

EXTRACTION METHOD FOR IMPROVING THE CHARACTERIZATION OF HIGH MOLECULAR WEIGHT COMPONENTS OF CARBONACEOUS SPECIES

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Abstract

The complete characterization of tarry and solid carbonaceous species characterized by a low H/C ratio, low volatility and high molecular weight (MW), is relevant in the fossil fuel combustion field for the control of the fuel and combustion process quality in terms of efficiency and environmental impact. It is also a key point for the development of detailed chemical and physical models of formation of the combustion-formed carbon particulate matter.

In previous work the chromatographic separation (Size Exclusion Chromatography, SEC) of carbonaceous species in MW-segregated fractions was set up and used in order to distinguish and quantify the contribution of different classes of components in a wide MW range.

This technique uses N-Methyl pyrrolidinone (NMP) that is a powerful solvent of high-MW carbonaceous species. However, the use of NMP makes difficult to perform subsequent spectroscopic and mass spectrometric analysis of the MW-segregated fractions due to its very low volatility and strong chemical interference. To avoid this inconvenience a liquid-liquid extraction method has been set up and tested to transfer the MW-segregated fractions from NMP to a volatile solvent as dichloromethane (DCM).

In this preliminary work the details of this extraction procedure applied on suitable standard species and mixtures are reported. The results of spectroscopic and mass spectrometric analysis performed on the NMP to DCM-transferred standards were compared with those obtained on the same standards directly dissolved in DCM to show the reliability and the effectiveness of the method.

Introduction

The wide Molecular Weight (MW) distribution of carbonaceous species constituting heavy fossil fuels and/or combustion formed particulates has been previously assessed by Size Exclusion Chromatography (SEC) [1,2].

This technique exploits the high solvent power of N-Methyl-pyrrolidinone (NMP) used for both solubilizing/suspending the samples and for the SEC separation. Overall, a low-MW fraction, constituted of Polycyclic Aromatic Hydrocarbons

(PAH) up to a MW of about 400 u and other heavier aromatic species (from 400 to 1000 u), has been separated from aromatic species and/or particles with a high-MW fraction (from 1E4 up to 1E11u).

SEC analysis also allows to get MW-segregated fractions that may be subjected to further analysis by mass spectrometric and spectroscopic diagnostics for their identification [3].

The low-MW segregated fraction (up to 1000u) coincides with the fraction of organic compounds adsorbed on the solid particulate and generally separated by simple extraction of the particulate with Dichloromethane (DCM). This fraction is relevant due to its toxicity related to the PAH content and in regard to its possible role as precursors of carbonaceous particles in combustion. It is not known if the heavier aromatic species (from 400 to 1000u) are composed of stacked PAH or oligomers of PAH, since their analysis cannot be done by conventional chromatographic techniques even if they are separated from the light PAH by SEC, because of the presence of the NMP solvent that obscures the mass spectrometric and spectroscopic regions of analytical interest.

In this work a liquid-liquid extraction procedure for transferring the high-MW species fraction from NMP to DCM has been set up and tested on standard species having aromatic structure simulating the structure of big PAH as coronene, oligomers of PAH as polyacenaphthylene and naphthalene pitch. Advanced diagnostics as Laser Desorption Ionization-Mass Spectrometry (LDI-MS) and UV-Visible spectroscopy suitable for the analysis of aromatic species in high MW range have been applied for the procedure testing.

Experimental

Samples

DCM and NMP solutions of coronene, polyacenaphthylene and naphthalene pitch (obtained from Mitsubishi Chemical Co. Ltd) were prepared (concentration 10-40 mg/l) and used for testing the liquid-liquid extraction procedure described in the following.

In order to verify the reliability and the effectiveness of the extraction procedure, UV-Visible spectra and LDI mass spectra measured on the DCM solutions have been compared with the spectra measured on the solutions obtained transferring the species from NMP solution to a DCM solution by liquid-liquid extraction.

