from 0.5–3.0 uL/min by a syringe pump (Harvard Apparatus Model 11). Except when otherwise indicated, all solvents were liquid chromatography (LC) grade from various suppliers. Additions to the solvent, e.g. acid or salt to increase conductivity, or differences in procedure, will be pointed out when relevant. The analyte material in each set of experiments will be identified in the description of those experiments.

3. Results and discussion

Examples to be shown include ESIMS analyses on samples of jet fuel, gasoline, crude petroleum, and coal, or solvent extracts therefrom. In the case of the crude oils and coal the spectra are very complex, but their peaks are clearly resolved by our modest quadrupole. We have not yet attempted to identify the parent species for any one peak. Indeed, we cannot even be sure that all the ions of any one peak are from the same parent. Even so, a lot of information on the identity of the parent molecules should be readily

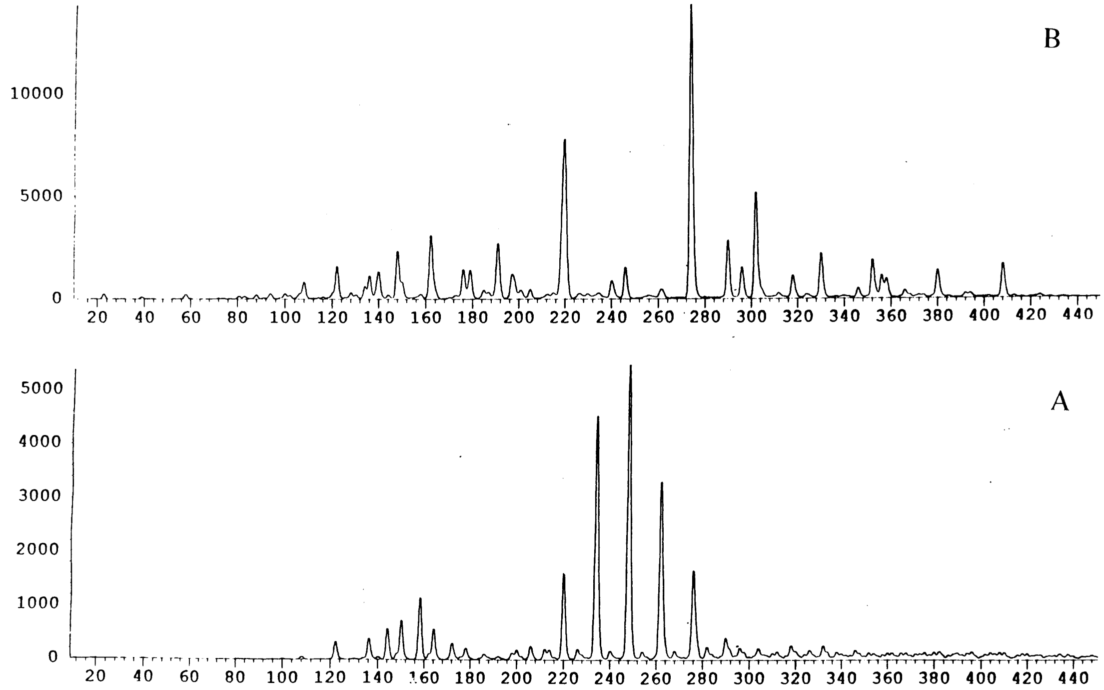

Fig. 3. ESI mass spectra for gasoline. Panel A is for unleaded "regular" (87 octane). Panel B is for unleaded "plus" (93 octane). In both cases sample liquid comprising a 10 vol % solution of fuel in acetone with 0.3 vol % of acetic acid was infused at 3 uL/min.

recoverable by MS/MS methods. These studies had their origin in our learning that the Air Force was interested in methods for assaying amounts of detergent additives in jet fuel so we began with samples of JP-8 kindly provided by Dr. Robert Mantz of Wright-Patterson AFB.

3.1. Experiments with jet fuel JP-8

We were well acquainted with the landmark electrospray experiments of K. Tang and A. Gomez, our former colleagues at Yale. Motivated by an interest in the combustion of sprays of small monodisperse droplets, they had found that the addition of antistatic compounds to hydrocarbon liquids made them conductive enough to be electrosprayed. Their experiments revealed many details of the dynamic behaviour of electrospray droplets, individually and collectively. Of special note were their historic photographs of charged droplets in the act of disruption by a Rayleigh instability [9]. They did not attempt to determine whether charged droplets of hydrocarbons could produce ions of the antistatic additive or any other species. When we learned of Air Force interest in analyzing jet fuels for additives, at least some of which were polar, the Tang and Gomez success in electrospraying hydrocarbons persuaded us that ESIMS would be worth trying. Moreover, we and others had often used relatively nonpolar compounds like chloromethanes as solvents for particular analytes. Our first experiments were with a sample of JP-8 containing 0.15% of di(ethylene glycol) monomethyl ether (DEGMME) as a detergent.

