



Direct analysis of $\delta^{13}\text{C}$ and concentration of dissolved organic carbon (DOC) in environmental samples by TOC-IRMS

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Dissolved organic carbon (DOC) plays an important role in carbon cycling in terrestrial and aquatic systems. Stable isotope analysis ($\delta^{13}\text{C}$) of DOC could provide valuable insights in its origin, fluxes and environmental fate. Precise and routine analysis of $\delta^{13}\text{C}$ and DOC concentration are therefore highly desirable. A promising, new system has been developed for this purpose, linking a high-temperature combustion TOC analyzer trough an interface with a continuous flow isotope ratio mass spectrometer (Elementar group, Hanau, Germany). This TOC-IRMS system enables simultaneous stable isotope (bulk $\delta^{13}\text{C}$) and concentration analysis of DOC, with high oxidation efficiency by high-temperature combustion for complex mixtures as natural DOC. To give $\delta^{13}\text{C}$ analysis by TOC-IRMS the necessary impulse for broad-scale application, we present a detailed evaluation of its analytical performance for realistic and challenging conditions inclusive low DOC concentrations and environmental samples.

High precision (standard deviation, SD predominantly < 0.15 permil) and accuracy ($R^2 = 0.9997$, i.e. comparison TOC-IRMS and conventional EA-IRMS) were achieved by TOC-IRMS for a broad diversity of DOC solutions. This precision is comparable or even slightly better than that typically reported for EA-IRMS systems, and improves previous techniques for $\delta^{13}\text{C}$ analysis of DOC. Simultaneously, very good precision was obtained for DOC concentration measurements. Assessment of natural abundance and slightly ^{13}C enriched DOC, a wide range of concentrations (0.2-150 mgC/L) and injection volumes (0.05-3 ml), demonstrated good analytical performance with negligible memory effects, no concentration/volume effects and a wide linearity. Low DOC concentrations (< 2 mgC/L), were correctly analyzed without any pre-concentration. Moreover, TOC-IRMS was successfully applied to analyze DOC from diverse terrestrial, freshwater and marine environments (SD < 0.23 permil).

In summary, the TOC-IRMS performs fast and reliable analysis of DOC concentration and $\delta^{13}\text{C}$ in aqueous samples, without any pre-concentration/freeze-drying. Flexible usage is highlighted by automated, online analysis, a variable injection volume, high throughput and no extensive maintenance. Sample analysis is simple, using small aliquots and with minimal sample preparation. Further investigations should focus on complex, saline matrices and very low DOC concentrations, to achieve a potential lower limit of 0.2 mgC/L. High-resolution, routine $\delta^{13}\text{C}$ analysis of DOC by TOC-IRMS offers opportunities for wide-scale application in terrestrial, freshwater and marine research to elucidate the role of DOC in biogeochemical processes and ecosystem functioning.