Introduction
Mass spectrometry has currently achieved a mass resolution capable of discerning chemical composition and structure in complex mixtures. However, whatever is the mass spectrometric system used, complex mixtures produce spectra with a huge number of peaks, which generally make difficult the data analysis.
In the present work, a method involving Fast Fourier Transform (FFT) analysis and a home-made software was applied for interpreting the mass spectra of complex PAH-laden samples derived from combustion systems and from heavy fossil fuels, thereby giving information on their composition.
FFT analysis allows individuating periodicities that can indicate preferential growth routes and/or fragmentation patterns related to the chemical composition [1].
The home-made software is able to sort large polycyclic aromatic hydrocarbons (LPAHs), which were found to be the major components in the complex mixtures, by their carbon number and double bond equivalence (DBE) number. A simplified model for representing the structure for each PAH type consists of two basic structural attributes: the aromatic core and the aliphatic side chains. Generally, molecules with the same DBE number but increasing number of carbon atoms can be assigned to a series of structures with similar aromatic cores but increasing length or number of aliphatic side chains. Iso-abundance plots were introduced to sort and visualize the molecular constituents into different types based on the carbon and double bond equivalence (DBE) numbers.
The differences between the different carbonaceous materials could be easily observed by comparing their iso-abundance plots [2].

Experimental
Samples. Soot was isokinetically collected in premixed laminar flames of ethylene produced on a commercial McKenna burner at atmospheric pressure with cold-gas-
flow velocity of 4 cm/s and C/O=1. The organic species adsorbed on soot were extracted with dichloromethane (DCM) and analyzed by mass spectrometric tools. More details on the experimental conditions and procedures are given elsewhere [3]. Two solid pitch samples were kindly provided by RÜTHERS Basic Aromatics GmbH (Castrop-Rauxel, Germany). These solid carbon samples were produced by the selection of suitable raw materials with low heteroatom content and appropriate thermal carbonization techniques. The petroleum pitch (ZL 250M, CAS NO.: 68187-58-6) and the coal tar pitch (CARBORES® P, CAS NO.: 121575-60-8) have softening points of 252 and 235°C, respectively.

**Laser desorption ionisation time of flight mass spectrometry (LDI-TOFMS)**

Positive Linear Laser Desorption Ionisation-Time-of-Flight Mass Spectrometry spectra were recorded on a 4800 Plus MALDI TOF/TOF Analyzer (Applied Biosystems, Framingham, MA). The target was prepared by depositing on the metallic sample plate a volume variable from 1 and 10 μl of a solution of the sample dissolved in DCM.

**Mass spectrometric tools**

**Fast Fourier Transform Analysis.** The Discrete Fourier Transform is a mathematical operation transforming one discrete function of the independent variable into another function, which is the representation of the original function in the domain of the inverse of the independent variable. In the case of mass spectra, the independent variable is represented by the mass m and therefore the Fourier transform will be a function of mass frequency (f = 1/m).

A Fast Fourier Transform (FFT) is an efficient way to compute the discrete Fourier transform (DFT). Therefore, the result of a FFT is simply equal to that of a discrete Fourier transform (DFT) performed on the same input. Many FFT software packages can give several output results, such as the magnitude, power, phase and amplitude of the transformed data. Among these results, the mean square amplitude power, represents the number of ions contributing to the mass frequency (f = 1/m).

In order to have a clearer physics meaning, the independent variable, the frequency f, may be converted to the mass period (m = 1/f).

In the present work a commercial graphic software (Origin) has been used offering a higher flexibility in the parameters choice for data analysis [1].

**Home-made software.** In order to assign the molecular formula to the main peaks detected in the mass spectra a purpose-built, home-made, computer software was used, by considering that the atomic weight of one H atom is 1.0086 Da and the accurate atomic weight of one C atom is 12.000 Da. While the carbon number n and hydrogen number m must be nominal numbers, there is only one probability for each individual exact mass to fit the theoretical molecular weight of chemical formula CₙHₙ fixed a certain accuracy in mass (in ppm). Based on the assigned elemental compositions, the carbon number and double bond equivalence (DBE) number were determined for each mass peak and iso-abundance graphs were drawn in the Origin software by plotting the DBE number and the relative intensity
against the carbon number. DBE number is defined following [4], as:

\[
DBE = C - \frac{(H/2)}{} + 1
\]

**Results and Discussion**

The LDI-TOFMS spectra of Carbores pitch, Petroleum pitch and soot extract, shown in Fig.1, extend from \( m/z \) 200 up to about 2000.

