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Analysis of Polar Components in Crude Oil by Ambient Mass Spectrometry

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1. Introduction

Crude oil is a naturally generated material comprising a very complex mixture of coexisting hydrocarbons and polar organic compounds. It is found in geologic formations below the Earth's surface and recovered mostly through oil drilling. It is refined and separated by distillation according to the various boiling points of the components resulting in a number of products, such as petrol, kerosene, and numerous chemical reagents that can be used to produce plastics, pharmaceuticals, and a wide variety of other materials. Due to the extreme complexity of the components of crude oil samples, the characterization of these constituents or their products has been a challenging research topic for analytical chemists.

Gas chromatography/mass spectrometry (GC/MS) is routinely used for identifying volatile and non-polar components in crude oil, and the characterization of trace polar components is usually achieved by liquid chromatography/mass spectrometry (LC/MS). However, recent advances in mass spectrometry have enabled the development of novel ionization techniques that are potentially useful in addressing some issues associated with conventional mass spectrometric technologies.

As shown in Table 1, conventional mass spectrometric ionization techniques, such as electron impact ionization (EI), field ionization (FI) (Beckey *et al.*, 1969; Hsu *et al.*, 2001), and field desorption (FD) (Stanford *et al.*, 2007), are suitable for the analysis of volatile or semivolatile compounds in crude oil. For compounds with higher boiling points (>500 °C), pyrolysis (Py) combined with GC/MS to produce characteristic fragments for identification is necessary (Shute *et al.*, 1984). For the purpose of characterizing polar components that cannot be achieved by Py/GC/MS, approaches that couple a HPLC system with atmospheric ionization sources, such as electrospray ionization (ESI) (Fenn *et al.*, 1989 & 1990), atmospheric pressure chemical ionization (APCI) (Carroll *et al.*, 1975), and atmospheric pressure photoionization (APPI) (Robb *et al.*, 2000), have been developed. Although some of the polar fragments can be separated and detected by the LC/MS approach, strong interaction between certain polar components with the stationary phase in the chromatographic system is still a problem. Directly introducing samples into the ionization source without passage through a chromatographic system may be a solution.

The direct analysis of trace polar components containing N, O, and S in crude oil has been achieved by ESI/MS and the interference with the ionization processes resulting from the presence of a large amount of non-polar components in the sample is not observed (Zhan *et al.*, 2000).

For ambient mass spectrometric approaches, techniques such as electrospray-assisted pyrolysis ionization (ESA-Py) (Hsu *et al.*, 2005), desorption electrospray ionization (DESI) (Takáts *et al.*, 2004), easy ambient sonic-spray ionization (EASI) (Haddad *et al.*, 2008), and atmospheric pressure laser-induced acoustic desorption chemical ionization (AP/LIAD-CI) (Nyadong *et al.*, 2011) have been used for the direct analysis of crude oil with minimal sample pretreatment. Such approaches prevent unexpected effects on the composition of crude oil samples during preparation. Another attractive feature of performing analyses under ambient conditions is the capacity for rapid sampling, thereby enabling opportunities for high-throughput analysis.

Within this context, ambient mass spectrometry is regarded as a potential analytical tool for “petroleomics” applications owing to its specific features that differ from conventional mass spectrometry. Such features support the selective characterization of trace polar components by constructing variable sampling methods and ionization models. In the present chapter, we focus on a recently developed ambient mass spectrometric approach for the rapid characterization of polar components in crude oil.

Technique name	Acronym	Environment	Analyte polarity	Reference
Pyrolysis/mass spectrometry	Py/MS ^I	Vacuum	Non-polar/Polar	Shute <i>et al.</i>
Gas chromatography × gas chromatography/mass spectrometry	GC×GC/MS ^I	Vacuum	Non-polar/Polar	Blomberg <i>et al.</i>
Pyrolysis/gas chromatography/mass spectrometry	Py/GC/MS ^I	Vacuum	Non-polar/Polar	Snyder <i>et al.</i>
Matrix-assisted laser desorption/ionization mass spectrometry	MALDI	Vacuum	Polar	Robins <i>et al.</i>
Electrospray ionization	ESI	Ambient	Polar	Zhan <i>et al.</i> , Klein <i>et al.</i> & Hsu <i>et al.</i>
Atmospheric pressure photoionization	APPI	Ambient	Polar/Non-polar	Purcell <i>et al.</i>
Atmospheric pressure chemical ionization	APCI	Ambient	Polar/Non-polar	Hsu <i>et al.</i>
Atmospheric pressure laser-induced acoustic desorption chemical ionization	AP/LIAD-CI	Ambient	Polar/Non-polar	Nyadong <i>et al.</i>
Easy ambient sonic-spray ionization	EASI	Ambient	Polar	Corilo <i>et al.</i>
Desorption electrospray ionization	DESI	Ambient	Polar/Non-polar ^{II}	Wu <i>et al.</i>
Electrospray-assisted pyrolysis ionization	ESA-Py	Ambient	Polar	Hsu <i>et al.</i>

I: The ionization sources: electron impact (EI), chemical ionization (CI), field desorption (FD), and field ionization (FI).
II: Analyses performed through discharge-induced oxidation reactions.

