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Liquid chromatographic isolation of individual carbohydrates from atmospheric and marine samples for stable carbon analysis and radiocarbon dating

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Carbohydrates are among the most abundant organic molecules in both aquatic and terrestrial ecosystems; however, very few studies have addressed their isotopic signature using compound-specific isotope analysis, which provides additional information on their origin (δ13C) and fate (Δ14C). In this study, semi preparative liquid chromatography with refractive index detection (HPLC-RI) was employed to produce pure carbohydrate targets for subsequent offline δ13C and Δ14C isotopic analysis. δ13C analysis was performed by elemental analyzer-isotope ratio mass spectrometer (EA IRMS) whereas Δ14C analysis was performed by an elemental analyzer coupled to the gas source of a mini carbon dating system (AixMICADAS). In general, four successive purifications with Na+, Ca2+, Pb2+, and Ca2+ cation-exchange columns were sufficient to produce pure carbohydrates. These carbohydrates were subsequently identified using mass spectrometry by comparing their mass spectra with those of authentic standards.
The applicability of the proposed method was tested on two different environmental samples comprising marine particulate organic matter (POM) and total suspended atmospheric particles (TSP). The obtained results revealed that for the marine POM sample, the δ13C values of the individual carbohydrates ranged from -18.5 to -16.8‰ except for levoglucosan and mannosan, which presented values of -27.2 and -26.2‰ respectively. For the TSP sample, the δ13C values ranged from -26.4 to -25.0‰ . The galactose and glucose Δ14C values were 19 and 43‰ respectively, for the POM sample. On the other hand, the levoglucosan radiocarbon value was 33‰ for the TSP sample. These results suggest that these carbohydrates exhibit a modern age in both of these samples, whereas the presence of levoglucosan and mannosan in the POM sample clearly indicates a terrestrial source from burning biomass processes. Radiocarbon HPLC collection window blanks, measured after the addition of phthalic acid (14C free blank), ranged from -988 to -986‰ for the abovementioned compounds, indicating a very small background isotopic influence from the whole purification procedure. Overall, the proposed method does not require derivatization steps, produces extremely low blanks, and may be applied to different types of environmental samples.