Fig. 1A shows the ESI mass spectrum obtained for this fuel when we sprayed 2 uL/min of a solution comprising one part of the JP-8 in 100 parts of acetonitrile (ACN) containing sodium bromide (NaBr) at a 0.1 millimolar concentration. The NaBr

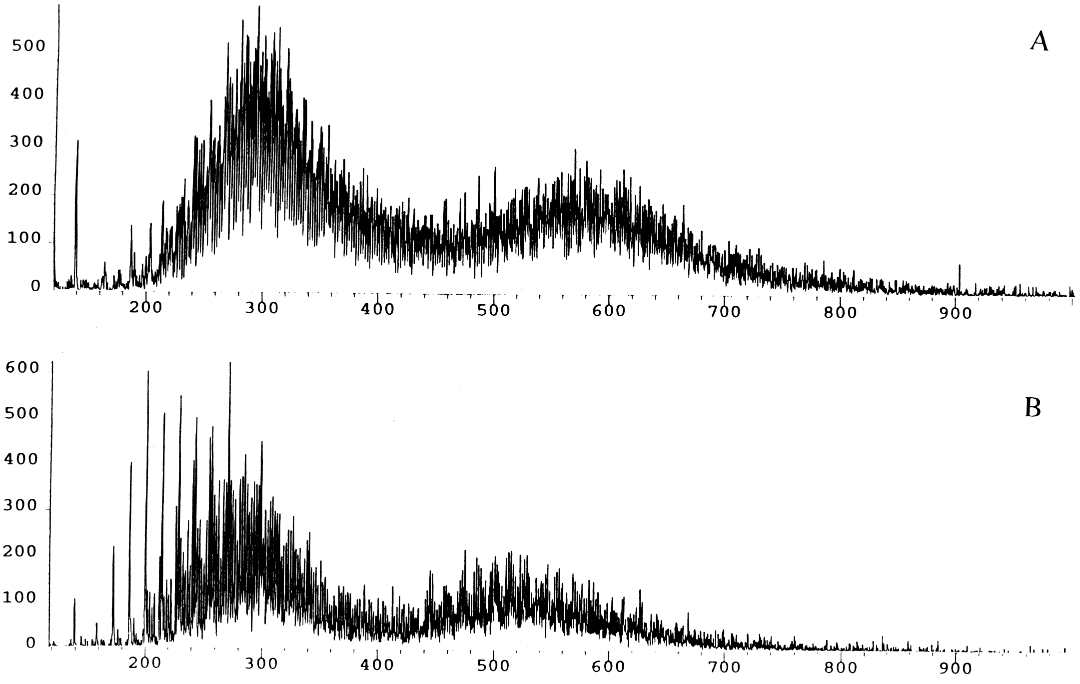

Fig. 4. ESI mass spectra for crude petroleum samples obtained by shaking 200 μL of oil with 1 mL of acetonitrile. One part of the supernatant liquid was further diluted with six parts of acetonitrile containing 0.4% acetic acid by volume and infused at 3 μL/min. The nozzle-skimmer potential difference was 70 V. Panel A is for the Alba crude, panel B for the Maya.

was added to increase solution conductivity and to supply Na+ cations that ionize poly(ethylene glycols) by binding to the interior O atoms [10]. The solution as sprayed contained only 150 ppm by weight of DEGMME but that was enough to give a strong peak at *m/z* = 143 in the spectrum of Fig. 1A corresponding to one molecule of DEGMME with one Na+ ion attached. The signal/noise ratio is so high that this material could probably be assayed at concentrations of ppb or less without much trouble. The other major peak in Fig. 1A is at *m/z* = 64 and corresponds to an Na+ ion solvated with one molecule of ACN.

