Capabilities of Asymmetrical Flow Field-Flow Fractionation coupled with MALS for the Detection of Carbon Nanotubes in Soot and Soil

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Introduction

Methods to characterize and quantify Multi-Walled Carbon Nanotubes (MWCNTs) from soil samples are still scarcely available to date. Quantification – depending on the used method – may be biased by soot ubiquitously present in soils and sediments. Differentiating between MWCNTs and soot is a big challenge as they are physically and chemically very similar, e.g. in terms of thermal stability or density.
Shape could however be a contrasting parameter for the detection of MWCNTs in pure soot or even soil. Therefore, we evaluated a shape factor ρ, derived from AF4-MALS measurements, for its capabilities to detect MWCNTs in these matrices.

Detection of MWCNTs in Soot

We used differently shaped particles (MWCNTs, soot, native soil particles) to depict the shape differentiation capabilities of AF4-MALS. The method used shall be addressed briefly: samples (particle powder, dry soil) were dispersed in 2 % Sodium deoxycholate/0.05% Sodium azide, sonicated and centrifuged at 17.500 g for 10 min. The supernatant half of the volume was then used as a working suspension. As an AF4 carrier, 10^{-5} M Ammonium nitrate/0.02% Sodium azide was used. For determination of the hydrodynamic radius (r_h) we used retention time calibration with different certified latex standards. The radius of gyration (r_g) was determined using the PN3621 21-angle MALS detector. Both parameters were combined to give a shape factor $\rho = r_g/r_h$ Soot showed a relatively homogeneous ρ-distribution over the peak area (Fig.1) with average values of approx. 0.9. This was expected as the soot dispersions consisted of fractal-like aggregates that deviated from spherical shape ($\rho > 0.775$). Once MWCNTs were added, ρ showed an increase that was concentration dependent. These results could be confirmed using automated electron microscopy and image analysis (see Gogos et al. 2014).

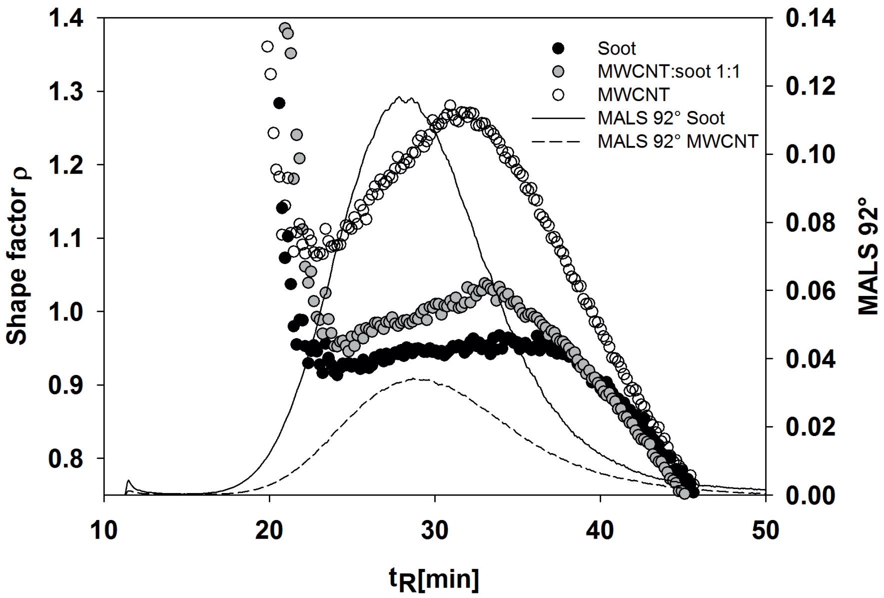

Figure 1: Fractograms obtained by AF4-MALS with shape factor ρ (symbols) for equal mass injections (5 µg) of a pristine long MWCNT, soot and a 1:1 mixture of both. Lines show the 92° MALS signal of pure soot (solid) and pure MWCNT (dashed).

Detection of MWCNTs in Soil

Native soil showed ρ-distributions comparable to soot (approx. 0.9, Fig. 2). Again, addition of MWCNT increased the resulting ρ values in a concentration dependent manner. Resulting method detection limits for MWCNTs in soils were in the order of 1.6 to 4 mg g^{-1}.

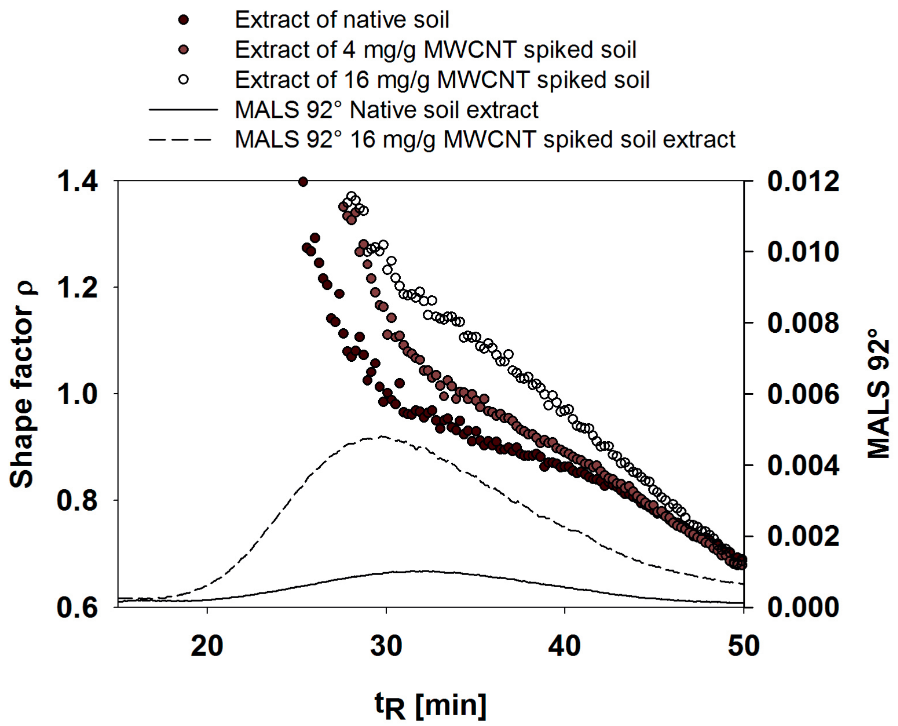

Figure 2: Fractograms obtained by AF4-MALS with shape factor ρ (symbols) of standard additions of a MWCNT to soil. Lines show the 92° MALS signal of native soil (solid) and soil + 16 mg g^{-1} MWCNT (dashed).

Conclusion

- Generation of a shape factor ρ from r_g and r_h values over time enables differentiation of MWCNTs and soot.
- Shape factor increment is dependent on the ratio between MWCNTs and soot in a mixture, i.e. ρ is concentration dependent.
- Soil particles extracted by the presented method are contrasting to MWCNTs in terms of ρ, allowing specific detection of MWCNTs in these complex matrices.
- Detection limits are still much higher than any currently predicted environmental concentration.

References

Gogos, A., Kaegi, R., Zenobi, R. and Bucheli, T. D., Environmental Science: Nano, 2014, 6(1), 584-594.