Table 1. Summary of ionization methods used in the analyses of crude oil.

2. Conventional analytical approaches for characterizing polar components in crude oil

Although gas chromatography/mass spectrometry (GC/MS) has been widely used in characterizing volatile and semivolatile components in different samples, many natural macromolecules are still not amenable to be characterized by GC/MS. However, these materials often yield volatile, gas chromatographable products upon controlled thermal degradation induced by pyrolysis (Anhalt *et al.*, 1975; Gutteridge *et al.*, 1987; Yang *et al.*, 2003). These volatile components characterized by Py/MS or Py/GC/MS may then serve as fingerprints for classifying or studying the composition of different species of macromolecules (Snyder *et al.*, 1990; Goodacre *et al.*, 1991; DeLuca *et al.*, 1993; Smith *et al.*, 1993). In general, the pyrolysis of a complicated mixture like crude oil produces a wide variety of chemical compounds ranging in polarity from non-polar to highly polar. The non-polar components, for example, saturated acyclic or cyclic terpenoids and aromatic hydrocarbons, are often used as biomarkers in organic geochemistry. The polar components, which are difficult to characterize by conventional Py/MS or Py/GC/MS, are seldom used for sample diagnosis or classification. Moreover, these complex polar compounds are nearly impossible to resolve by GC and are often referred to as unresolved complex mixtures (UCMs) (Panda *et al.*, 2007). With the aim of resolving UCMs, two-dimensional GC/MS (GCxGC/MS) was developed to provide higher resolution for the separation of these compounds. This approach has been applied to the characterization of many compounds, including the different hydrocarbon isomers in crude oil (Blomberg *et al.*, 1997; Hua *et al.*, 2004; von Mühlen *et al.*, 2006).

For certain materials (e.g., synthetic polar polymers), the polar pyrolysates may contain useful diagnostic structural information (Williamson *et al.*, 1980; Marshall *et al.*, 1983; Shiea *et al.*, 1996; Galipo *et al.*, 1998). Unfortunately, during pyrolysis processes, many polar macromolecules are broken down to fragments that cannot be detected by GC/MS because they are retained in the pyrolysis zone, the injection system, or the capillary column owing to their high polarity or high molecular weight (Moss *et al.*, 1980; Holzer *et al.*, 1989). Even when the polar pyrolysates do enter the separation column, they often display peak tailing, poor reproducibility, and long elution times. In many cases, no chromatographic peaks are even observed in this fraction (Derbyshire *et al.*, 1989; Manion *et al.*, 1996).

Directly introducing the gaseous pyrolysates into the ionization source of a mass spectrometer may be a way to circumvent the chromatographic problems that affect the analysis of polar pyrolysates, but the ionization of trace polar pyrolysates in samples that contain a large amount of non-polar compounds still remains a challenge. As is generally known, when electron impact ionization (EI) is used to ionize samples, non-polar ion signals always overwhelm those of polar components – the so-called “ion suppression effect” (Tang *et al.*, 1991).

Electrospray ionization (ESI), developed by Fenn (for which he received the 2002 Nobel Prize in Chemistry), is an atmospheric ionization method used to characterize polar compounds through continuous infusion of a solution to which a high DC voltage (ca. 3–4 kV) is applied. By electric field forces, a Taylor cone is induced leading to the generation of a large number of charged droplets forming the protonated analyte ions from an ESI emitter. In this way, compounds consisting of functional groups with high proton affinity can be effectively

ionized, in contrast to less or non-polar compounds. The characterization of polar hydrocarbons containing N, S, and O in crude oil samples by low or high resolution electrospray ionization mass spectrometry has been reported (Klein *et al.*, 2003; Hsu *et al.*, 2011).

In addition to ESI, matrix-assisted laser desorption/ionization (MALDI) developed by Tanaka in 1987 (for which he received the 2002 Nobel Prize in Chemistry) is an alternative method for ionizing large biomolecules, such as proteins and peptides. In MALDI, the sample solution mixes with the UV-absorbing organic matrix solution (usually in equal volumes). After drying, the crystals containing a large amount of matrix and sample molecules are irradiated with a pulsed laser. The matrix absorbs the energy supplied by the pulsed laser to assist the ionization of analytes. Although the MALDI analysis is performed under vacuum, a characterization of the chemical components in crude oil has been reported (Robins *et al.*, 2003). Unlike the traditional polar and acidic matrices, such as sinapinic acid, α -cyano-3-hydroxycinnamic acid, and 2, 5-dihydroxybenzoic acid, non-polar matrices, including anthracite and 9-cyanoanthracene, are more effective for characterizing crude oil fractions as they provide higher quality MALDI mass spectra. In addition, no interfering matrix ions are observable in the resulting spectra.

