



## **Black carbon determination by chemical oxidation and $^{13}\text{C}$ NMR spectroscopy**

W. Hockaday and P. Hatcher

Department of Chemistry, and Environmental Molecular Science Institute, Ohio State University, 100W. 18<sup>th</sup> Ave. Columbus, Ohio 43210, USA (hatcher@chemistry.ohio-state.edu / Fax: (614) 688-5920)

Although the morphology, surface functionality, and carbon cluster size of the black carbon (BC) present in environmental samples vary along the combustion continuum, a common structural property among pyrogenic carbon is the condensed aromatic carbon core or backbone. Hence, spectroscopic measurement of condensed aromatic carbon is a means to quantify BC. The application of  $^{13}\text{C}$  NMR spectroscopy provides structural information, allowing the analyst to consider the inherent variation in natural organic matter (NOM) samples. This also reduces the risk of overlooking artifacts generated by techniques used to isolate the BC from NOM. Interferences with the spectroscopic determination of pyrogenic aromatic carbon include the aromatic carbon in natural biopolymers; notably, lignin and tannin. Lignin and tannin phenols are efficiently removed from natural samples by chlorite oxidation, as confirmed by pyrolysis mass spectrometry (Simpson and Hatcher, 2004). Seven samples from the "Standard Collection of BC" were analyzed by  $^{13}\text{C}$  CP MAS NMR spectroscopy and total organic carbon analysis before and after chlorite oxidation.

BC values for two standard soils are lower than those obtained by the UV photo-oxidation/NMR technique of Skjemstad. Also of note, is the finding that the low temperature wood char sample contained no BC, while the grass char, produced under identical pyrolysis conditions, contained only 10% BC/TOC as determined by the chlorite oxidation/NMR technique. This result highlights the ability of this technique to identify the dependence of BC content upon starting material composition for BC formed at the same point on the combustion continuum. One difficulty with the NMR technique was realized during the analysis of the standard hexane soot. The  $^{13}\text{C}$  NMR spectrum of the hexane soot exhibited excessive peak broadening in the aromatic re-

gion, presumably due to electrical conductivity, and free radical content (Akhter *et al.* 1985) of this sample. This may not be problematic in environmental samples where graphitic carbon is more dilute, however radical scavenging methods are being investigated as a means to improve quantification using NMR, as enumerated by spin counting experiments.

### **References**

Akhter, M., Chughtai, A., Smith, D., 1985. The structure of hexane soot I: Spectroscopic studies. *Applied Spectroscopy* 39(1), 143-153.

Simpson M., Hatcher, P., 2004. Overestimates of black carbon in soils and sediments. *Naturwissenschaften* 91, 436-440.