The conditions for the spectrum of Fig. 1B were identical with those of 1A except that the potential difference between the capillary exit and the skimmer was increased from 60 to 120 V. As a result the peak at *m/z* = 64.1 in Fig. 1A is absent in Fig. 1B because all the solvated Na+ ions were completely desolvated by the higher energies of the ion-neutral collisions in the jet. Consequently, there were enough "bare" Na+ ions to form a substantial peak at *m/z* = 24. Similarly, the peak at *m/z* = 143 is substantially smaller than in 1A because the collision energies were high enough to fragment a lot of the ions comprising adducts of Na+ and DEGMME. The higher voltage also improved the focusing so that the very tiny peaks at *m/z* = 300.9 and 425.1 in 1A are more pronounced in 1B. Note that the ordinate scale in 1B is expanded by a factor of 3 so that, for example, the measured abundance of ions with *m/z* values of 143 in 1B is actually only about 1/7 of that in 1A. We have not attempted to identify the ions with *m/z* values of 300.0 and 425.1. Indeed, many more peaks become distinguishable when we expand the ordinate scale, as is clear in Fig. 2, which shows a resulting magnification of that portion of the spectrum in 1B between *m/z* values of about 140 and 440. The signal/noise ratio is high enough to reassure us that all

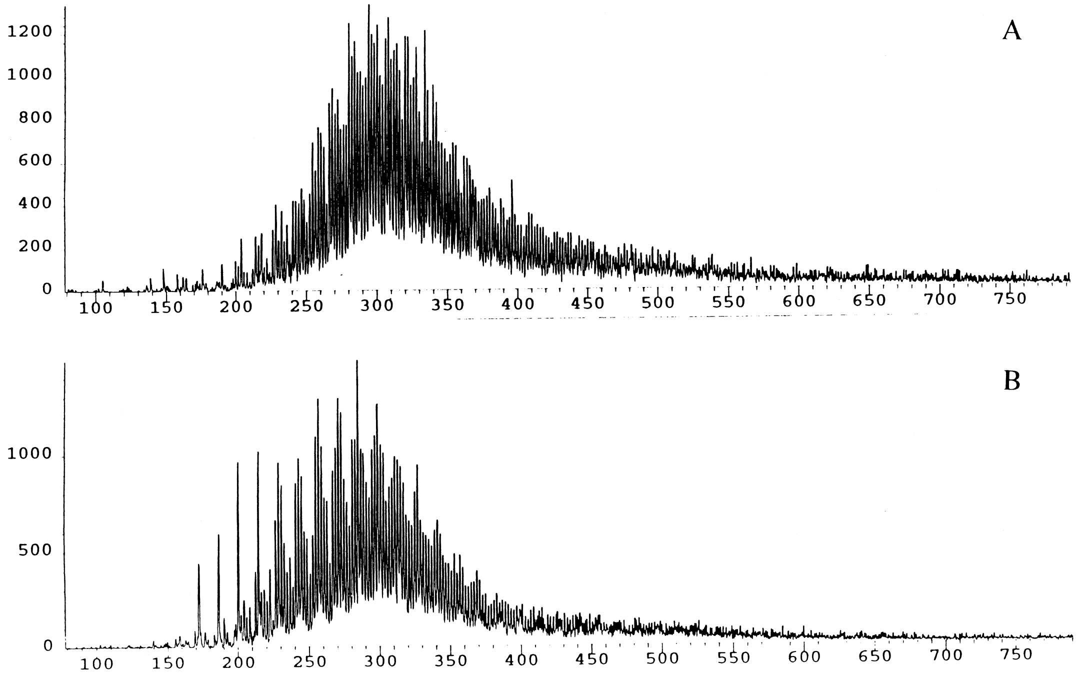

Fig. 5. Everything is the same as in Fig. 4 except that the nozzle-skimmer potential difference was 130 V. Again, panel A is for the Alba crude, panel B for the Maya.

the major peaks are real in the sense that they are due to trace components in the fuel. The desolvation due to countercurrent drying gas plus the doubling of capillary-skimmer voltage for Fig. 1B makes the presence of peaks due to solvent clusters unlikely. Also, blank experiments with "pure" solvent showed no solvent cluster ions. (Note: the ordinate scale in Fig. 1B is expanded one hundred times relative to that in Fig. 1A.) We made no attempt to identify any of these trace components, but as mentioned, MS/MS experiments could probably identify most of them. This ability of ESIMS to "see" polar compounds while ignoring hydrocarbons provides a new perspective on the characterization of hydrocarbon products.

3.2. Experiments with gasoline

The components of entering feedstock that leave the refinery in gasoline are essentially all nonpolar hydrocarbons. But what the motorist buys at the pump usually contains small quantities of polar molecules that are components of additives such as detergents, corrosion inhibitors, antiknock agents, and oxygenated compounds thought to promote "clean" burning. One or more of some of these additives are statutory requirements in some areas. There is thus a growing need for simple and effective methods of analyzing gasoline for these additives, many if not most of which are polar. We tried ESIMS on two samples of gasoline. Fig. 3A shows the spectrum obtained with unleaded "regular" (87 octane) gasoline after tenfold dilution with acetone containing 0.3% acetic acid to provide conductivity. The spectrum of Fig. 3B was obtained with unleaded "super" (93 octane) similarly diluted with acetone and "spiked" with acetic acid. We have not attempted to identify the ions of the peaks but these spectra clearly reveal a lot about the polar components of these gasolines. If prices go low enough, mass spectrometers could be attractive analyzers for liquid fuels.

