



## **Preparative chromatography for specific $\delta^{13}\text{C}$ isotopic analysis of individual carbohydrates in environmental samples**

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Carbohydrates are among the most abundant organic molecules on the Earth and are present in all geochemical systems. Despite their high abundance in the environment, very few studies assessed their origin using molecular carbohydrate isotopic analyses. In contrast with bulk stable isotope analysis (BSIA), which gives the isotopic signature of the entire sample without any specification about its chemical composition, compound specific  $^{13}\text{C}$  isotopic analysis of individual sugars (CSIA) offers valuable information about the origin of single molecules. Previous investigations used gas or liquid chromatography coupled with isotope ratio mass spectroscopy (GC-IRMS; HPLC-IRMS) for CSIA of sugars however the former requires  $\delta^{13}\text{C}$  corrections due to the carbon added to the sugar (derivatization) while the later does not provide always adequate separations among monosaccharides. Here we used cation preparative chromatography ( $\text{Ca}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Na}^{+}$ ) with refractive index detection in order to produce pure monosaccharide targets for subsequent EA-IRMS analyses. Milli-Q water was used as eluant at a flow rate  $0.6 \text{ ml min}^{-1}$ . In general, three successive purifications ( $\text{Ca}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ca}^{2+}$ ) were sufficient to produce pure compounds. Pure monosaccharides were compared with authentic monosaccharide standards using  $^1\text{H}$  NMR and/or mass spectroscopy. The detection limit of our technique was about  $1 \mu\text{M/sugar}$  with a precision of  $\sim 10\%$  ( $n=6$ ). Blanks run with Milli-Q water after three successive purifications resulted in carbon content of  $0.13$  to  $2.77 \mu\text{gC}$  per collected sugar. These values are much lower than the minimum required amount ( $5 \mu\text{gC}$ ) of the EA-IRMS system with a precision of  $\pm 0.35 \text{ ‰}$ . Application of our method to environmental samples resulted in  $\delta^{13}\text{C}$  values of glucose, fructose, and levoglucosan in the range of  $-24$  to  $-26 \text{ ‰}$  (PM10 atmospheric particles), and  $-15 \text{ ‰}$  to  $-22 \text{ ‰}$  for arabinose, glucose, and xylose (marine high molecular dissolved organic matter). These results fall in the range of previous reported values for terrestrial and aquatic ecosystems.