Recently, Marshall *et al.* presented results for the characterization of polar compounds in crude oil samples by laser desorption/ionization-ion mobility/mass spectrometry (LDI/IM/MS). In this approach, a Fourier transform ion cyclotron resonance (FT-ICR) was used to obtain high resolution mass spectra (Fernandez-Lima *et al.*, 2009). The distribution of polar compounds in the crude oil samples was studied. Atmospheric pressure chemical ionization (APCI) combined with HPLC has been used to characterize naphthenic acids, which are known to be corrosive to the containers and pipelines used in the petroleum industry (Hsu *et al.*, 2000). Atmospheric pressure photoionization (APPI) combined with a 9.4 T FT-ICR and HPLC has demonstrated utility for characterizing both polar and non-polar components that cannot be ionized by ESI (Purcell *et al.*, 2006). The results indicate that APPI is capable of ionizing both polar and non-polar components in crude oil. In the mean time, the problem of the high complexity of the crude oil components can be solved by using a high resolution FT-ICR to detect the ions generated by APPI. Although APCI and APPI are useful tools for ionizing chemical compounds with different polarities, complicated sample pretreatments are needed to remove insoluble particles in the sample prior to HPLC/MS analysis.

3. Ambient mass spectrometric approaches

Ambient ionization mass spectrometry is another recently developed ionization method and possesses the following features: (1) rapid sample switching, (2) minimal or no sample pretreatment, and (3) ability to analyze solid, liquid, or gaseous samples (Huang *et al.*, 2010). To date, certain ambient ionization mass spectrometric techniques have been used to characterize either non-polar or polar components in petroleum and crude oil without tedious pretreatments.

3.1 Desorption electrospray ionization mass spectrometry (DESI-MS) for crude oil analysis

Desorption electrospray ionization mass spectrometry (DESI-MS), an alternative to ESI-based ambient mass spectrometry, has been used to analyze petroleum samples. Under

typical DESI conditions, the technique is only suitable for the detection of polar components. However, in a separate study, Cooks *et al.* reported that discharge-induced oxidation reactions occurred for non-polar components when betaine aldehyde was added to the DESI spraying solution (Wu *et al.*, 2010). The oxidation reactions transformed hydrocarbons to oxidized components of low-polarity, such as alcohols or ketones. In the mean time, the so-called reactive-DESI approach was developed to enhance the detection sensitivity for these oxides. This was achieved by replacing the spray solution with one that contains functional groups with higher proton-affinity (Cotte-Rodríguez *et al.*, 2005). The study indicated that saturated hydrocarbons can still be ionized by DESI under ambient conditions. Although accompanying dehydrogenation may make the method unsuitable for characterizing the extent of unsaturation, a rapid and accurate determination of the carbon distribution in the saturated hydrocarbons of petroleum distillates is demonstrated.

3.2 Easy ambient sonic-spray ionization mass spectrometry (EASI-MS) for crude oil analysis

Easy ambient sonic-spray ionization mass spectrometry (EASI-MS), developed by Eberlin *et al.*, has also been applied to the analysis of crude oil samples. The samples were directly exposed to a flow of nitrogen gas along with the spray reagent. The moist surfaces of the crude oil samples were then desorbed and subsequently ionized to generate analyte ions that were detected by a mass spectrometer (Corilo *et al.*, 2010). The process of ion formation in EASI-MS is mainly supported by the production of bipolar solvent droplets using a nebulizer to generate a supersonic spray, and the high electric voltage applied in conventional ESI is not used to form the charged droplets. The performance of EASI-FT-ICR MS for characterizing crude oil samples has been found to be almost as fast as ESI/FT-ICR-MS and provide similar compositional information on the polar components and comparable spectral quality to that of a commercial ESI device.

3.3 Atmospheric pressure laser-induced acoustic desorption chemical ionization/mass spectrometry (AP-LIAD/CI/MS) for crude oil analysis

A laser-induced acoustic desorption (LIAD) device combined with a chemical ionization source was employed for the analysis of crude oil distillates under atmospheric pressure. In general, LIAD, a matrix-free and laser-based approach, is usually performed under vacuum conditions. The desorption process in LIAD is induced by the action of a shockwave that is generated as a pulsed laser irradiated on the backside of a metal foil. As the energy is transferred from the metal foil to the sample, which is deposited on another side of the foil, it induces the desorption of analytes. By the interaction of the analyte with an ion cloud generated by a chemical ionization (CI) process, analytes with a wide range of polarity are successfully ionized. Marshall *et al.* have combined an atmospheric pressure AP-LIAD/CI with a 9.4 T FT-ICR/MS to perform high resolution chemical analyses under ambient conditions. It was demonstrated that not only polar but also non-polar compounds in the crude oil distillates could be successfully characterized by this AP-LIAD/CI/FT-ICR/MS approach.