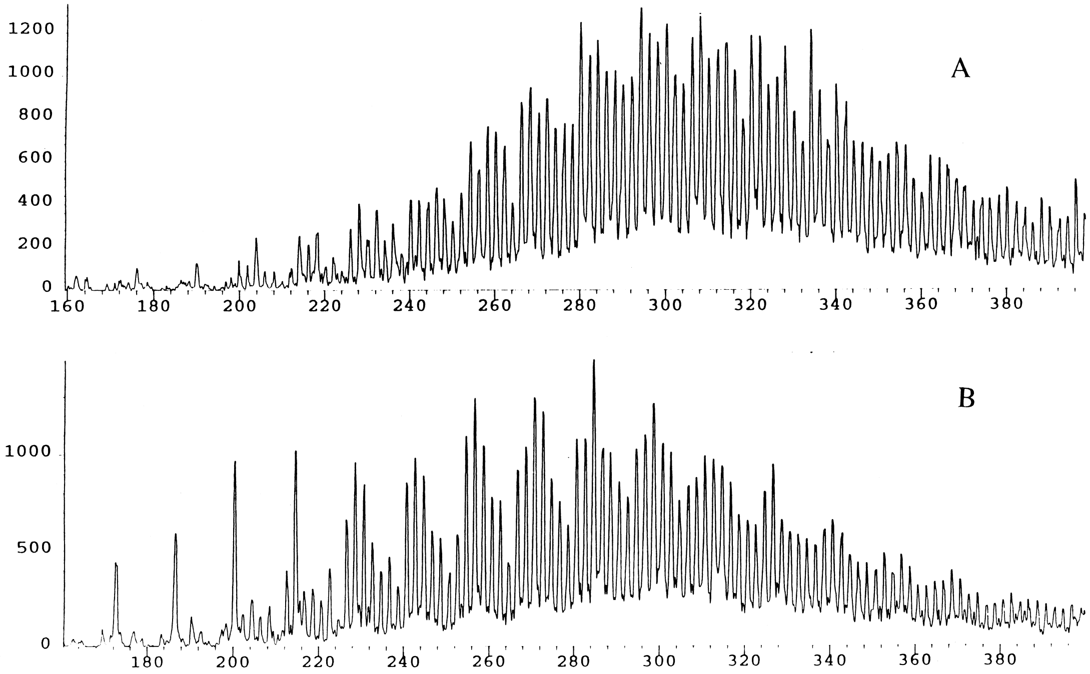

Fig. 6. The sections of the spectra in Fig. 5 between *m/z* values of 160 and 180 but with the *m/z* scale "stretched" so as to increase the apparent resolution.

3.3. Experiments with crude oil

Encouraged by the results with JP-8 and gasoline we decided to look at crude oil. Professor Peter Kilpatrick of the Department of Chemical Engineering at North Carolina State University kindly provided us with samples of two "heavy" crude oils, "Alba" from the North Sea Basin and "Maya" from a major oil field in Mexico, along with some of the "asphaltene fraction" of each one. The resulting spectra are shown in Figs. 4–10, briefly described in what follows.

Fig. 4A and B show spectra obtained when about 200 uL of crude were shaken with 1 ml of acetonitrile (ACN). The supernatant solution was diluted six times with ACN and acidified with acetic acid (0.4% by volume) to increase conductivity. The diluted solution was injected at 3 uL/min with a potential difference of 2.7 KV between needle and capillary entrance. Spray current was 40 nA. The potential drop from capillary exit to skimmer was 70 V. Panel A is for the Alba crude, panel B for the Maya.

Conditions for the spectra in Fig. 5A and B were identical with those for the spectra in Fig. 4A and B except that the capillary-skimmer potential difference was increased from 70 V for the spectra in Fig. 4 to 130 V for the spectra in Fig. 5. Thus the ion-neutral collision energies in the jet were almost doubled for the spectra in Fig. 5. Therefore, the ions of the latter were more completely stripped of solvent molecules and/or other loosely bound species. Such stripping probably accounts for the disappearance of the "hump" whose peak is at an *m/z* value between 500 and 600 in Fig. 4 but is absent in Fig. 5. It could also account for the increase in abundances (peak heights) for ions with *m/z* values below 400 in Fig. 5 relative to those in Fig. 4. That is to say, such a stripping of solvent molecules (or other loosely bound groups) from the ions with *m/z* values above 400 in Fig. 4A and B, would increase the abundances of "cleaner"

