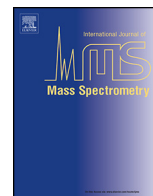




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Penning ionization-FT-ICR: Application to diesel fuel analysis

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ABSTRACT

The Penning ionization (PeI) source uses atoms of rare gases or molecules (N₂) excited to give a flux of metastable atoms or molecules (A*) able by collision to ionize a target molecule (M) on the condition that the process is exothermic (*i.e.*, IE(M) < EE(A)). As electron ionization, PeI allows the ionization of apolar species such as saturated hydrocarbons yielding molecular ions. In this work we present the application of vacuum PeI source coupled with a FT-ICR instrument for the characterization of a diesel fuel. Argon and krypton, as metastable gas, allow reducing significantly the fragmentation extent compared to electron ionization. Unlike with an atmospheric pressure source, the use of a vacuum source allows a good control of the ionization conditions with the absence of oxygen or other reactant such as water.

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1. Introduction

The use of mass-spectrometry for the analysis of petroleum compounds has been the subject of recent reports [1,2]. The group of Marshall showed in particular the interest of the ultra-high resolving power of the FT-ICR for the analysis of crude oil or other highly complex mixtures [3–6]. The ultra-high mass resolving power and mass accuracy of the FT-ICR allows to separate each isobaric ion and to determine their elemental composition. In addition, FT-ICR method allows fast analysis through determination of heteroatom class, double bound equivalent and carbon atom number without chromatographic separation. Knowledge of the amount of heteroatom containing compounds is of particular importance owing to the current international regulations [7].

Crude oil distillation isolates saturated and aromatic hydrocarbons as a function of their boiling point. Petroleum-derived diesel fuel is typically the fraction that boils between 200 and 400 °C (at atmospheric pressure) constituted by about 75% saturated hydrocarbons, and 25% aromatic hydrocarbons [8]. The typical carbon atom number for common diesel fuel is between 10 and 22 [9]. Compounds present in diesel fuel, are therefore are mainly apolar species. Soft atmospheric ionization techniques such as electrospray (ESI) or atmospheric pressure chemical ionization (APCI) yield mainly to the ionization of the most polar compounds yielding

significant ionization discrimination [8]. The characterization of these species is however important owing in particular to their role in environment [7]. Positive ion mode ESI yields mainly to the ionization of basic nitrogen-containing species (*i.e.*, pyridine homologues) [8,10]. In the same way, negative ESI mode leads to the detection of acidic species [11,12]. APCI however allows the ionization of more apolar compounds especially with the presence of aprotic solvents such as toluene or isooctane [13,14]. Although very useful, these soft ionization methods do not provide an overall representation of the different compound families present in a mixture. The development of ionization source that can ionize efficiently apolar compounds such as saturated hydrocarbons is still the subject of several investigations [15–23].

To overcome this problem low-energy electron ionization (EI)-FT-ICR (10–20 eV) has been used successfully [4,24]. Such EI conditions allow limiting fragmentations, but this is at the expense of sensitivity and reproducibility [5,25]. Field ionization (FI) and field desorption (FD) were also used for the analysis of petroleum compounds [21]. Atmospheric pressure photoionization (APPI) has been shown to allow ionization of various species not observed in ESI such as polycyclic aromatic hydrocarbons (PAHs) or furans [26]. However, APPI tends to produce competitively both M⁺ and MH⁺ molecular species (*i.e.*, molecular ions and protonated molecules, respectively), which complicate the mass spectra.

A hybrid quadrupole-FT-ICR equipped with an electrospray source has been recently coupled, in our laboratory, with a Penning ionization source (PeI) [27]. Penning ionization [28] was introduced in 1927 and was reconsidered more recently (as the *metastable atom bombardment* source, MAB) by the group of Bertrand [29]. It was

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Table 1
Excitation energy values of gases in their metastable state (eV).

Gaz	EE(A ^m) ^a	IE(A) ^b
Helium	19.82	24.59
Argon	11.55	15.76
Krypton	9.92	14.00
Nitrogen	8.52	15.58
Xenon	8.32	12.13

^a Excitation energy with long lifetime [40].^b Ionization energy [34].

successfully coupled to various instruments such as sector and time of flight instruments [30–32]. Penning ionization uses a quantized energy for ionization and it allows to control the available energy in 8–20 eV range. PeI includes therefore all energy ranges found in conventional ionization sources such EI, and FD/FI. It allows a control of the fragmentations and can allow selective ionization by use of different rare gases or nitrogen characterized by different excitation energy levels. Helium yields relatively high internal energy deposition and results are very close to 70 eV electron ionization (Table 1). Argon or krypton is characterized by lower excitation energy and yields to fragmentations close to FI. High ionization efficiency, such as EI, can be obtained with PeI but this depends on various parameters such as gas flow and discharge current [27].