![Figure 1. LDI-TOFMS of Carbores pitch, Petroleum pitch and soot extract.](image)

The spectra of Carbores pitch and soot extract are rather similar presenting a sequence of major ion peaks with a spacing of \( m/z \) 24 superimposed on a sequence of minor ion peaks which present the same spacing of \( m/z \) 24; the spacing between the major and the minor ion peaks is 12. However, the Carbores pitch spectrum is more crowded of peaks with respect to the soot extract spectrum and the double sequence of 12 and 24 gaps can not be clearly observed at higher molecular masses. As can be observed from Fig. 2, the FFT analysis puts in evidence the presence of two gaps, at \( m/z \) 12 and 24, but in the case of Carbores pitch also a gap at 14 is present. The gap of \( m/z \) 24 can be attributed to a neat sequential addition of C2 as an ethylene bridge, while a gap of \( m/z \) 12 between the two sequences can be attributed to the insertion of a methylene (-CH2-) into a bay region of angular PAH. For soot extract, the two sequences have been attributed in a previous work [5] to even- and odd-numbered PAH up to about \( m/z \) 1000. Therefore, it can be speculated the presence of the same sequences extended up to \( m/z \) 2000 both for the soot extract and for Carbores pitch. The occurrence of a \( m/z \) gap 14 (CH2) can indicate the presence of a series of LPAHs with the same aromatic core size but increasing number of short aliphatic groups, such as methyl and ethyl.

In the case of Petroleum pitch, the spectrum appears even more complex and crowded of peaks therefore hindering an easy extrapolation of repetitve spacing without mathematical tools. The application of FFT analysis revealed the only presence of \( m/z \) gap of 14, as shown in Fig. 2. The higher complexity of pitch
spectra with respect to the flame-formed sample is testified also by the presence of a gap at \( m/z = 1 \), which is largely prevalent with respect to the other gaps (more for Petroleum pitch than for Carbores pitch) whereas is lower with respect to the remaining gaps in the case of Carbores pitch (see Fig. 1):

![Figure 2. FFT analysis of Carbores pitch, Petroleum pitch and soot extract.](image)

From the home-made software created for the assignment of the molecular formula, carbon number for each molecule, as well as the DBE number and the relative intensity of each species, were obtained and iso-abundance graphs were drawn in the Origin software by plotting the DBE number and the relative intensity against the carbon number.

![Figure 3. Iso-abundance plots of DBE number vs. carbon number of hydrocarbon classes in Carbores pitch, Petroleum pitch and soot extract.](image)
Iso abundance plots for Carbores pitch, Petroleum pitch and soot extract are reported in Fig. 3. Each dot in an iso-abundance plot represents one kind of hydrocarbons with the same chemical formulas while the abscissa is the total carbon number and the ordinate is the DBE number of that species. The relative content (percentage) of each species is calculated based on the mass peak intensity ratio to the sum intensity of all mass peaks in the corresponding spectrum. The abundance of the hydrocarbon species can be estimated by comparing the colour of the dot with the colorimetric scale.

The overall appearance of the plots for the three samples show interesting features: first, the Petroleum pitch globally shows higher intensities especially in the nC range between 30 and 50, where it exhibits also significant intensity differences. By contrast, Carbores pitch show a much less change of peak intensity along all the range. For soot extract, the exception is represented by the presence of some peaks with the higher intensity (red point on the right graph in Fig.3) which correspond to the even PAH sequence of the well-known stabilomers grid in the range m/z 400-522 [6]. Moreover, the variety of LPAH species observed in Carbores pitch and soot extract is smaller with respect to Petroleum pitch as the iso-abundance plot distribution is narrower. For the three samples, the total carbon numbers mainly range from 20 to 65 and the DBE numbers from 15 to 50 for Carbores pitch and soot extract, and from 20 to 50 for Petroleum pitch. This is in line with the suggestion that the degree of unsaturation rapidly increases with the carbon number and molecular weight [7]. As an example, naphthalene molecule presents a DBE of 7 with nC 10 whereas coronene has a DBE of 18 with nC 24.

For quantifying the differences among the three samples, it was used a planar limit line, introduced by Kim et al. [8] as a means to predict and understand the molecular structure of compounds in crude oil. The planar limit lines are generated by connecting maximum DBE numbers at given carbon numbers and are thus also relevant to the growth of the most fused molecules during carbonization. The slope of planar limit lines, namely DBE/carbon number ratios, for the linear and nonlinear integration of benzene rings to the precursor aromatic unit is 0.75 and 1, respectively. Aromatic cores formed by a successive incorporation of saturated cyclic rings to the aromatic rings yields a line with a slope of 0.25. The aromaticity increase is mainly due to a change in the distribution of the species in compositional space toward higher DBE values.

Planar limit lines have also been generated for Carbores pitch, Petroleum pitch and soot extract, and the slopes are reported in Table 1. The slope obtained for the Carbores pitch is 0.7133, which indicates that LPAHs in the coal tar pitch are mainly formed by the linear and nonlinear extension with benzene rings. The slope for the Petroleum pitch is 0.6434. This indicates that, besides the growth of the aromatic core structures by integration of aromatic rings, the formation of saturated cyclic rings or the addition of saturated alkyl chains is also a possible reaction.
Table 1. Slopes of planar limit lines of Carbores pitch, Petroleum pitch and soot extract.

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<tr>
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<th>Carbores pitch</th>
<th>Petroleum pitch</th>
<th>Soot extract</th>
</tr>
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<tbody>
<tr>
<td>$\alpha$</td>
<td>0.7133</td>
<td>0.6434</td>
<td>0.8101</td>
</tr>
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As observable in Table 1, soot extract presents a slope of 0.8101, much higher with respect to the two pitches, indicating a higher aromatic nature of the sample. It allows speculating the structure of flame-formed SOF as mainly constituted by LPAHs with highly condensed aromatic cores and either no or short aliphatic side chains.

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References

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