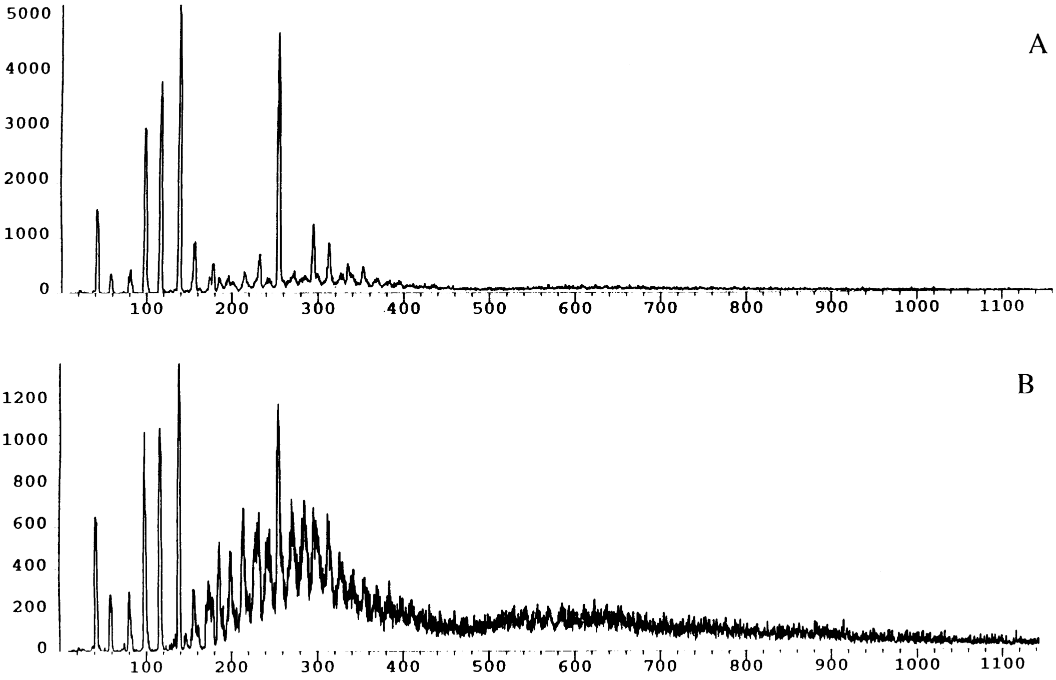

Fig. 7. Panel A shows the electrospray mass spectrum obtained with an extract of 50 uL of Alba crude in 1 mL of acetone. The supernatant liquid was mixed with an equal volume of pure acetone and acidified with 0.4% by volume of acetic acid. An identical procedure with Maya crude produced the spectrum in panel B.

and, therefore, lighter ions at *m/z* values below 400 in Fig. 5. In both Figs. 4 and 5, panel A is for the Alba crude and panel B for the Maya.

Fig. 6 comprises the spectra of Fig. 5 in the *m/z* range from 200–400 on an expanded scale and shows that the apparent congestion of the spectra of Figs. 4 and 5 is due to peaks that can be resolved by our quadrupole, which has an effective resolving power of about 1 *m/z* unit, under the conditions of these experiments. It is provacative that most of the peaks in Fig. 6 seem to form coherent sequences with *m/z* values differing by two units, i.e. two H atoms. Each increment of two units corresponds to the addition of a hydrogen molecule to a double bond, i.e. one less double bond in an alkyl chain of particular length on the parent polar molecule. The periodic tallest peaks in Fig. 6 are 14 units apart on the *m/z* scale, corresponding to addition of a CH2 group to such a chain. As is apparent from these speculations we have assumed throughout that all the ions we have detected are singly charged. We have not proved this assumption in any absolute way but it is consistent with all of our observations on these materials.

Fig. 7 shows ESI mass spectra for an extract of 50 uL of the Alba (panel A) and Maya (panel B) crudes in 1 mL of acetone. The supernatant liquids were mixed with an equal volume of pure acetone and acidified with 0.4% acetic acid by volume before spraying. There are noticeably fewer peaks in these spectra as compared to those of Fig. 4 for which the solvent was ACN, not acetone. These differences are consistent with what seemed to be the case when the solutions were prepared, i.e. that the crudes were more soluble in ACN. It is also noteworthy that differences between the spectra of Alba and Maya crudes are much greater in Fig. 7 when acetone was the solvent than in Figs. 4 and 5 when ACN was the solvent. These differences underline the rather obvi-