Extraction procedure

The condition necessary for applying the liquid-liquid extraction procedure proposed in this work is that, similarly to the organic species generally adsorbed on the particulate, the selected standard samples be soluble both in DCM and NMP and insoluble in water. This is just the case of aromatic samples of low/moderate MW as PAH, polyacenaphthylene and naphthalene pitch. Overall, the procedure, described step by step in the following, is based on the higher affinity/miscibility of the NMP toward water and on the immiscibility of DCM in water. The standard

sample dissolved in NMP is mixed with comparable amounts of both water and DCM. As NMP mixes with water, two liquid immiscible phases (NMP/water and DCM) separate each from other and the species, originally solubilized in NMP, preferentially migrate and transfer in the lower DCM phase.

Step 1 - 4ml of distilled water and 2 ml of DCM are added to 4ml of the NMP solution of standard species. The mixture is vortexed for 5min and then centrifuged (3000 rpm) in order to separate the lower DCM liquid phase, where solute sample is transferred, from the upper NMP/water phase.

Step 2 – To purify the DCM phase from residual traces of NMP, 4ml of distilled water are added to the DCM phase obtained from step 1 and the mixture vortexed and centrifuged as in the step 1 removing the upper water phase. This step is repeated twice on the DCM phase separated from the water to remove all the traces of residual NMP and obtain the DCM-extracted solution where the sample has been transferred.

Measurements

Ultraviolet-Visible spectra were measured on a HP8453 spectrophotometer. UV-Visible spectra in the 190-1100nm wavelength range using 1-cm path-length quartz cuvette. The UV absorption of DCM limited the spectra acquisition to the 250-1100nm wavelength detection range.

Atmospheric pressure laser desorption mass spectrometry (LDI) was performed on a MSD-TRAP-SL by Agilent Technologies.

The samples were placed on the AP-LDI target plate and heated at 60 °C for 30 min to ensure the complete evaporation of residual solvent. The intensity of the nitrogen laser ($\lambda=337$ nm) used for desorption/ionization was about 200 μ J/pulse. A typical analysis consisted of 100–150 co-added mass spectra collected on the whole spot surface (1–2mm in diameter) to average the sample non-homogeneity effect. More details on the AP-LDI-MS system used are given in previous work [2].

Results

Figure 1 shows the comparison of the height-normalized UV-Visible spectra of coronene, polyacenaphthylene and naphthalene pitch measured on the standard DCM solutions and on the DCM-extracted solutions obtained after the liquid-liquid extraction of the NMP solutions.

The UV-Visible spectra of the DCM-extracted solutions of all standard species, obtained by liquid-liquid extraction, present the same shape in respect to the reference DCM solutions indicating that the extraction procedure was effective in transferring all the standard samples from NMP to DCM.

Consistently with this experimental evidence, also the comparison of the normalized AP-LDI mass spectra of the standard species measured on the DCM solutions with the DCM-extracted solutions obtained after the liquid-liquid extraction procedure shows the same typical mass peaks (left part of Fig.2).

