Automation of $^{13}C/^{12}C$ ratio measurement for freshwater and seawater DOC using high temperature combustion

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We provide a detailed description of the hyphenation of an Aurora 1030C high temperature catalytic conversion DOC analyzer, a GD-100 CO2 trap and an open-split IRMS which has made possible the high-throughput, automated measurements of 13C/12C ratios and DOC concentrations for a wide range of aquatic samples. Precision of 13C/12C ratios increases exponentially with sample concentration reaching 0.2‰ or better for high concentration samples (>5 µg mL-1), comparable to that obtained in a conventional elemental analyzer-IRMS setup. The high system blank is the limiting factor in obtaining maximal system performance; optimal system blanks values are in the order of 0.2 µg C with an isotopic signature varying from -20 to -12 ‰ during the lifetime of the combustion column. With appropriate blank correction procedures, accurate analyses (0.5‰ or better) can be obtained on concentrations as low as 0.5 µg DOC mL-1, representing the lower limit typically observed in aquatic systems. Sample matrix does not affect reproducibility or accuracy; this method is amenable to both freshwater and seawater samples. Although no certified DOC standards exist for δ13C, we analyzed a consensus reference material from a deep-ocean environment (CRM Batch 13 Lot # 05-13, Hansell 2013) and found a $\delta^{13}C$ value of –19.86 ± 0.44‰ (n = 4), which corroborates previously reported values for a similar sample (Bouillon *et al* 2006) and is consistent with its marine origin.