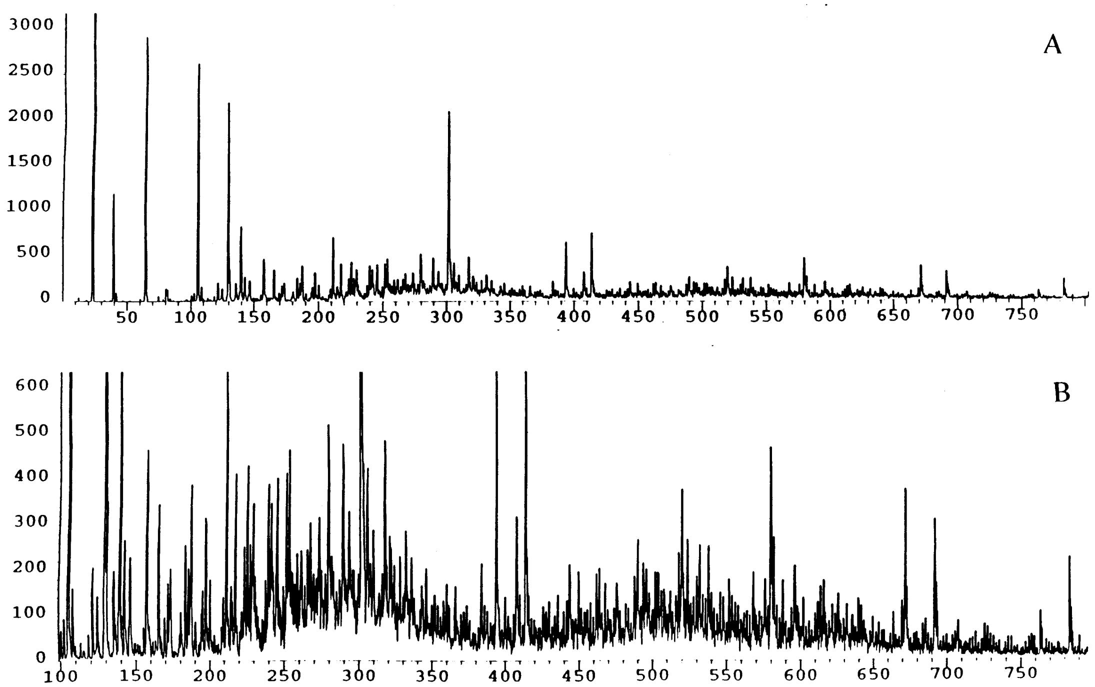

Fig. 8. Panel A shows the electrospray mass spectrum obtained with the supernatant liquid resulting from shaking 16.8 mg of the solid asphaltene fraction of Alba crude with 1 mL of acetonitrile containing 0.4% acetic acid by volume. The spectrum of panel B was obtained in the same way except that the "gain" on the detector was increased so that the complexity of the asphaltene composition is more fully revealed.

ous expectation that solvent composition as a variable might play a useful role in characterizing fossil fuels and their derivatives.

Fig. 8 shows spectra from a solution obtained by mixing 16.8 mg of the solid asphaltene fraction of the Alba crude in 1 ml of ACN with 0.4% acetic acid by volume. Panels A and B were taken under the same conditions except that for B the detector gain was increased in order to make the rich complexity of the spectrum more apparent.

Fig. 9A shows a negative ion spectrum for the acetone solution of Maya crude as prepared for the spectrum in Fig. 7B, which is repeated in Fig. 9B, so as to provide easy comparison of the negative and positive ion spectrum for the same acetone solution of the Maya crude. [All the other spectra (Figs. 1–8) are for positive ions.] Differences between the proclivities of component species to form negative and positive ions must be largely responsible for the differences in appearance between the spectrum of Fig. 9A and its positive ion counterpart in Fig. 9B. (same as Fig. 7B).

Fig. 10 shows "difference spectra" obtained by subtracting a spectrum for Maya crude from one for Alba crude, both obtained with the same operating conditions. Panel A shows such a difference spectrum for the spectra in Fig. 4 with low capillary-skimmer potential difference (70 V). Panel B shows the analogous difference spectrum for the spectra in Fig. 5 obtained with a higher capillary-skimmer potential difference (130 V). These "difference spectra" support the idea that the distribution of polar species in a particular crude oil, as revealed by ESIMS, is a unique characteristic or "fingerprint" by which the crude can be identified. If the "difference spectrum" of two samples shows no peaks, they must have identical compositions and be from the same source. It is unlikely that such a difference spectrum will ever

