JOURNAL OF MASS SPECTROMETRY
*J. Mass Spectrom.* 2007; **42**: 874–880
Published online 29 May 2007 in Wiley InterScience
(www.interscience.wiley.com) DOI: 10.1002/jms.1217

JMS

# Laser desorption/ionization techniques in the characterization of high-molecular-weight oil fractions – Part 2: De-asphalted Oils

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Received 30 November 2006; Accepted 21 March 2007

**The composition of the de-asphalted oil fraction obtained from two different Italian fields was studied by laser desorption/ionization mass spectrometry. These fractions were treated with different solvent mixtures, and subfractions containing saturates, aromatic and polar compounds were obtained and analyzed by the same instrumental approach.**

**The investigation showed clear differences between the samples coming from the two oils. The instrumental approach did not lead to an accurate description of the different components in terms of elemental composition and structures; however, valid information could be obtained on the molecular weight distribution of the components of the different fractions. Copyright © 2007 John Wiley & Sons, Ltd.**

**KEYWORDS:** laser desorption/ionization; de-asphalted oils; hydrocarbons

## INTRODUCTION

The study of the composition of crude oils is of great interest, as it gives information on the age and dimension of the oil field.[1] However, the analysis of crude oils is always a hard challenge because of the complex and heterogeneous nature of the oil itself.[2]

The development of new ionization methods has led to a revolution in the compositional analysis of oil. On one hand the use of desorption/ionization techniques allows a fast overview of the molecular weight distribution of the different components present in the oil samples, and on the other, accurate mass measurements lead to an easy identification of heteroatom-containing components. In the latter case, Fourier-transform ion cyclotron resonance (FT-ICR) is particularly effective.[3] In the analysis of a crude oil, it allowed the identification of more than 11 000 species, evidencing heteroatom diversity, aromaticity and alkyl substitutions. A very recent Rodgers presentation at the 17th International Mass Spectrometry Conference[4] compared the results that can be achieved by FT-ICR and linear ion traps in terms of compositional class, characterization of naphthenic acids (and their change with respect to thermal treatments) and solution-phase aggregates.

Laser desorption/ionization techniques lead surely to less specific results, but can give information on the molecular weight distribution of the oil components. To simplify this analysis, prefractionation of the crude oils is performed.[5] This is usually achieved by the addition of a low-boiling hydrocarbon (i.e. *n*-pentane, *n*-heptane), leading to the precipitation of the heaviest petroleum components (asphaltenes). As shown in Scheme 1, this approach allows the separation of the so-called de-asphalted oils (DAO, maltenes) which in turn, by selective solvent extraction, can be fractionated into three different classes of compounds: saturates (paraffin/wax), aromatics and resins (or polar compounds).

The stability of the asphaltenes is influenced by the composition of the DAO fraction, and consequently the study of the nature of its subfractions is of great interest for the oil industry to understand and solve problems, e.g. the solid precipitation during production, transportation and storage of petroleum fluids.[6] As the solubility class definition for each fraction is a function of the solvents used for its separation, the composition includes a broad distribution of molecular structures, not always completely comparable with that obtained with a different separation procedure.

In a previous paper, we tested the power of LDI-MS for the characterization of asphaltenes. It was found that the molecular weight distribution of the components of asphaltenes coming from two different Italian oil fields (1 and 2) could be distinguished.[7] However the LDI approach showed some severe limitations, due to the drop in instrumental resolution, possibly due to space-charge phenomena occurring either in the ion source region or during the flight

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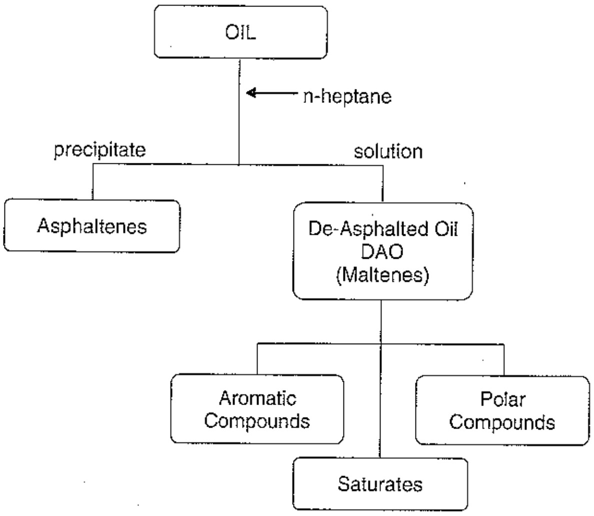

**Scheme 1.** Oil fraction separation scheme.

time. An extensive study on the instrumental parameters (delay time, laser power, sample thickness) led to spectra of increased quality. A parallel investigation, performed by surface-enhanced laser desorption/ionization (SELDI),[8] indicated that sample–surface interaction is an important parameter. The analysis of asphaltene fractions obtained by gel permeation chromatography (GPC) and the consequent analysis of less complex mixtures gave better results.