3.4 Electrospray-assisted pyrolysis ionization/mass spectrometry (ESA-Py/MS) for crude oil analysis

To characterize polymers and trace polar components in crude oil samples, we previously developed an interface to combine electrospray ionization mass spectrometry (ESI/MS) with a pyrolytic probe. This technique successfully detects the polar pyrolysates that are released from synthetic polymers, which are constructed from polar units and crude oil. We refer to this technique as “electrospray-assisted pyrolysis ionization/mass spectrometry (ESA-Py/MS)” (Hsu *et al.*, 2005 & 2007).

The pyrolyte products generated by a commercial Curie-point pyroprobe are conducted to the tip of a capillary where charged droplets are continuously produced by electrospraying an acidic methanol solution. The ionization of the polar pyrolysates is suggested to occur through (1) ion-molecule reactions (IMRs) between the gaseous pyrolysate molecules (M) and protons (H^+) or protonated methanol species [e.g., $(H_3O)^+$, $(MeOH)H^+$, $(MeOH)_2H^+$] and/or (2) polar pyrolysate molecules dissolving (or fusing) in the charged methanol droplets, followed by electrospray ionization from the droplets to generate protonated analyte molecules (MH^+).

The ESA-Py mass spectra are then used to rapidly distinguish synthetic polymer standards that differ in the nature of their building units, degree of polymerization, and copolymerization coefficients. In addition, a petroleomic application of ESA-Py/MS was also demonstrated. Trace polar compounds that coexist with large amounts of non-polar hydrocarbons in crude oil, amber, humic substances, and rubber samples were selectively ionized without any chromatographic separation or complicated pretreatment processes.

According to the ionization features of ESI, the ionization of polar pyrolysates in an ESA-Py source may go through IMRs and/or an ESI process. Only those compounds containing polar functional groups can be ionized. Non-polar compounds, such as saturated, unsaturated, cyclic, acyclic, or aromatic hydrocarbons possess no functional groups that receive a proton in the source and cannot be detected during the ESA-Py/MS analysis. Thus, this technique may be useful for a rapid characterization of polar components within fossil fuels and other materials that generate traces of polar pyrolysates together with large amounts of non-polar hydrocarbons. Herein, we show the results that were obtained using ESA-Py/MS to selectively detect trace polar components in the pyrolysates of different crude oil samples. The samples of different origins are then rapidly distinguished by their ESA-Py mass spectra. In addition, analyses of samples using ESI/MS were also performed, and the results were compared with those obtained using the ESA-Py/MS approach.

Other ambient mass spectrometric approaches, such as low temperature plasma mass spectrometry (LTP/MS) and direct analysis in real time mass spectrometry (DART/MS), have been used to characterize less polar components in olive oil samples. The use of organic solvents and/or additional reagents in the source is unnecessary, except for the use of helium gas for discharging (García-Reyes *et al.*, 2009; Vaclavik *et al.*, 2009). The results indicate that both techniques are potentially useful for characterizing polar components in petroleomics applications.

3.5 Electrospray-assisted pyrolysis ionization/mass spectrometry (ESA-Py/MS) combined with statistical methods for crude oil analysis

Recently, we modified the existing ESA-Py source to simplify the operation. During this ESA-Py analysis, a drop of untreated crude oil sample ($10\ \mu\text{L}$) was deposited on the Teflon block. The analytes in the sample were desorbed by inserting an electric soldering iron probe heated at $350\ ^\circ\text{C}$. The desorbed gaseous analytes then moved into an ESI plume located 5 mm above the top of the sample. Trace polar compounds (M) in the gaseous analytes were then ionized. The schematic of the modified ESA-Py/MS system is displayed in Fig. 1. An acidic methanol solution (50% aqueous methanol with 1% acetic acid) was continuously electrosprayed from an ESI emitter at high voltage (4 kV).