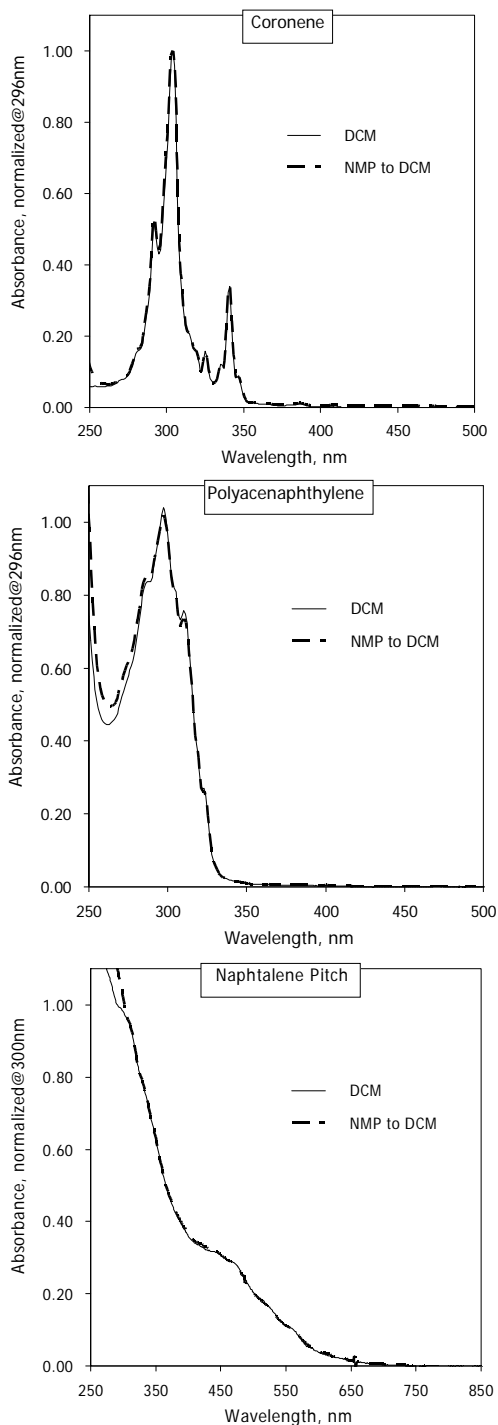


Figure 1. Normalized Uv-visible spectra of standards directly dissolved in DCM (solid lines) and after the extraction from NMP to DCM (dashed lines).