In the present investigation, we studied the DAO fractions of the same oils (samples **1a** and **2a**) by laser desorption/ionization. These fractions were treated with three different solvents mixtures to yield the subfractions containing saturates, aromatics and polar compounds. We focused our attention to aromatic (samples **1b** and **2b**) and polar (samples **1c** and **2c**) species.

## EXPERIMENTAL

### DAO sample preparation

Asphaltenes were precipitated from the corresponding oils (from two different Italian oil fields, samples **1** and **2**) with *n*-heptane according to the following procedure. Four hundred milliliters of *n*-heptane was carefully mixed with 10 ml of oil by a 10-min sonication. The suspension was filtered with a 0.5 µm Millipore filter, applying a differential vacuum of 0.3 bar. The asphaltenes were collected on the filter. From the filtered solution, *n*-heptane solvent was removed by rotavapor to obtain the DAO containing the maltene fraction (samples **1a** and **2a**). The maltenes were separated on a 1.0 cm i.d. column (50 cm length), packed for 4/5 with silica (silica gel 923, Grace) and the upper 1/5 of the volume with basic alumina ($Al_2O_3$ 90, Merck). Both resins were activated at 150 °C overnight. The solvent, or a mixture thereof, was used with increasing polarity, sequentially. A first subfraction composed of saturates was eluted with 25 ml of *n*-hexane, while the second one (i.e. the aromatic fraction, samples **1b** and **2b**) was eluted with 50 ml of a mixture of toluene and *n*-hexane (70 : 30). Finally, the third subfraction, yielding the polar compounds (samples **1c** and **2c**) contributing to the maltenes, was eluted with 60 ml of a mixture of ethanol : diethyl ether : chloroform (30 : 30 : 40). The solvents were removed by evaporation in order to obtain the undiluted subfractions.

### LDI analysis

LDI measurements were performed using a Voyager–DE STR (Applied Biosystem, Foster City, CA, USA) instrument operating in positive linear mode and equipped with a UV laser (nitrogen laser, $\lambda = 337$ nm). Maltenes and their subfractions were dissolved in chloroform to give a 10-mg/ml solution. For LDI analysis, 1 µl aliquot of each solution was placed on the plate and the solvent was evaporated in air. The DE operating conditions were: acceleration potential: 20 kV; grid potential: 93%; delay time: 250 ns. External calibration was performed using the $[M + H]^+$ ions of 2,5-dihydroxybenzoic acid (DHB) and angiotensin II at $m/z$ 155 and 1047, respectively.

## RESULTS AND DISCUSSION

As already found in the previous investigation on asphaltenes, the analysis of DAO samples (**1a** and **2a**) with a MALDI approach (data not shown) did not lead to results better than those obtained under LDI conditions. MALDI spectra obtained with different matrices (1,8,9-trihydroxyanthracene, 2,5-dihydroxybenzoic acid, 2-(*p*-hydroxyphenylazo)benzoic acid) were always of a quality lower than that achieved by LDI, owing to strong interactions between the matrices and the analytes. For this reason, the present investigation was carried out by the latter approach.

The LDI spectra of samples **1a** and **2a** are reported in Fig. 1. They appear of poor diagnostic quality for asphaltenes; in fact, even under the best instrumental conditions (delay extraction time 250 ns, grid potential 93%) the resolution is particularly low. This aspect can be ascribed to the large number of ionic species differing by a few mass units (or fractions of mass units), leading to severe space-charge phenomena either inside the source (during delayed extraction) or during the flight path from the source to the detector. Furthermore the proximity in $m/z$ value of the different ions can induce saturation at the detector level.