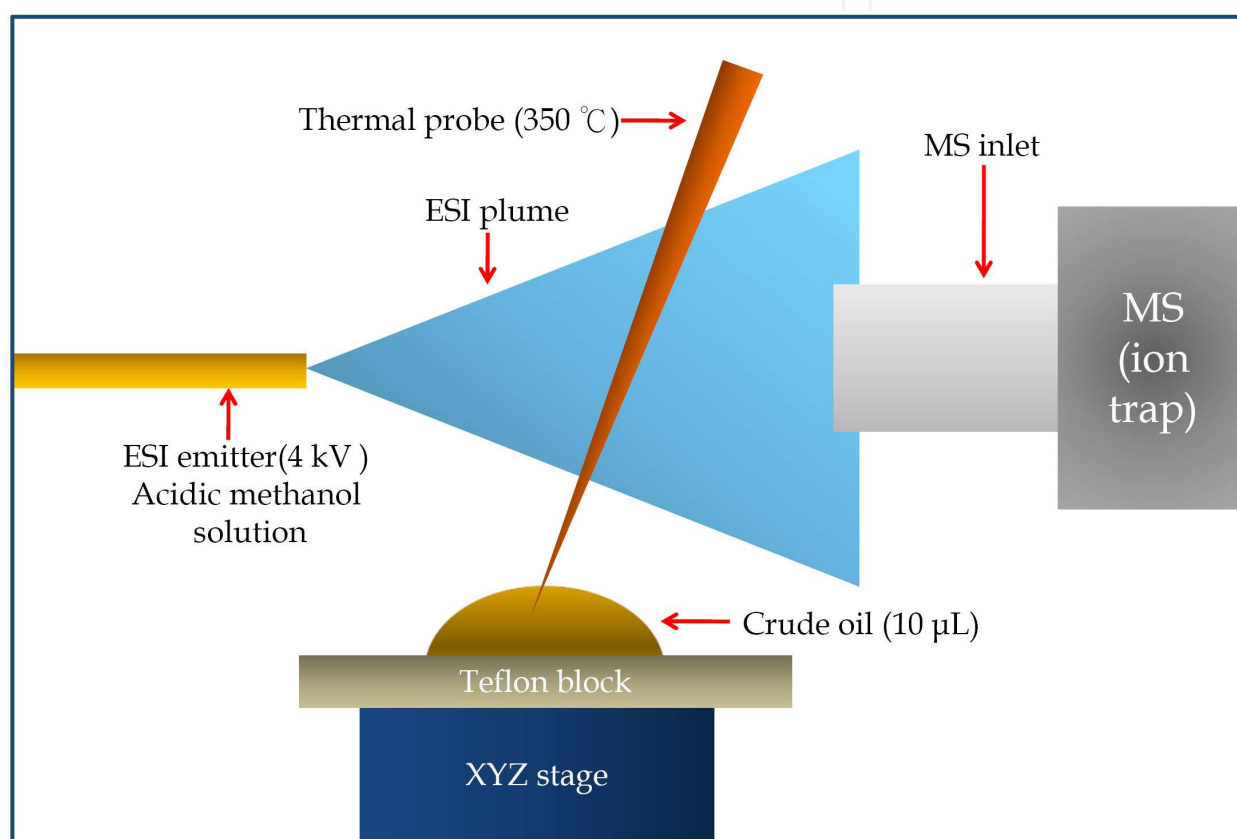


Fig. 1. Schematic illustration of the ESA-Py/MS system for crude oil analysis.

As described previously, the major components of the desorbed analytes are non-polar hydrocarbons, and their lack of functional groups that can accept a proton in the ESA-Py source results in the absence of hydrocarbon ion signals. Instead, the ions produced in the source are from trace polar components in the crude oil samples. Fig. 2 displays the ESA-Py/MS spectra of six crude oil samples from different origins. Samples A1 and A2 are from different depths of a well drilled in Africa, samples B1 and B2 are from different fields in a sedimentary basin of Asia, and samples C1 and C2 are from different basins in Taiwan. As shown in Fig. 2, all samples show significant responses for lower molecular weight components in the mass spectra. These low molecular weight compounds are presumed to be polar compounds owing to their high volatility. For sample correlation, it is demonstrated that oil samples of different origins are rapidly distinguished by their positive

ion ESA-Py mass spectra. It is noted that samples A1 and A2, which are from the same well, show high similarity in their ESA-Py/MS mass spectra.

