

Isolation and ^{14}C analysis of humic-like substances (HULIS) from ambient aerosol samples

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Keywords: Carbonaceous Aerosols, radiocarbon, source apportionment.

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Humic-like substances (HULIS) are an unresolved complex mixture of organic compounds, which accounts for 12-60% of the total organic carbon (OC) in ambient aerosols (Graber *et al.*, 2006). As the characterization of HULIS is still incomplete and because their composition and amount is strictly method dependent, a meaningful comparison of different studies about this class of compounds is difficult. More detailed information on atmospheric HULIS and thus a significant effort towards standardized characterization and isolation methods is required. The information on the radiocarbon (^{14}C) content would allow the source discrimination of biogenic and biomass-burning emissions from fossil-fuel combustion (Szidat, 2009), thus contributing a share to a better understanding of these carbonaceous aerosol constituents.

The evaluation of different isolation approaches resulted in a straightforward HULIS extraction procedure for subsequent ^{14}C analysis by accelerator mass spectrometry (^{14}C -AMS). The presented methodology corresponds to a modified method of Varga *et al.* (2001). The complete procedure is summarized as a flow chart in Fig. 1.

In brief, aerosol samples on quartz-fiber filters are water extracted, filtered through a $0.2\mu\text{m}$ PTFE filter and concentrated by lyophilisation. The sample is redissolved in ultrapure H_2O and acidified to pH 2 before loading the sample on a preconditioned HLB Oasis solid phase extraction (SPE) cartridge. During a washing step with 0.1M HCl, inorganic salts and small molecular weight acids are removed. The HULIS fraction is afterwards eluted with methanol (MeOH) and concentrated under a gentle stream of N_2 . The eluate is redissolved in ultrapure water, frozen at -18°C and then lyophilized to remove remaining MeOH. The dried SPE eluates are combusted in a thermo-optical OC/EC analyser and the formed CO_2 is concentrated cryogenically in glass ampoules. The CO_2 trapped in the ampoules is transferred to the ^{14}C -AMS system via a gas inlet system (Szidat *et al.*, 2014)

First tests showed that unexpected contaminations eluted from the SPE cartridges and the use of organic solvents complicated the HULIS isolation and sample preparation

for ^{14}C analysis. Procedure blanks were significantly lowered by removing released fine material from the SPE with an additional filtration step. The eluent (MeOH) was effectively removed by the additional steps of drying and lyophilisation. The remaining procedure blank was quantified in terms of its mass and its $^{14}\text{C}/^{12}\text{C}$ ratio by isotopic dilution analysis using a fossil and a modern standard (Fluka humic acid and IHSS Suwannee river humic acid respectively). Consequently the sample mass for the AMS measurement should be $\geq 20\mu\text{g C}$ for a reasonable precision of the ^{14}C data.

The validity of this HULIS isolation method is demonstrated on a filter set with 13 aerosol samples collected during different summer and winter conditions. The ^{14}C measurements will give a first insight into sources of HULIS emissions and formation.

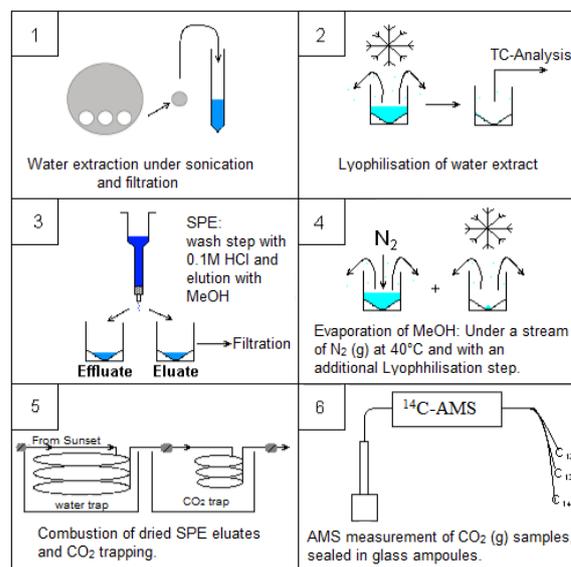


Figure 1. Flow chart of the HULIS isolation procedure for subsequent ^{14}C -AMS measurement.

Graber, E.R. and Rudich, Y. (2006) *Atmos. Chem. Phys.*, **6**, 729-753.

Szidat, S. (2009) *Chimia* **63**, 157-161.

Varga, B., Kiss, G., Ganszky, I., Gelencser, A., Krivacsy, Z. (2001) *Talanta*, **55**, 561-572.

Szidat, S., Salazar, G.A., Vogel, E., Battaglia, M., Wacker, L., Synal, H.-A., Türler, A. (2014) *Radiocarbon*, **56**, 2, 561-566.