However the DAO LDI spectra of Fig. 1 show clear differences with respect to those obtained from the asphaltene fractions. In particular, a higher abundance of low-molecular-weight species is observed for the DAO samples. As an example, while the integral of the region of $m/z$ 100–680 is 53% of the whole distribution for sample **1a**, the integral of the same region in the asphaltene spectra of the same oil sample is 21%. While for asphaltenes the maximum of the distribution was found at $\sim m/z$ 700, in the case of DAO samples it is shifted down to $\sim m/z$ 300.

Comparing the LDI spectra of samples **1a** and **2a**, several features can be found. In the low $m/z$ region a completely different distribution is observed. In the case of sample **1a** (Fig. 1A), the lower resolution can be ascribed to a large number of ionic species with mass differences of 1–2 Da (or even lower, due to the presence of heteroatom-containing species). Their higher density necessarily leads to space-charge phenomena, which seem to be less relevant in the case

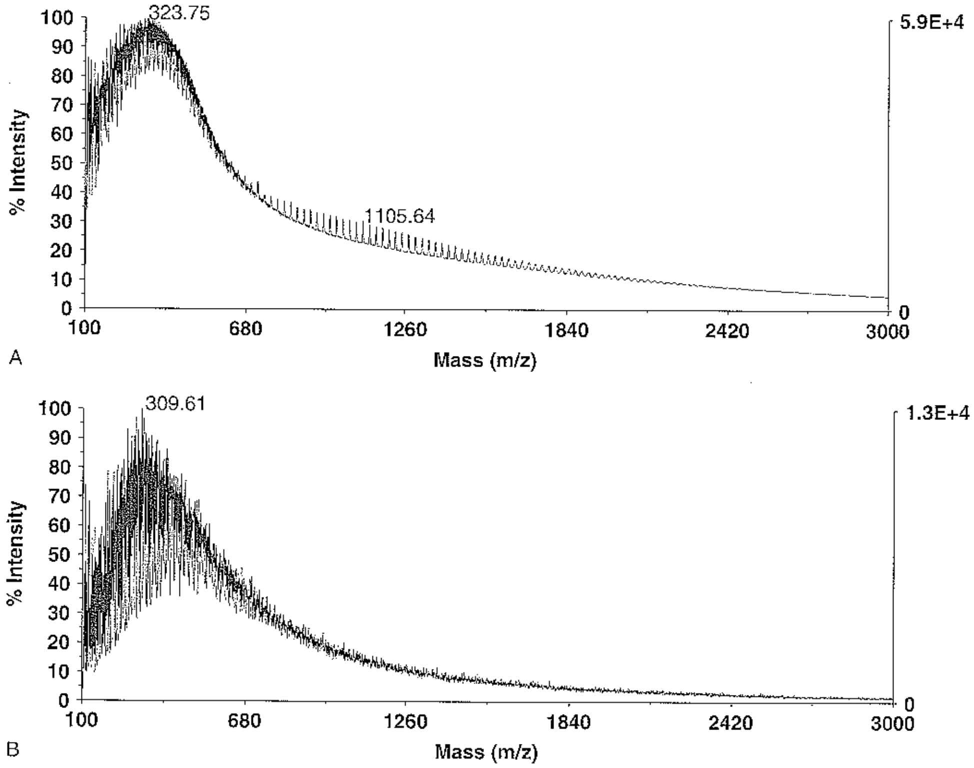

**Figure 1.** (A) DAO Sample **1a**, spectrum LDI, range 100–3000; (B) DAO Sample **2a**, spectrum LDI, range 100–3000.

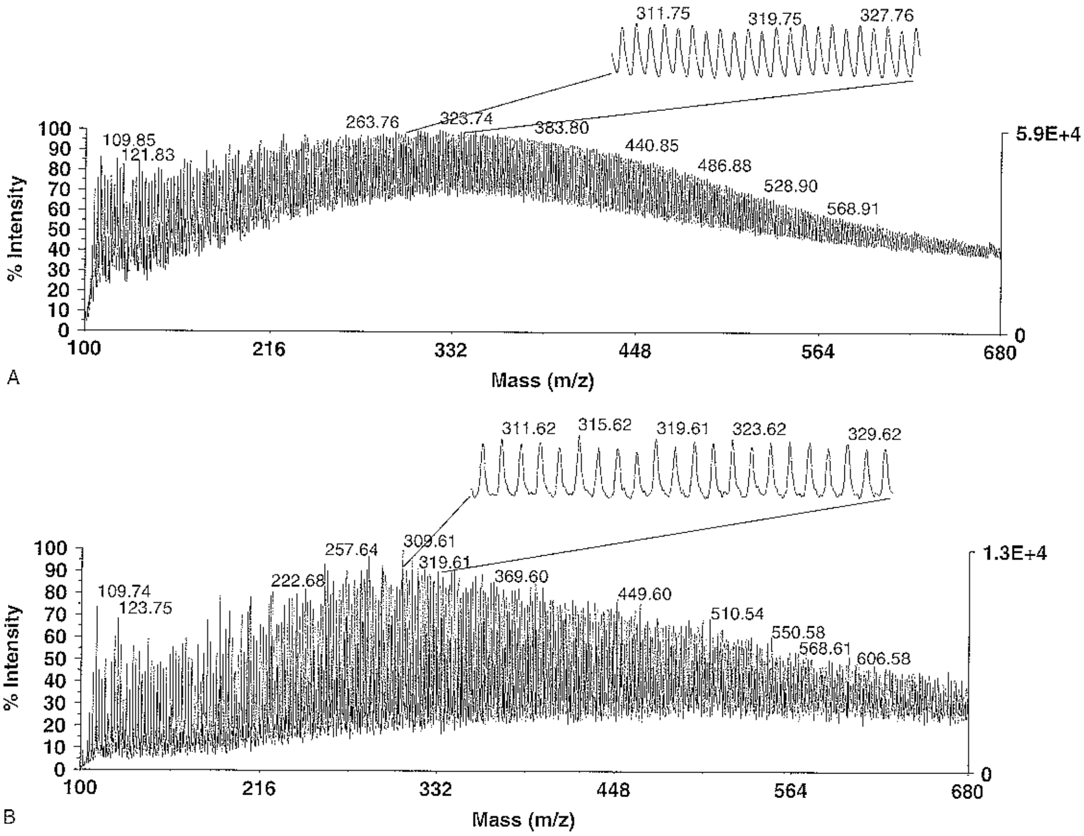

**Figure 2.** (A) DAO Sample **1a**, spectrum LDI, range 100–680; (B) DAO Sample **2a**, spectrum LDI, range 100–680.

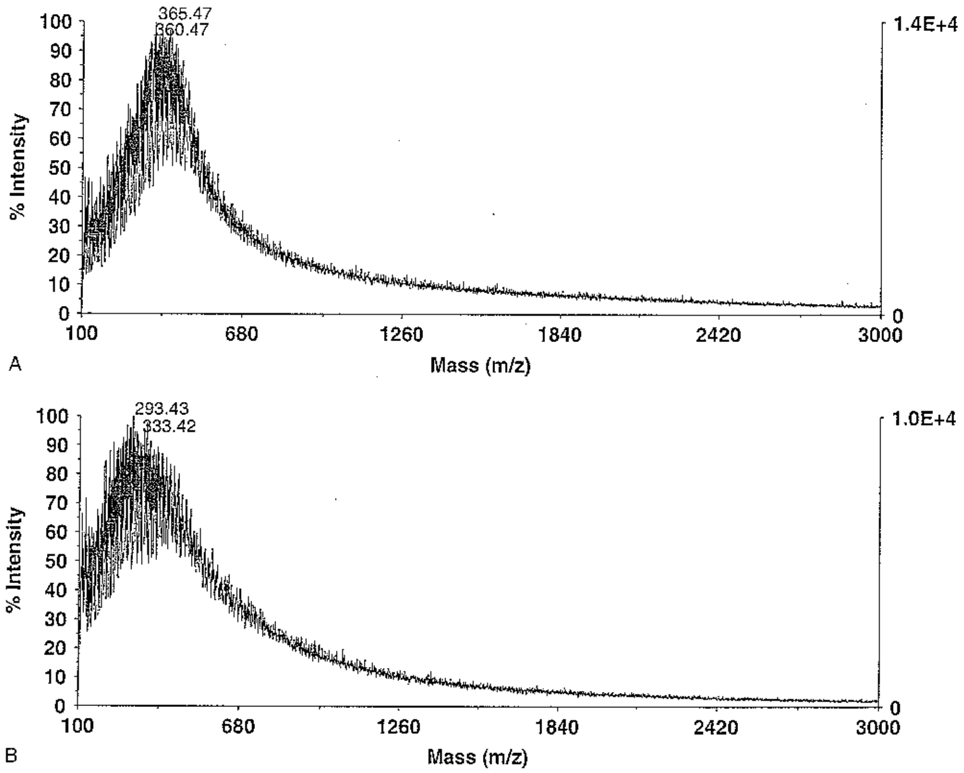

**Figure 3.** (A) Aromatic fraction Sample **1b**, spectrum LDI, range 100–3000; (B) Aromatic fraction Sample **2b**, spectrum LDI, range 100–3000.

