

QUANTITATIVE ANALYSIS OF AROMATIC HYDROGEN FOR DETERMINING THE STRUCTURE OF POLYAROMATIC SYSTEMS TYPICAL OF CARBON MATERIALS. CASE STUDY: ANTHRACENE OIL

C. Russo, F. Stanzione, A. Tregrossi, A. Cijolo

carmela.russo@irc.cnr.it

Istituto di Ricerche sulla Combustione (IRC-CNR), P.le Tecchio 80, Napoli, Italy

Polyaromatic systems constitute the basic structural units of many natural, industrial and anthropogenic carbon materials as coal, heavy petroleum-derived fractions, carbon black, pitch, soot, graphene-like materials, etc.. The number of aromatic hydrogens and their distribution at the edge of the polyaromatic moieties feature their structure and reactivity. It is, thus, important to differentiate and quantify the different kinds of aromatic hydrogen. This can be done by specific techniques sensitive to hydrogen neighbors, (i.e. the number of different environments the hydrogen atoms are in) as XRD analysis, NMR and FT-IR spectroscopy. In this work a FT-IR based method was implemented for the quantitative analysis of aromatic hydrogen considering anthracene oil as a case study for testing the technique. Anthracene oil is distilled from coal tar and is composed of high-boiling three- to five-ring aromatic compounds with masses lower than 300u that could be completely quantified by GC-MS analysis. A map of the aromatic hydrogen distribution in the anthracene oil could be obtained for the comparison with the aromatic hydrogen as measured by the FT-IR method used in this work.

The FT-IR spectroscopic analysis is sensitive to different carbon-hydrogen bonding producing different C-H vibration peaks in the FT-IR spectrum. For aromatic hydrogen, the corresponding C-H stretching gives rise to a high-frequency absorption around 3000 cm^{-1} , while aromatic C-H out-of-plane (OPLA) bending modes occur between 600 and 1000 cm^{-1} . The detailed analysis of specific OPLA vibrational bands occurring in the anthracene oil FT-IR spectrum was carried out. On the basis of the literature and by comparison with the measured spectra of aromatic standard species, isolated hydrogens (SOLO) were assigned to the peaks detected in the $890\text{-}870\text{ cm}^{-1}$ range (9-methyl-anthracene at 886 cm^{-1} , anthracene at 884 cm^{-1}) whereas two-adjacent hydrogens (DUO) peaks are located between 850 and 810 cm^{-1} (1-methyl-pyrene at 840 cm^{-1} , coronene at 847 cm^{-1} , phenanthrene at 817 cm^{-1}). Three-adjacent hydrogens (TRIO) peaks are located in the $790\text{-}750\text{ cm}^{-1}$ region (1-methyl-pyrene at 755 cm^{-1} , acenaphthene at 784 cm^{-1} , fluoranthene at 775 cm^{-1}). Four-adjacent hydrogens (QUATRO) peaks are detected in the $750\text{-}720\text{ cm}^{-1}$ region (9-methyl-anthracene at 723 cm^{-1} , anthracene at 725 cm^{-1} , phenanthrene at 731 cm^{-1} , fluoranthene at 746 cm^{-1}).

The quantitative FT-IR analysis involved the spectral deconvolution of the aromatic C-H bending region and the calculation of calibration factors of diverse aromatic standard species. The distribution of aromatic hydrogen derived from GC-MS analysis was calculated and compared with that derived from FT-IR analysis.

The results showed a good agreement and the FT-IR method appear to be promising and useful for the analysis of carbon edges of more complex carbon materials.