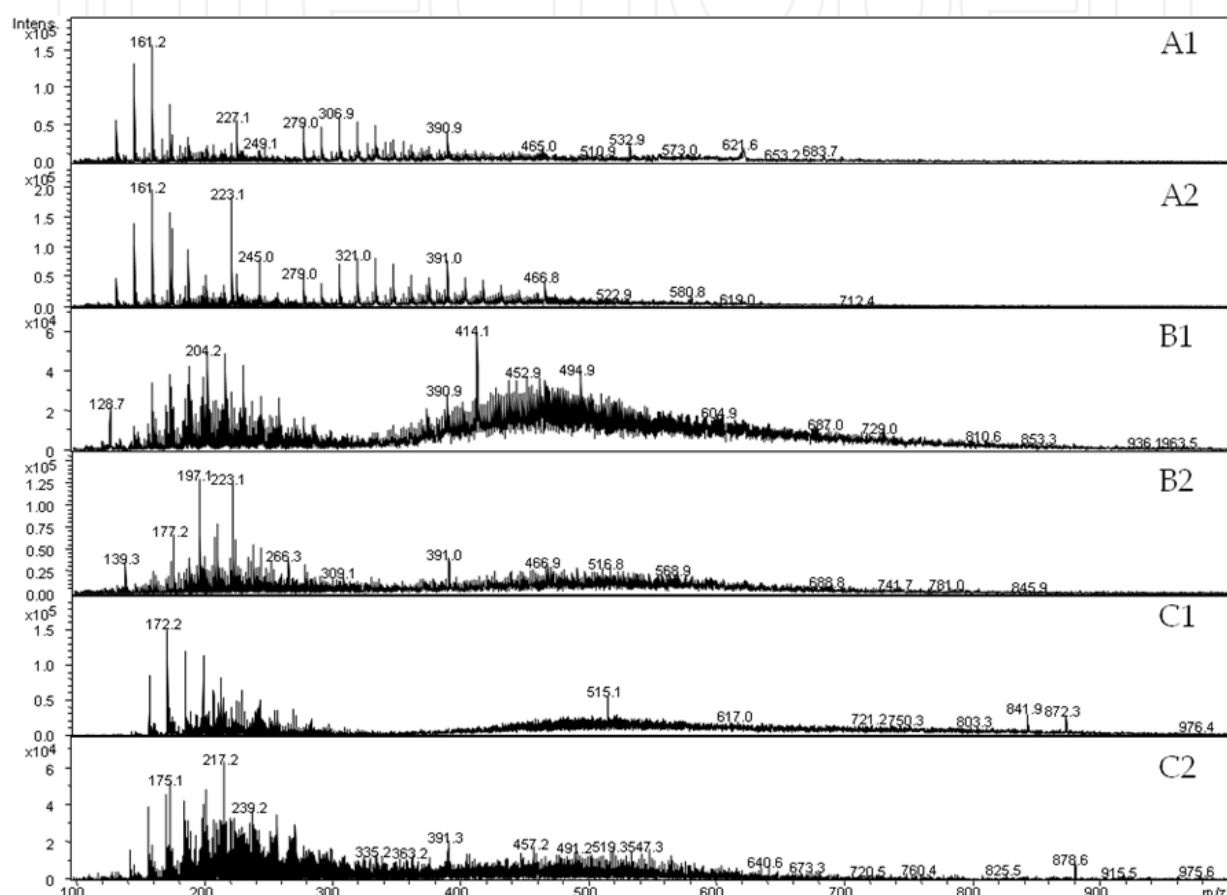


Fig. 2. The ESA-Py/MS spectra recorded from six crude oil samples. Samples A1 and A2: different depth of a well drilled in Africa; samples B1 and B2: different fields in a sedimentary basin of Asia; samples C1 and C2: different basins in Taiwan.

ESA-Py/MS analyses of each crude oil sample were performed in triplicate, and the results were further processed using a multivariate statistical method, principle component analysis (PCA). The results of the statistical analysis are shown in Fig. 3. In the sample groupings, A1 and A2 overlap, indicating that these two samples are closely related. This result is in agreement with the sample origins in which samples A1 and A2 are from the same drilling well but acquired at different depths. Although sample B2 was collected from a different geological region than samples A1 and A2, it contains components that are more

similar to those in samples A1 and A2 than to those in sample B1. The remaining samples (B1, C1, and C2) form individual groups independent from each other, reflecting their different origins.

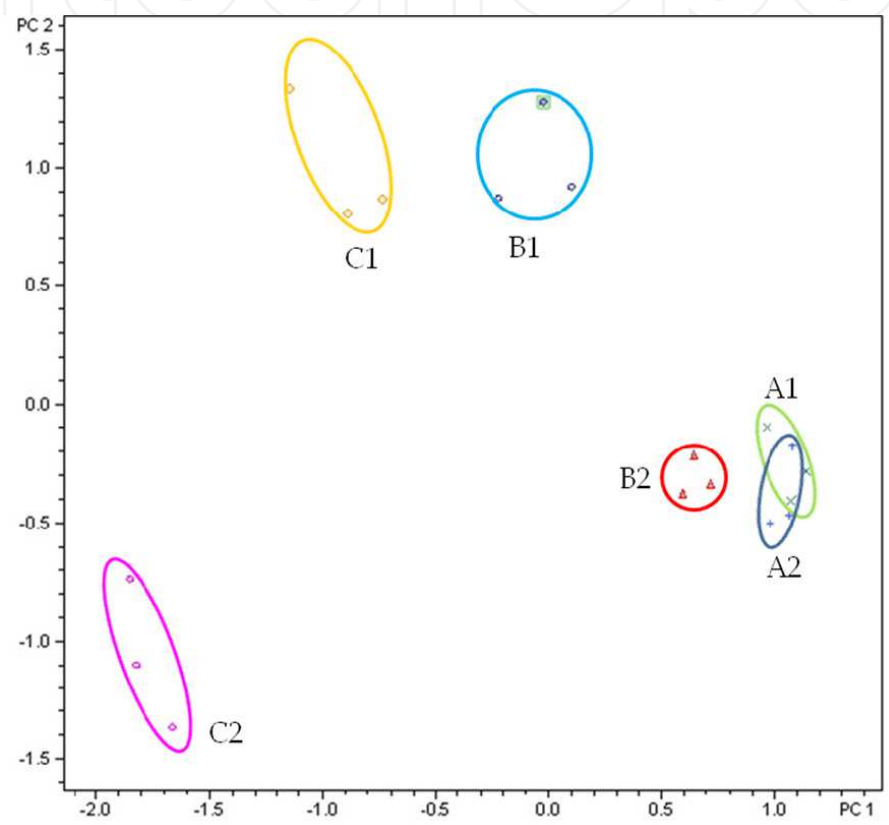


Fig. 3. The PCA diagram of ESA-Py/MS results from six crude oil samples.