of sample **2a**. This aspect is well described by the expanded $m/z$ view reported in Fig. 2. As can be seen by the insets presented in parts (A) and (B), a peak is present for each $m/z$ value, and surely some of the peaks are due to different isobaric species with different elemental composition and, consequently, with different values of accurate mass.

In the case of sample **1a**, a series of peaks with mass differences of 24 Da are observed in the mass range 700–1800 (Fig. 1). This behavior was considered characteristic for asphaltene fractions and ascribed to the presence of polyaromatic compounds of 'graphitic' nature and/or the occurrence of aggregation phenomena, typical of the asphaltene fractions. In principle, these species could be generated by laser-induced decompositions, but their absence in the case of sample **2** might indicate that they represent molecular species present in the DAO fraction of sample **1**. Experiments performed with different laser powers led to analogous spectra, suggesting that laser-induced decomposition could play a role in the production of the 24-Da-spaced series of ions. In other words, the laser energy necessary to desorb and ionize the species of interest is also high enough to activate decomposition reactions. The maintenance of these high molecular species only in the case of sample **1a** is an unexpected behavior. Considering that the oil sample treatment leading to the DAO samples **1a** and **2a** was rigorously the same, it follows that sample **1a** either contains a higher concentration of these species (so that its fractionation becomes a more difficult task) or its chemical composition favors the 'trapping' of these species in the DAO fraction.

The subfractionation of DAO by a toluene/$n$-hexane mixture led to samples **1b** and **2b**, enriched in aromatic compounds (Scheme 1). The related spectra are reported in Figs 3 and 4. First of all, the disappearance of the species at high molecular weight with mass differences of 24 Da is evident. Considering the subfractionation procedure, it follows that they must be insoluble in toluene/$n$-hexane.

A different distribution of molecular species is observed for samples **1b** and **2b**. In both cases, a molecular weight distribution between 100 and 700 Da is observed, but, while in the first case a symmetrical distribution centered at $m/z$ 360 is observed, in the latter case an unsymmetrical distribution with a maximum corresponding to $m/z$ 290 is present. This aspect is well depicted in Fig. 4. In other words, sample **2b** seems to be richer in low-molecular-weight components. In fact, in this case the relative abundances of the ionic species in the $m/z$ range 100–300 are in the range 60–100%, while in the case of sample **1b** they are in the range 30–60%. The same figure shows some similarities and differences between the samples: (1) first of all, in both cases peaks corresponding to every $m/z$ value are present, owing to the high complexity of the samples under analysis; (2) in the case of sample **2b**, the components with molecular weight higher than 400 seem to be better defined than those present in the case of sample **1b**. In fact, as can be seen from the spectra of Fig. 4B, in this case the oligomeric series (mass differences of 14 Da) with different hydrogen deficiencies is readily evident, suggesting a higher homogeneity of this sample.

The polar fractions (samples **1c** and **2c**) (Scheme 1) led to the LDI spectra reported in Fig. 5. In this case, for sample **1c**,