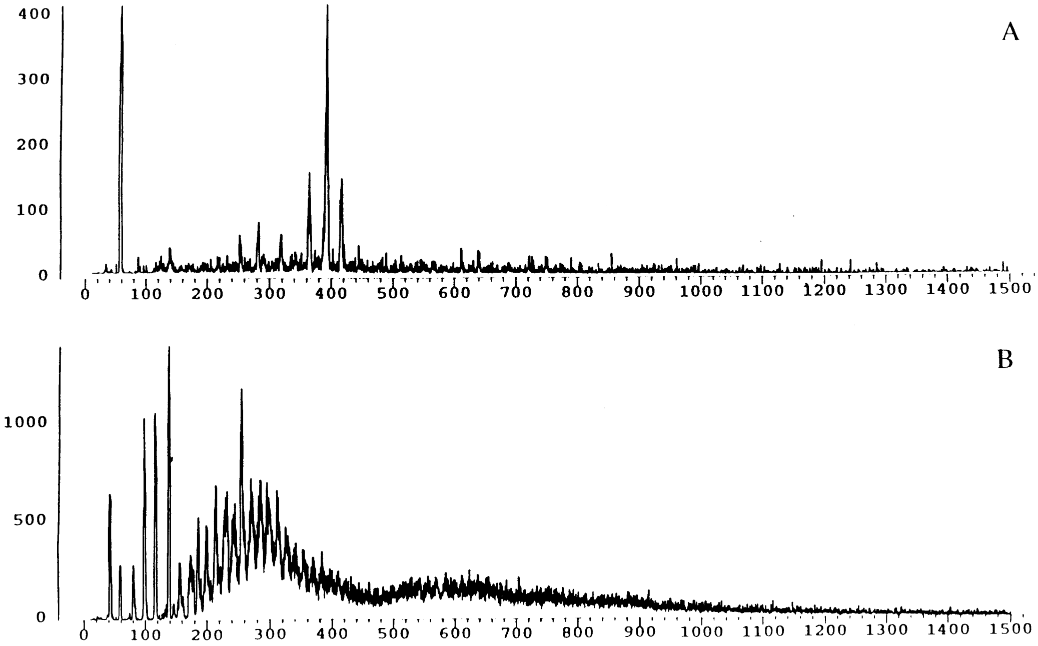

Fig. 9. Panel A shows a negative ion electrospray mass spectrum obtained with the same acetone solution of Maya crude used to produce the positive ion spectrum in Fig. 7B. That positive ion spectrum of Fig. 7B is reproduced in Fig. 9B for easy comparison of positive and negative ion spectra on the same sample, i.e. acetone solution of Maya crude.

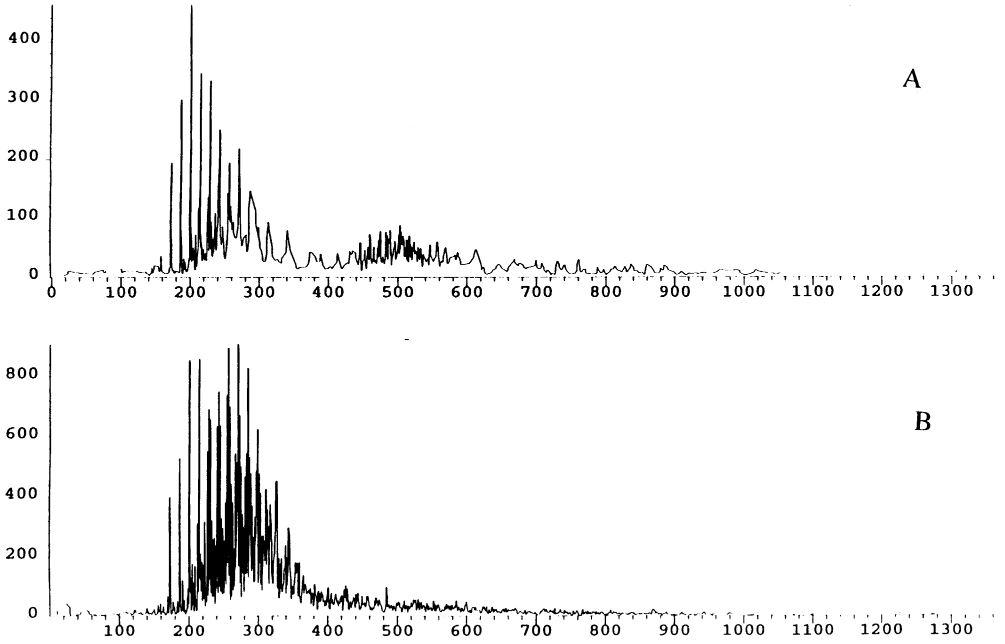

Fig. 10. Panel A shows the "difference spectrum" obtained by subtracting the spectrum of panel A from the spectrum of panel B in Fig. 4, to characterise the "differences" between the Alba and Maya crudes. Panel B was obtained by performing an analogous subtraction with the spectra of Fig. 5 that were obtained with a nozzle-skimmer potential difference of 130 V instead of 70 V as in Fig. 4.