In this study, a low resolution ion trap mass spectrometer (Bruker Esquire 3000+ ion trap mass spectrometer) equipped with a conventional ESI source was also used to analyze the methanol-soluble fraction of the same crude oil samples. The crude oil samples were ultrasonically mixed with methanol to extract the polar components. The methanol extract was concentrated and analyzed using ESI/MS. The ESI/MS spectra of the crude oil samples are shown in Fig. 4. As can be seen in the figure, several ion signals were observed in the ESI mass spectra, probably resulting from the dissolution of more polar components in the methanol solvent by the action of ultrasonication. Additionally, for the same reasons, the signals for polar components of higher molecular weight are found to be more intense than those for lower molecular weight components.

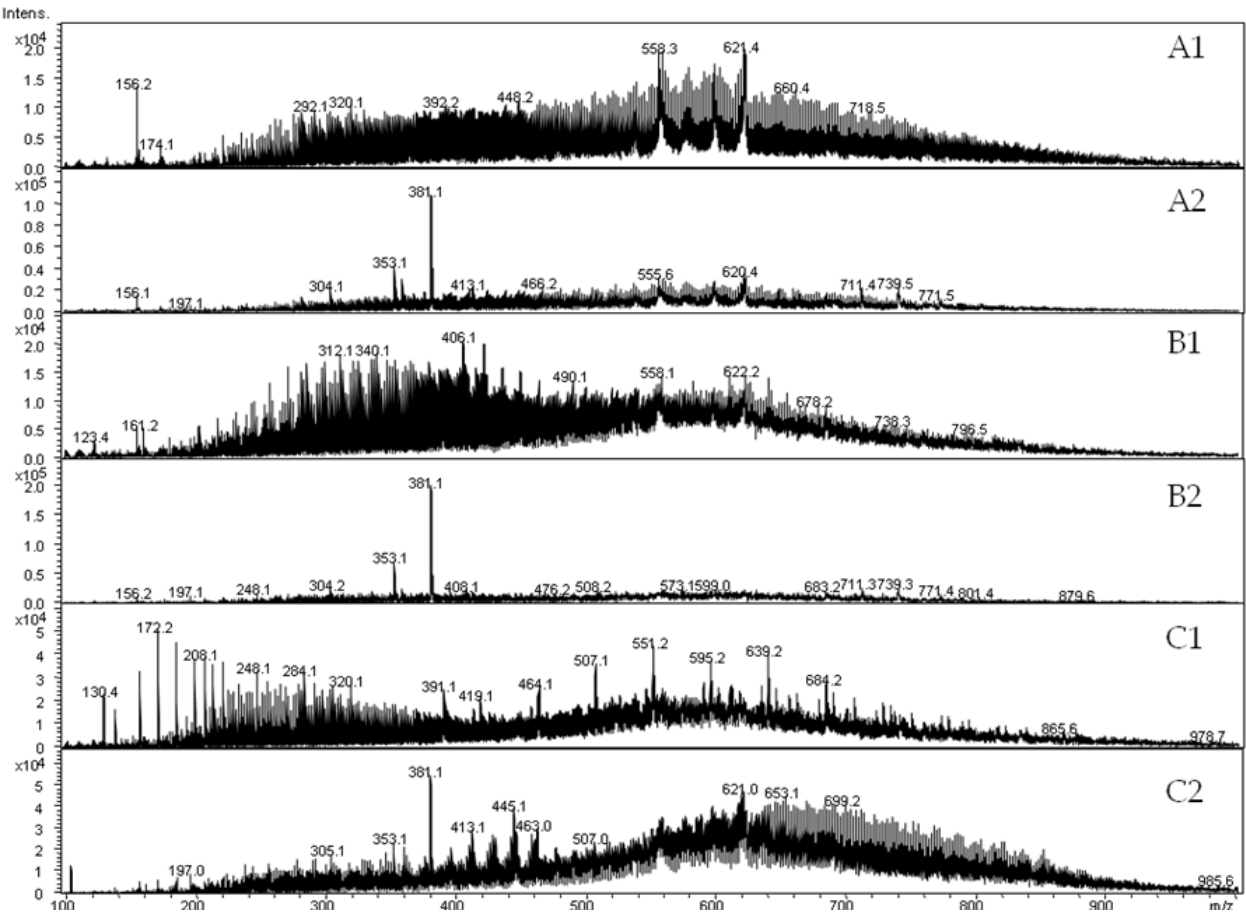


Fig. 4. The ESI mass spectra recorded from six crude oil samples.