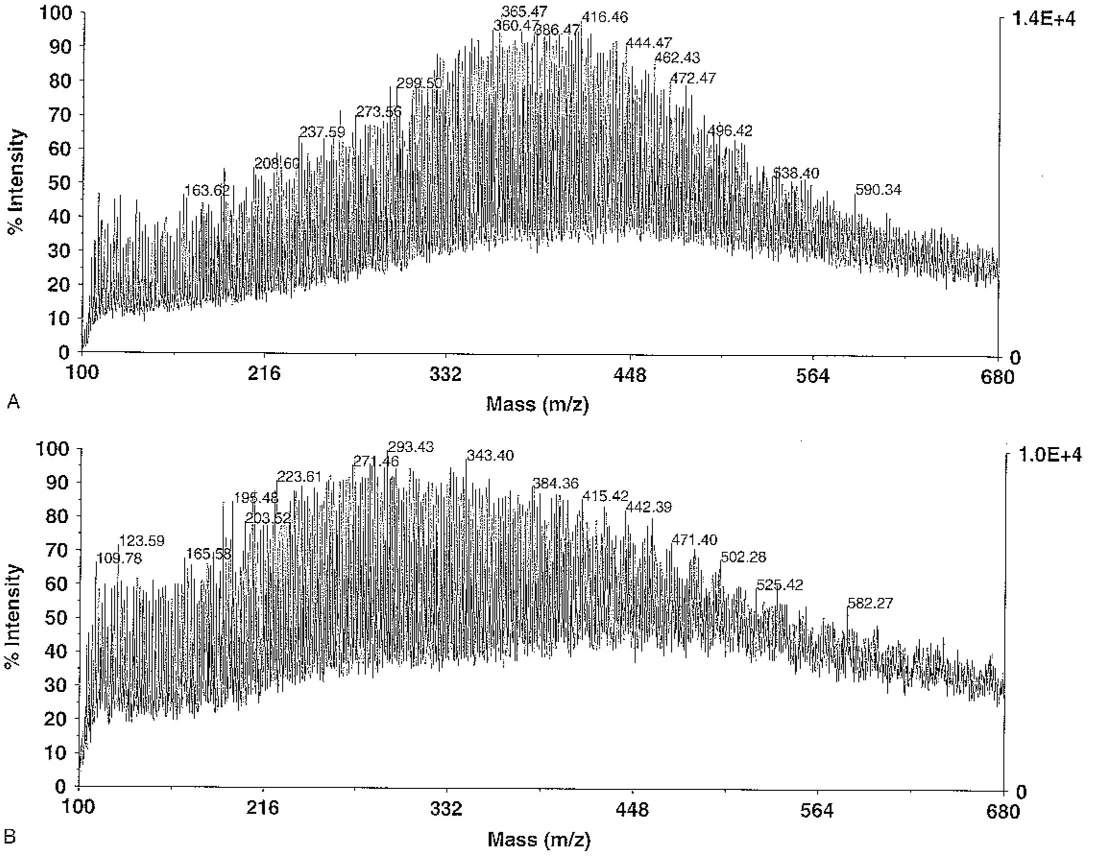

**Figure 4.** (A) Aromatic fraction Sample **1b**, spectrum LDI, range 100–680; (B) Aromatic fraction Sample **2b**, spectrum LDI, range 100–680.

