



## First results from a novel methodological approach for $\delta^{18}\text{O}$ analyses of sugars using GC-Py-IRMS

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Although the instrumental coupling of gas chromatography-pyrolysis-isotope ratio mass spectrometry (GC-Py-IRMS) for compound-specific  $\delta^{18}\text{O}$  analyses is commercially available for more than 10 years, this method is hardly applied by isotope researchers so far. Using GC-Py-IRMS, Zech and Glaser (2009) and Zech et al. (2013; 2012) developed and applied a method, which allows determining  $\delta^{18}\text{O}$  of hemicellulose-derived sugar biomarkers extracted from soils and sediments. However, the used methylboronic acid (MBA) derivatization is suitable only for pentoses and deoxyhexoses, not for hexoses.

Here we present first GC-Py-IRMS results for TMS-(trimethylsilyl)-derivatives of plant sap-relevant sugars (glucose, fucose, sucrose, raffinose) and a polyalkohol (pinitol) produced using BSTFA (N,O-Bis(trimethylsilyl)trifluoroacetamide) as the derivatization reagent. Particularly, we focus on sucrose, which is the most important transport sugar in plants and hence of utmost relevance in plant physiology and in tree-ring studies. Replicate analyses of sucrose standards with known  $\delta^{18}\text{O}$  values suggest that the  $\delta^{18}\text{O}$  measurements are not stable over several days. A calibration (including a drift correction) against an external sucrose standard is hence essential when measuring sample batches. Furthermore, we observed a large dependence of the  $\delta^{18}\text{O}$  values on the analyte amount (area), which needs to be considered by a respective correction procedure. Tests with  $^{18}\text{O}$ -enriched water do not provide any evidence for oxygen exchange reactions between water and sucrose, glucose and raffinose.

Finally we present the first application of compound-specific  $\delta^{18}\text{O}$  analyses from natural samples, namely from seven needle extracts (soluble carbohydrates) from a Siberian study area. Both the  $\delta^{18}\text{O}$  amplitude and values of sucrose are considerably higher (32.1‰ to 40.1‰ compared to the  $\delta^{18}\text{O}$  amplitude and values of bulk needle extract (24.6‰ to 27.2‰). We found positive correlation (although statistically not significant) for  $\delta^{18}\text{O}$  of sucrose ( $n = 7$ ) and bulk  $\delta^{18}\text{O}$  ( $R = 0.62$ ),  $\delta^{13}\text{C}$  of sucrose ( $R = 0.55$ ) and maximum day temperature ( $R = 0.58$ ) and negative correlation for  $\delta^{18}\text{O}$  of sucrose and cloudiness ( $R = -0.80$ ). This highlights the great potential of compound-specific  $\delta^{18}\text{O}$  analyses of sucrose for (paleo-) climate studies.

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