

Molecular characterization of potentially interfering materials when studying “Black Carbon” forms. The combined use of Analytical Pyrolysis, Solid state- ^{13}C Nuclear Magnetic Resonance and thermogravimetric techniques

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Due to geochemical and environmental implications, there is an increased interest in the study of the different forms of refractory organic matter (ROM) widely widespread in soils, water and sediments. Included in the refractory OM pool are kerogens, humic-like materials as well as the so-called “black carbon”(BC). These materials might remain sequestered in soils and sediments (slow geological C cycle) from thousand to million of years, being considered as an important sink for atmospheric CO₂ (fast C cycle) and part of the “missing C” in the global C budget. As pointed out by many authors [1] there is therefore a need to develop accurate and comparable analytical protocols to determine the amount of BC stored in different environmental matrices. However, despite the significant improvements achieved in the analytical techniques and a considerable effort devoted recently to characterise sedimentary organic carbon, a large fraction of it remains bio-chemically uncharacterised [2].

Black carbon (BC), the product of incomplete combustion of fossil fuels and biomass, is considered the most stable form of C within the ROM. In this work we present a comprehensive study of 4 samples of different materials potentially interfering in the analysis of BC. Those materials consist of melanoidin, shale, lignite coal and bituminous coal. This study deals with the analytical characterization of those materials by using different analytical techniques including thermogravimetry (TG), TG coupled with differential scanning calorimetry (DSC), solid state ^{13}C CP-MAS nuclear magnetic resonance (NMR) spectroscopy and Pyrolysis coupled with gas chromatography-mass spectrometry (Py-GC/MS).

Thermal analysis (TG, TG-DSC) provided mainly information about the proportions of labile, recalcitrant and refractory OM forms, whereas Py-GC/MS and ^{13}C NMR provided complementary windows of structural information on the bulk matrices and their OM fractions. Good agreement was observed between recalcitrant C as determined by TG analysis and the aromatic content measured by ^{13}C NMR. Results indicated a high BC content in the bituminous coal. Analytical Pyrolysis results showed an important presence of aromatic compounds in samples rich in BC like material. By using analytical pyrolysis (Py-GC/MS) it was also possible to directly identify, with no pretreatment, several specific compounds released which could allow a clear identification of potentially BC-interference reference material. Other markers were also identified which provide information about OM origin.

References:

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2. J.I. Hedges, R.G. Keil and R. Benner, *Org. Geochem.*, 27 (1997) 195.