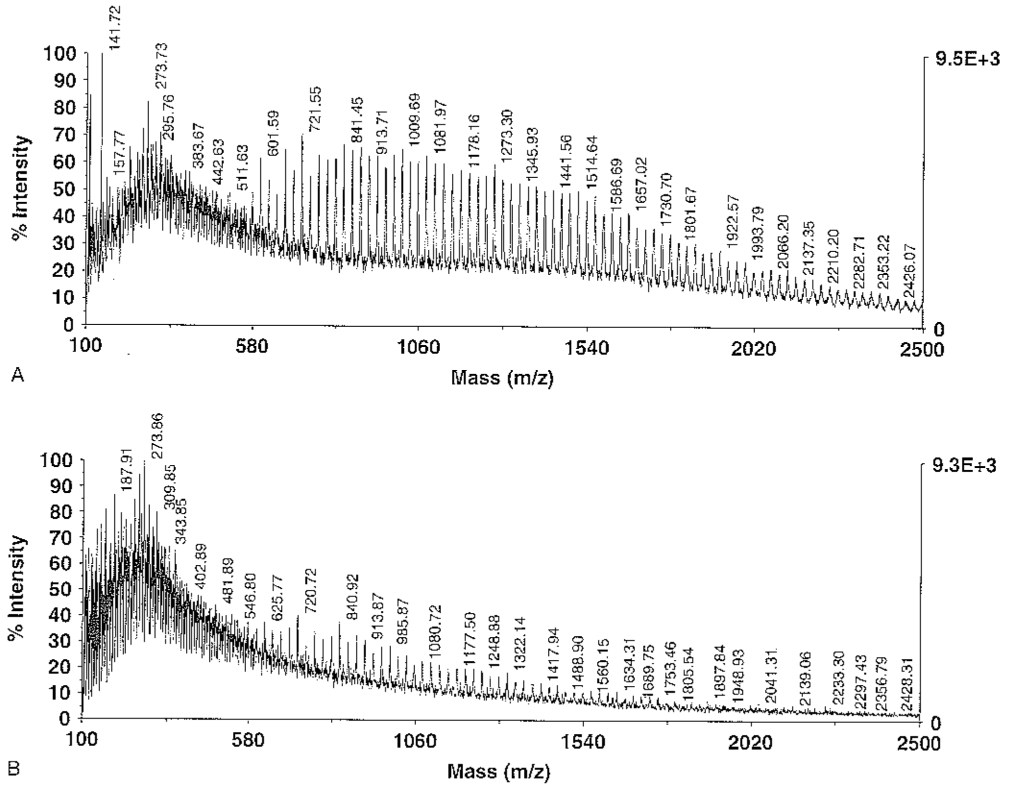

**Figure 5.** (A) Polar fraction Sample **1c**, spectrum LDI, range 100–2500; (B) Polar fraction Sample **2c**, spectrum LDI, range 100–2500.

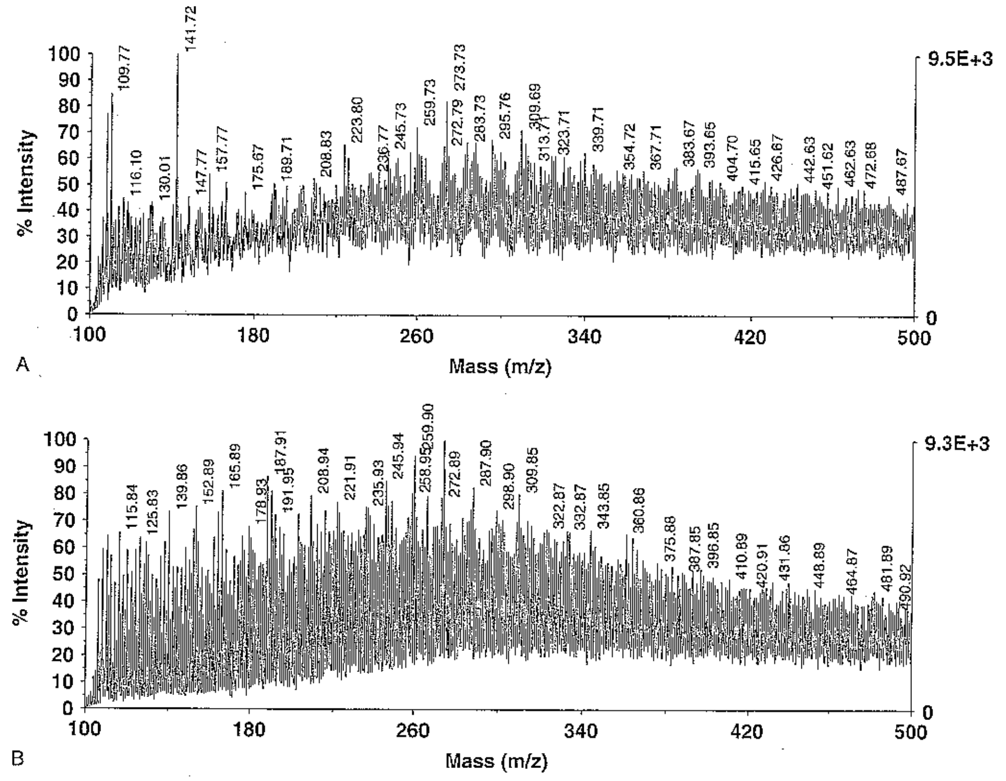

**Figure 6.** (A) Polar fraction Sample **1c**, spectrum LDI, range 100–500; (B) Polar fraction Sample 2c, spectrum LDI, range 100–500.

