

Thermal characterization of organic matter along a (hypothetical) coalification gradient

Ornella Cavallo (1), Maria Rosaria Provenzano (1), and Claudio Zaccone (2)

(1) Dept. of Soil, Plant and Food Sciences, University of Bari “Aldo Moro”, University of Bari, Bari, Italy (ornella.cavallo@uniba.it), (2) Dept. of the Sciences of Agriculture, Food and Environment, University of Foggia, Foggia, Italy

Geochemical transformations of organic carbon (C) in aquatic and terrestrial ecosystems are important starting points for genesis of peats, brown coals and other coal precursors. The humification process plays a key role in biogeochemical transformations of organic C and, as a result, in the first stages of coal precursors formation.

Thermal analysis was used by Schnitzer and other scientists since 1950-1960s, in order to investigate the stability of several organic materials of industrial value including peat and coal. What soil scientists found was the general occurrence of two exothermic peaks (exotherm 1 and 2) due to decomposition and combustion reactions of organic compounds having different thermal stability and, consequently, different degree of humification.

Thermogravimetric analysis (TG) was carried out on different samples reproducing a “hypothetical” coalification gradient as follows: peat (IHSS Pahokee peat standard), fulvic acid (FA), a peat humic acid (HA), leonardite (IHSS Gascoyne standard) and charcoal. An aliquot of about 20 mg of each sample was heated in a ceramic crucible from 50 to 850°C at 30°C min⁻¹, at a gas flow rate of 30 mL min⁻¹ using a PerkinElmer TGA4000 thermobalance. Samples were analysed both under nitrogen and under synthetic air. All analyses were carried out in triplicate and the average coefficient of variation was <1.5%. Weight losses (in %) were determined within 200-400°C (WL₁) and 400-600°C (WL₂) temperature ranges, and the ratio between WL₂/WL₁ calculated for all samples. This ratio has been often used as a highly sensitive parameter to describe chemical changes induced by the bio-transformation of organic materials. Finally, the temperature at which half of the exothermic mass loss has occurred (TG-T₅₀) was also calculated.

Preliminary results obtained from TG analysis under air showed that WL₂/WL₁ ratio was lower for the FA sample and higher for leonardite and charcoal, following the order FA<peat~HA<leonardite<charcoal. When nitrogen was used as gas carrier, a different stability order to the thermal degradation was obtained, with HF and HA showing a lower WL₂/WL₁ ratio (HF<HA<peat<charcoal<leonardite). Anyway, a positive and significant correlation ($p < 0.05$) was found between WL₂/WL₁ ratios obtained with both gases.

TG-T₅₀ was found to be lower for peat and higher for leonardite and charcoal samples (peat<HA~FA<leonardite<charcoal) when air was used as carrier gas, whereas, for most of these matrices, it was not possible to determine this value when nitrogen was used.