



Rapid online equilibration method to determine the D/H ratios of nonexchangeable hydrogen in cellulose

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An improved method for determination of deuterium to hydrogen (D/H) ratios of nonexchangeable hydrogen in cellulose is presented. The method is based on the equilibration reaction of hydroxyl hydrogen of cellulose and water vapour of known isotopic composition. The equilibrated cellulose is pyrolysed and the total D/H ratio determined by subsequent online IRMS. With a mass balance system the D/H ratio of nonexchangeable hydrogen is recalculated after an empirical calibration has been performed yielding a mean exchangeability of 0.239 and an equilibrium fractionation factor of 1.082 between hydroxyl hydrogen of cellulose and water hydrogen at 110°C. Equilibration takes 10min per sample. Results obtained by this online equilibration method agree very well with values obtained by nitration technique ($R^2=0.995$). The uncertainty of the equilibration method is $\pm 4\%$, resulting from a single standard deviation of $\pm 2.8\%$, for the equilibration determined by standard cellulose and 2.8% , due to the variable exchangeability of hydroxyl hydrogen in cellulose due to crystalline areas. The latter uncertainty may be lowered by minimising crystallinity of the cellulose. Advantages of this new technique are (i) the considerably reduced sample amount required (as low as 0.2 mg, ideally 0.5 mg compared to 20 mg for the conventional nitration technique); (ii) an approximately 100-fold reduced process time and (iii) there is no need of hazardous chemicals as it is the case for the nitration technique.