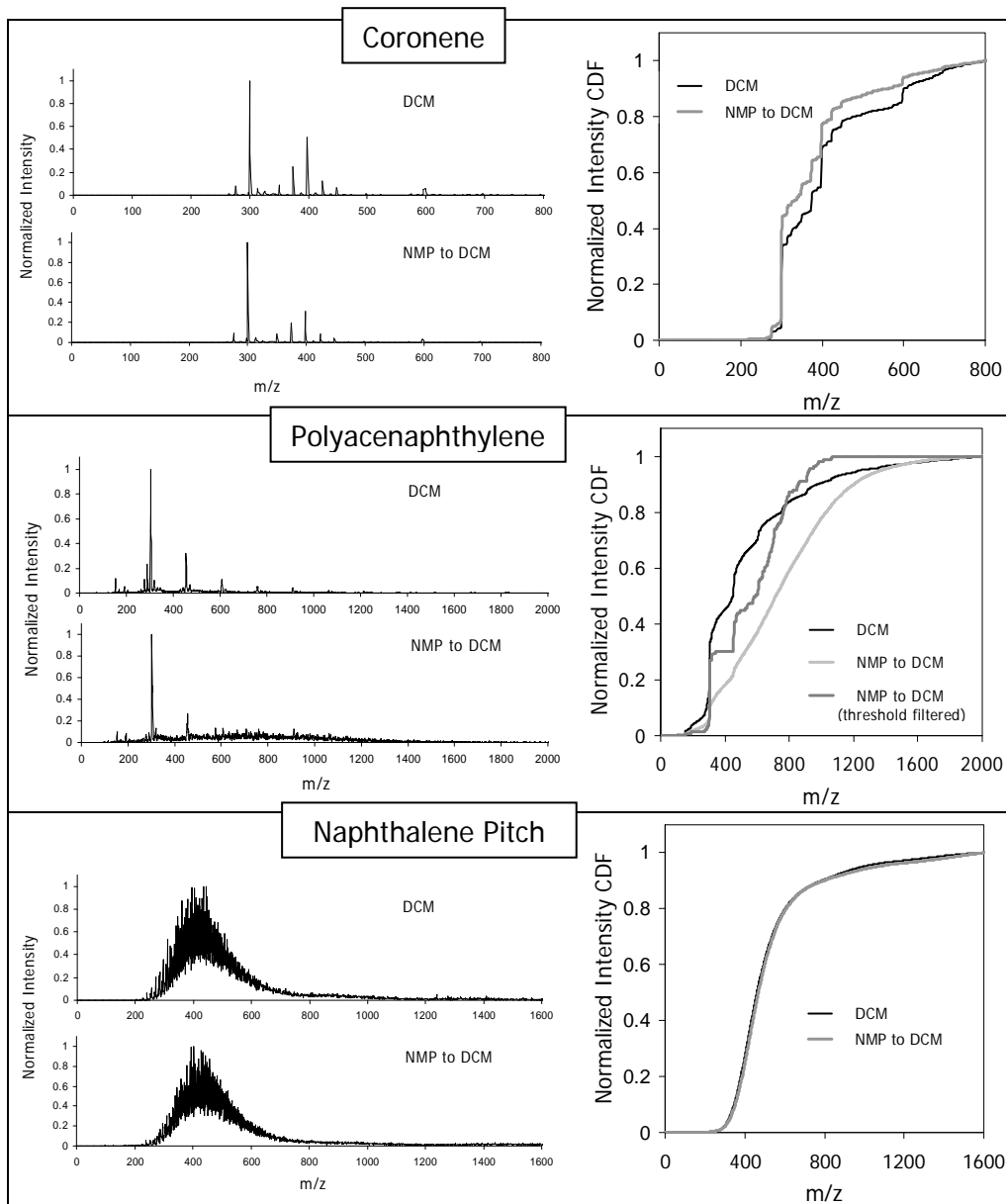


Figure 2. Normalized AP-LDI mass spectra of standard species directly dissolved in DCM and after the extraction from NMP to DCM and their normalized cumulative density functions. For polyacenaphthylene is also reported the CDF of threshold filtered AP-LDI mass spectrum after the extraction.

The comparison of the cumulative density functions (CDF) of the AP-LDI mass spectra, reported in the right part of Fig. 2, put better in evidence the similarity between the mass spectra of coronene and naphthalene pitch in the DCM and in the DCM extracted solutions. This confirms that the extraction procedure for these species is effective as before observed by UV-Visible spectroscopy.

For polyacenaphthylene the presence of a background in the mass spectrum of the DCM-extracted solutions results more evident by comparing the CDF. Filtering the normalized mass spectrum by imposing a suitable threshold on the intensity, the CDF of DCM solution and DCM-extracted solutions also reported in Fig. 2, become quite similar. Thus it appears that mass spectrometry is more sensitive than UV-Visible spectroscopy to verify the efficiency of the treatment process and the possible modifications on the samples induced by the liquid-liquid extraction procedure. The source of this noise in the case of polyacenaphthylene could be due to some interactions between NMP and polyacenaphthylene molecules. This effect requires further work for understanding if the liquid-liquid treatment modifies in some way the polyacenaphthylene and the procedure will be further tested on other standard species. However, these preliminary results appear to be promising for transferring carbonaceous species (e.g. heavy fossil fuels and combustion-formed carbonaceous species) and/or their MW-segregated fractions dissolved in NMP to a more volatile and easily removable solvent as DCM allowing their further detailed analysis .

Conclusions

In order to apply analytical and spectroscopic techniques to characterize heavy carbonaceous species and/or their MW-segregated fractions dissolved in a low volatile solvent as NMP, it is necessary to transfer these materials from the NMP solvent (used for the dissolution/separation) to a volatile solvent as DCM.

For this purpose a liquid-liquid extraction method has been set up and tested to transfer the MW-segregated fractions from NMP to DCM. In this preliminary work the results of this extraction procedure applied on suitable standard species as coronene, polyacenaphthylene and naphthalene pitch are reported.

The comparison of UV-Visible spectra measured on the solutions of standard solute species, dissolved in DCM, with the spectra measured on the solutions deriving from the extraction procedure (DCM-extracted solutions), indicates that this procedure is effective in transferring the standard species from NMP to DCM, and does not induce any modification to the optical properties of the standard species in the spectral region investigated.

The comparison of the LDI mass spectra measured on the DCM and on the DCM-extracted solutions gives quite good results for coronene and naphthalene pitch. In the case of polyacenaphthylene the extraction procedure appears to cause interference in the LDI mass spectrometric analysis. This demonstrates the higher sensitivity of LDI mass spectrometry for checking the efficiency of the liquid-liquid extraction procedure and the occurrence of modifications to the sample

during the treatment.

The procedure appears to be promising for transferring carbonaceous species (e.g. heavy fossil fuels and combustion-formed carbonaceous species) and/or their MW-segregated fractions dissolved in NMP to a more volatile and easily removable solvent as DCM allowing their further detailed analysis.

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