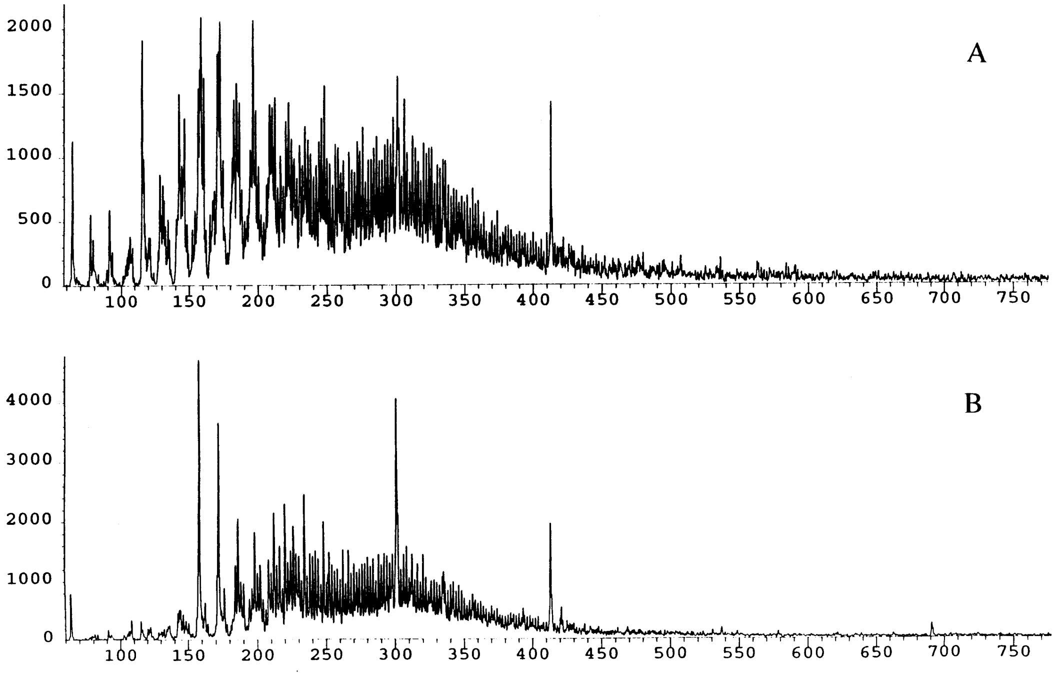

Fig. 11. Panel A shows the electrospray mass spectrum for a solution obtained by leaching 5 g of coal of unknown origin (after pulverizing with a mortar and pestle) with 18 mL of acetonitrile. The nozzle-skimmer potential difference was 170 V. The spectrum in panel B was obtained in exactly the same way except that the nozzle-skimmer potential difference was 220 V.

show no peaks, but as experience increases, and data for various crudes are accumulated, it should be possible to determine limiting values for the number and height of peaks in a difference spectrum below which the minuend and subtrahend samples could be safely attributable to the same source. The point is that ESIMS spectra promise to be convenient indicators for comparing different samples whenever a quantitative comparison would be useful for some purpose, e.g. fixing responsibility for surreptitious oil spills.

3.4. Experiment with coal

The only immediately available sample of coal was a piece that had been lying around in the back room of the local hardware store and was of unknown origin. We ground up a 5 gm piece with a mortar and pestle and leached the resulting powder with 18 mL of acetonitrile containing 0.4% acetic acid. The leachate was infused into the ES source at 2 uL/min. Fig. 11A shows the spectrum obtained when the nozzle skimmer potential difference was 170 V. For 11B it was 220 V. The closely spaced but fully resolved peaks are two units apart on the *m/z* scale corresponding to the mass of a hydrogen molecule if we assume the ions are singly charged. As was the case for the crude oil spectrum in Fig. 6, a possible explanation for this pattern is that the polar parent molecules may have hydrocarbon chains with varying numbers of double bonds.

4. Summary and conclusions

Because the major components of fossil fuels and their derivatives are nonpolar hydrocarbons, they have apparently been considered "off limits" for analysis by electrospray ionization mass spectrometry. The exploratory experiments described here show that many of these materials have a sufficiently high content of polar species for ESIMS to provide spectra that contain a substantial amount of information on the composition and character of these important materials. The implications and applications of this finding remain to be evaluated but the preliminary results strongly suggest that ESIMS may have found an unexpected new window of opportunity for examining and characterizing a class of materials that play crucial roles in modern society.

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