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

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General Information

ID0037

Application	Environmental
Technology	AF4-UV-MALS
Info	Postnova AF2000 MT, PN3621 MALS, PN3241 UV-Vis/DAD
Keywords	Asymmetrical Flow Field-Flow Fractionation, Multi Angle Light Scattering, Carbon Nanotubes, Shape Factor

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 [1].

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).

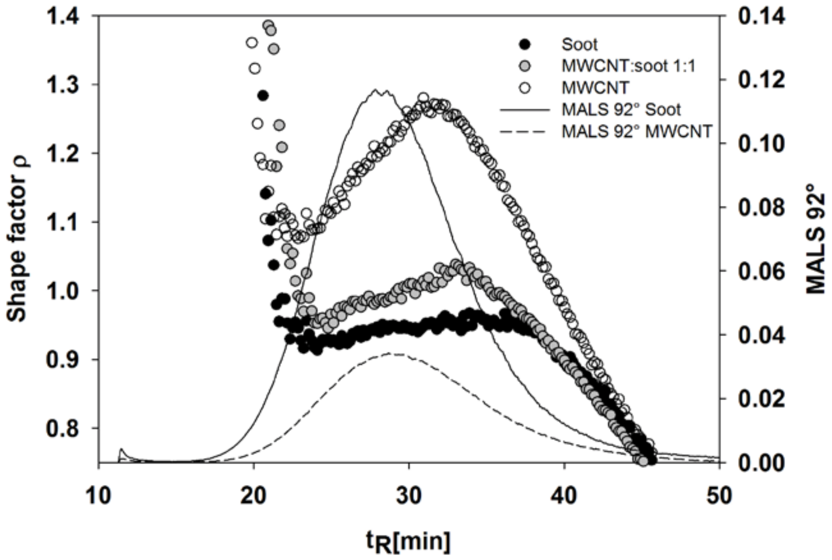

Figure 1: Fractograms obtained by AF4-MALS with shape factor ρ (symbols) for equal mass injections (5 µg) of a pristine long MWCNT, soot and a 1:1 mixture of both. Lines show the 92° MALS signal of pure soot (solid) and pure MWCNT (dashed).

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}.

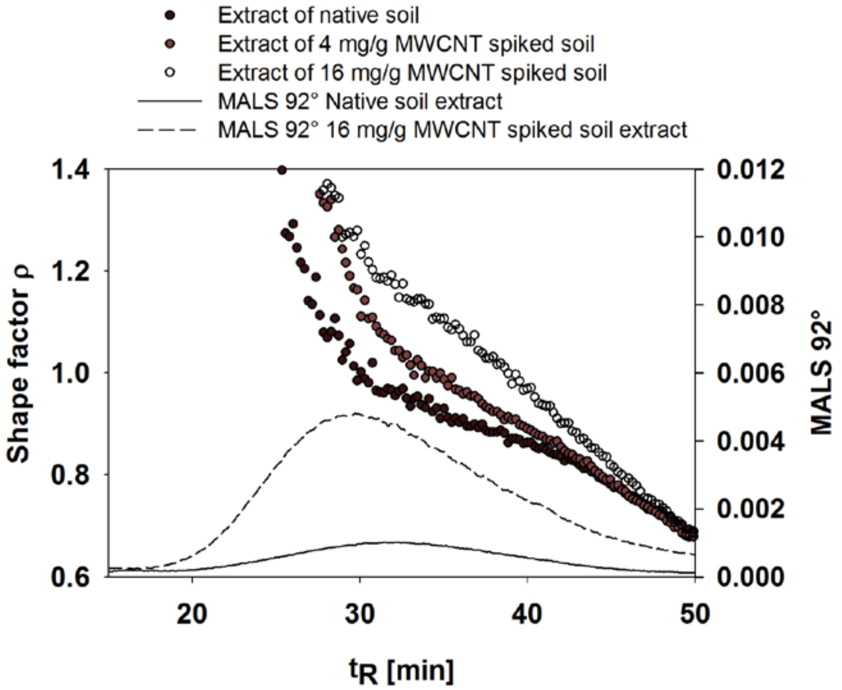

Figure 2: Fractograms obtained by AF4-MALS with shape factor ρ (symbols) of standard additions of a MWCNT to soil. Lines show the 92° MALS signal of native soil (solid) and soil + 16 mg g^{-1} MWCNT (dashed).

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

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