The PeI source uses excited atoms of rare gases or excited molecules (N₂) to give a flux of metastable neutrals (A*) able by collision to ionize a target molecule (M) on the condition that the process is exothermic (*i.e.*, IE(M) < EE(A)), Eq. (1).



$$E_{\text{int}}(M^{+\bullet}) = EE(A) - IE(M) - KE(e^-) \quad (2)$$

$E_{\text{int}}(M^{+\bullet})$: internal energy transferred to the molecular ion; EE(A): excitation energy of metastable atoms or molecules; IE(M): ionization energy of molecule M; and KE(e⁻): kinetic energy of ejected electron.

The molecular ion internal energy (Eq. (2)) depends on the molecule ionization energy (IE) and on the excitation energy (EE) of the gas metastable state (Table 1). Thus, by the choice of the gas, the rate constant of fragmentations can be relatively well controlled with an energy maximum of $E_{\text{int}}^{\text{max}}(M^{+\bullet}) = EE(A) - IE(M)$.

Recently, commercial atmospheric pressure ionization sources related to Penning ionization (such as direct analysis in real time, DART) have demonstrated their interest for ionization of compounds with low polarity [22,33]. Although these sources are efficient and flexible, they operate at atmospheric pressure, which imply a limited control of the ionization conditions. In the present work the use of a vacuum PeI source presents several advantages. First, it allows avoiding side reactions with species present in air such as O₂ or water that may lead to the formation of protonated or oxidized compounds [18]. Second, the production of the metastable atoms is carried out externally which allow deflecting all ionic species such as He^{+•}. In fact, if this ionic species are not removed from the metastable atom flux, charge exchange processes may take place together with Penning ionization [27].

In this work, we were interested in demonstrating the interest of the Penning ionization/FT-ICR coupling for complex hydrocarbon mixture analysis. Argon and krypton were used for Penning ionization and the results were compared to electron ionization. The coupling with the FT-ICR instrument allows efficient identification of species present in complex mixtures such as diesel fuel. This is easily performed by the separation of different isobaric ions and attribution of unique elemental composition.

2. Methods

2.1. Chemicals

High purity gases (Alphagaz™): krypton and argon have been purchased from Air Liquide (Nanterre, France). All chemicals have been purchased from Aldrich (Saint Quentin Fallavier, France).

2.2. Sample preparation

300 μL of commercial diesel fuel was dissolved with 200 μL of chloroform. 2 μL of this solution was deposited on a quartz tube and introduced in the EI/PeI source using a direct introduction probe. During acquisition the probe was heated from ambient temperature to 400 °C with a gradient of 1 °C/s.

2.3. Mass spectrometry

Experiments were conducted on a modified hybrid Qh-FT-ICR instrument (Bruker ApexQe, Bremen, Germany) equipped with an actively shielded 7 T superconducting magnet that was combined with a homemade EI/PeI source. The latter was composed of a modified Nermag EI source bloc and a MAB gun (Dephy technology). A Varian turbomolecular pump was used to obtain a vacuum of 10⁻⁵ mbar in the source housing. These conditions do not produce even-electron molecular species. Consequently, the observed even-electron species can be attributed exclusively to fragment ions. Details of the instrumental setup have been published elsewhere [27]. Energy levels of used gases are: Kr (9.92 eV), and Ar (11.55 eV). All mass spectra were acquired in the broadband mode from *m/z* 100 to *m/z* 1000. The image signal was amplified and digitized using 1 M data point resulting in the recording of a 0.48 s time domain signal, which was transformed into the corresponding frequency domain by Fourier transform (one zero fill and Sine-bell apodization). Under these conditions the resolving power obtained was between 400,000 (*m/z* 100) and 140,000 (*m/z* 250). The used resolving powers are enough to distinguish isobaric ions containing (or not) sulfur atom.

Perfluorotributylamine (FC43) was used for external mass calibration yielding typically less than 2 ppm *m/z* measurement error. After mass spectrum acquisition, internal calibration was performed from confidently assigned signals allowing to obtain better than 200 ppb along the *m/z* range of interest. All mass spectra have been background subtracted. The background mass spectra were defined from the means of the TIC last scans.

Determination of elemental composition of each signal was carried out using DataAnalysis 4.0 software. All elemental compositions containing up to 2 N, 4 O, 2 S and 1 ¹³C have been considered. The maximum error tolerance was 0.5 ppm. By this way a unique elemental composition was attributed for each signal. Manual filtering was however required in the few cases that yielded more than one possibility. All signals corresponding to species containing ¹³C have been removed from the peak list. Type (Z), corresponding to the hydrogen deficiency relative to alkanes was determined from the C_nH_{2n+2}X, equation in which X denotes heteroatoms.

3. Results and discussion

Experiments have been conducted with a commercial diesel fuel that is expected to present mainly hydrocarbons with also limited amount of species presenting heteroatoms such as sulfur, nitrogen and oxygen. Fig. 1 presents the PeI mass spectra recorded from this diesel fuel recorded under EI, PeI(Ar) and PeI(Kr) conditions. After internal mass calibration, mass accuracy on the *m/z* ratio range of interest is generally better than 200 ppb.

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