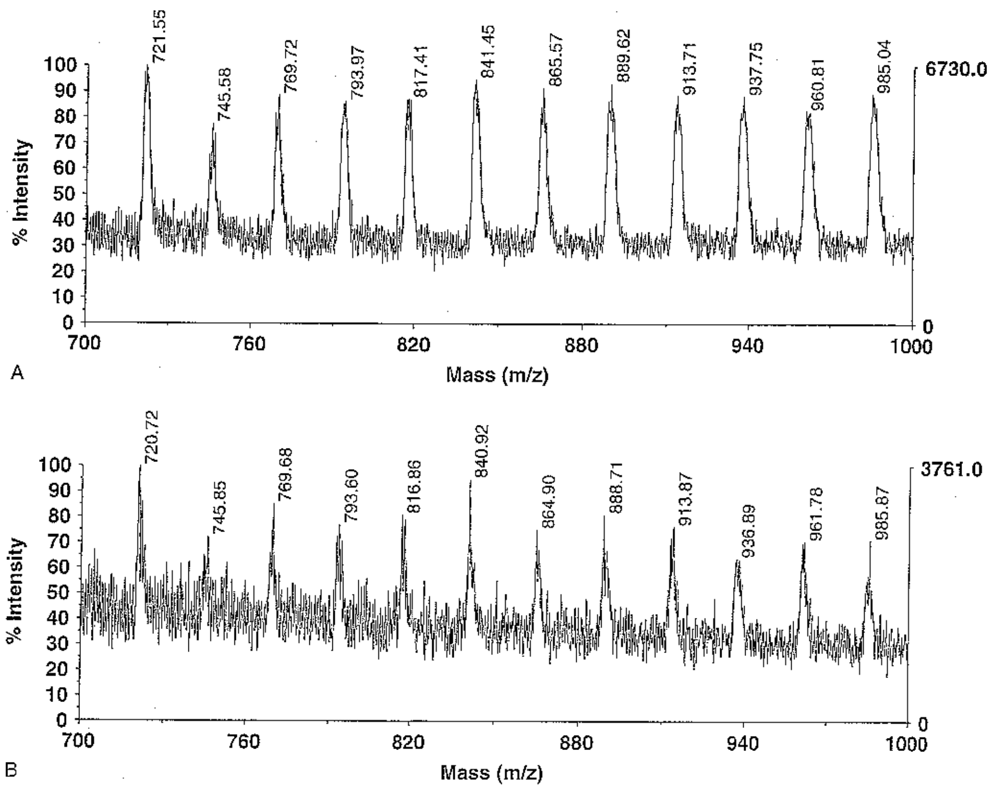

**Figure 7.** (A) Polar fraction Sample **1c**, spectrum LDI, range 700–1000; (B) Polar fraction Sample 2c, spectrum LDI, range 700–1000.

besides a complex distribution in the molecular weight range 100–500 Da (but surely less complex than that observed for samples **1b** and **2b**), most of total ion current is still due to the 24-Da-spaced series already established in the unfractionated DAO (sample **1a**). It is worth noting that these species were not detectable (or detectable at such a low level as to be lost in the spectrum complexity) in the case of sample **2a**. Figure 5(B) shows that after fractionation the 24-Da-spaced series is present even though at a lower extent than for sample **2c**. This result is quite surprising: in fact, the solvent extraction employed for obtaining **1c** and **2c** would exclude the presence of nonpolar compounds. The data shown by Fig. 5 are partially in agreement with this conclusion. In fact, the low-molecular-weight distribution is surely less complex than that observed for DAO (samples **1a** and **2a**, Fig. 1) and for the 'aromatic' fraction (samples **1b** and **2b**, Fig. 3). In principle, because of its chemical nature, the polyaromatic fraction responsible for the 24-Da-spaced series would be present in samples **1b** and **2b** and not, as it has been observed, in **1c** and **2c**. This behavior can be explained either by the presence, in their structure, of heteroatoms, or by the intrinsic complexity and dimension of the molecules belonging to the series, which makes difficult their extraction from the DAO samples. However, in the case of **1c** and **2c** the resolution shows a clear increase, proving that the samples under investigation are less complex than the others.

The complexity of the low $m/z$ region (100–500) is well shown by the expanded view of the spectra reported in Fig. 6. Interestingly, in the case of **1c** two ions predominate (Fig. 6): just as a hypothesis the most abundant species at $m/z$ 142 and that at $m/z$ 110 (85%) can be ascribed to the presence of $C_6H_4(SH)_2$ and $C_6H_5SH$ molecules. This data is in agreement with the elemental analysis data, indicating that crude oils **1** and **2** contain high amount of sulfur, 2.61 and 5.31% wt. S, respectively.

Finally, two further comments must be made on the mass spectra of samples **1c** and **2c**:

1. The low-molecular-weight region (Fig. 6) indicates a lower complexity of sample **1c** with respect to **2c**;
2. In the case of **2c** the 24-Da-spaced series shows the presence of species with different hydrogen deficiency and/or containing heteroatoms (Fig. 7).

In conclusion, the present investigation on the DAO fraction of oils of two different Italian fields shows that LDI is able to differentiate them, evidencing significant differences in their aromatic fraction or in the polar compounds.

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