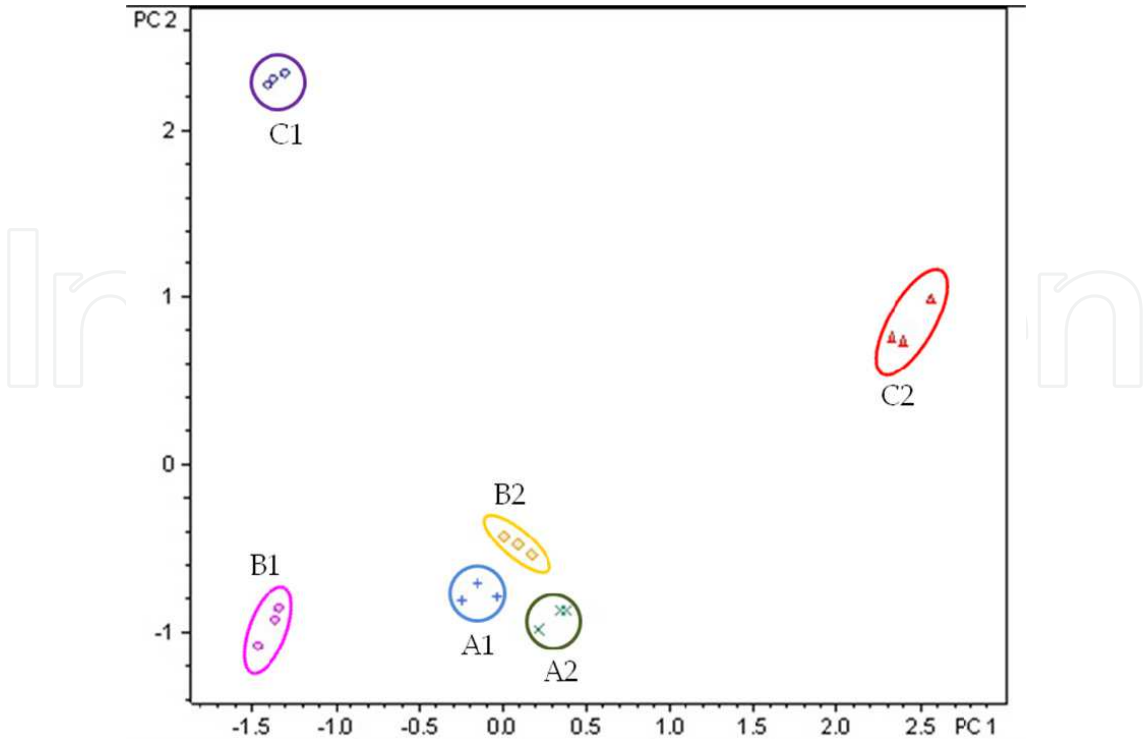


Fig. 5. The PCA diagram of ESI mass spectra results from six crude oil samples.

The PCA diagram based on the ESI mass spectra results from six crude oil samples is shown in Figure 5. In general, the distribution of samples on the PCA diagram is similar to that shown in Figure 3, excluding samples A-1 and A-2, which overlap in the ESA-Py/MS and PCA analyses. Although ESI/MS can be used to ionize more trace polar components, the required sample pretreatment and potential for blocking the ESI emitter (a capillary column) should be considered as possible difficulties associated with this analytical technique.

4. Conclusions

One of the most promising advantages of crude oil characterization by ambient mass spectrometry combined with a statistical processing method is the potential to rapidly analyze and distinguish the components and origins of the crude oil samples with minimal or no sample pretreatment. The technique also helps to reduce unexpected modifications to the composition of oil samples that may occur during sample pretreatment. The results obtained indicate that ESA-Py/MS, an ambient mass spectrometry method, is a useful technique for rapidly characterizing trace polar components in crude oil. With the assistance of modern statistical analysis (PCA), the crude oil samples from different origins are well classified.

5. References

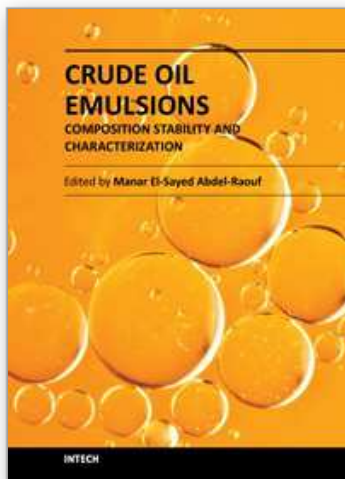
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Petroleum "black gold" is the most important nonrenewable source of energy. It is a complex mixture of different phases and components. Refining it provides a vast number of organic compounds, all of them of which are used to produce petroleum based products for numerous applications, from industry to medicine, from clothing to food industries. We can find petroleum based products all around us. This book deals with some important topics related to petroleum such as its chemical composition and stability. It is well-known that the chemical composition of crude oil differs according to the site of production, and its grade varies from waxy to asphaltenic crude. Both of them are refined to produce different products. The stability of crude oil on aging and transportation is governed by several factors and these factors are included within this book. Some new technologies for petroleum characterization are also introduced. This book is aimed at researchers, chemical engineers and people working within the petroleum industry.

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