11th Applied Isotope Geochemistry Conference, AIG-11 BRGM

Novel tool for simultaneous carbon and nitrogen stable isotope analyses in aqueous samples

Eugen Federherr\textsuperscript{a}, Robert J. Panetta\textsuperscript{b,*} Lutz Lange\textsuperscript{a}, Hans J. Kupka\textsuperscript{a}

\textsuperscript{a}Elementar Analysensysteme GmbH, Hanau, 63452, Germany
\textsuperscript{b}Isoprime, Ltd., Cheadle Hulme, SK8 6PT, United Kingdom

Abstract

The quantitative and isotopic analysis of dissolved matter (e.g. dissolved organic carbon, total dissolved nitrogen, etc.) is of particular importance since this pool is a prime conduit in the cycling of N and C. Studying the two elemental pools simultaneously is of importance, as the transformation and transport processes of N and C are inextricably linked in all biologically mediated systems. Dissolved Carbon concentration and isotopic composition can now be determined routinely through coupling of high temperature combustion (HTC) systems to isotope ratio mass spectrometry (IRMS). However the analysis of $\delta^{15}$N of Total Dissolved Nitrogen is fraught with limitations: low concentration makes lyophilisation followed by EA/IRMS laborious and subject to contamination; wet chemical oxidation-IRMS runs the risk of incomplete conversion and cannot distinguish dissolved N$_2$ from Total Dissolved Nitrogen. Further development of our HTC system lead to the implementation of the $\delta^{15}$N determination which is now coupled into a novel total organic carbon (TOC) analyzing system. An integrated, innovative purge and trap technique (peak focusing) for nitrogen with aluminosilicate adsorber and thermoelectric cooling element based system, in combination with high injection volume (up to 3 mL) significantly improves sensitivity. Down to 1ppm and less total nitrogen can be measured with precision of $\pm 0.5\%$. To decrease the background caused by physically dissolved nitrogen a new, membrane-based, degasser was designed for online separation of physically dissolved nitrogen. This novel HTC system, “iso TOC cube”, provides an innovative tool with large potential in investigation of biogeochemical carbon and nitrogen cycles.

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Keywords: Total dissolved nitrogen; stable isotopes; biogeochemistry

* Corresponding author. Tel.: +44-161-488-3681; fax: +44-161-488-3699.
E-mail address: Robert.panetta@isoprime.co.uk
1. Main text

The investigation of transformation and transport processes of carbon and nitrogen in ecosystems plays a vital role in understanding their biogeochemical dynamics. Consequently, suitable and accurate methods for quantitative as well as stable isotopic analysis of carbon and nitrogen in waters and aqueous solutions play a significant role. There has been much effort over the last decade to establish the routine analysis of $\delta^{13}C$ of dissolved organic carbon (DOC) through the coupling of total organic carbon analyzers with isotope ratio mass spectrometers (TOC-IRMS)\textsuperscript{1-4}. Though some samples such as seawater remain a challenge, most aqueous samples can now be measured routinely via this approach.

The analysis of $\delta^{15}N$ of dissolved nitrogen still has large limitations. Its low concentration makes Elemental Analysis coupled to Isotope Ratio Mass Spectrometry (EA/IRMS) laborious, time and sample consuming. Systems based on wet chemical oxidation-IRMS bare the risk of sensitivity loss as well as of fractionation due to incomplete mineralization. A TOC-IRMS system for determining $\delta^{15}N$ in natural waters has been described\textsuperscript{5}. The authors note that the high solubility of molecular nitrogen in water remained a technical challenge, and kept the lowest detection limit above 20 ppm N. Therefore additional off-line separation steps to distinguish between physically dissolved nitrogen and bound nitrogen are still required.

Here we describe the further development of our isoTOC system to the determination of $\delta^{15}N$ in addition to $\delta^{13}C$ of aqueous solutions. An integrated, innovative purge and trap technique (peak focusing) for nitrogen with aluminosilicate adsorber and thermoelectric cooling, in combination with high injection volume (up to 3 mL) significantly improves sensitivity. Detection limits of 1 ppm of total nitrogen can be measured with precision of $\leq 0.5\%$. To help decrease the contribution of physically dissolved nitrogen a new, membrane-based, degasser was designed for online separation of physically dissolved nitrogen.

1.1. Instrumentation

The entire system consists of three parts: the TOC analyzer, the interface and the isotope ratio mass spectrometer (see Fig. 1). The TOC analyzer (isoTOC cube) is derived from the commercially available high temperature conversion (HTC)-TOC analyzer varioTOC cube (Elementar Analysensysteme GmbH) which was modified and adapted to meet the requirements for IRMS, namely, to improve the system sensitivity, to minimize instrumental background as well as the blank contribution, and to ensure the absence of isotopic fractionation within the system.\textsuperscript{4} Samples, filled in 40-mL borosilicate glass vials, are introduced using a 32-position autosampler into the combustion system by means of a 5-mL syringe and a multiway valve. The combustion is performed at 850 $^\circ$C by oxygen and supported by a catalyst (Pt on ceramic carrier material). A reduction step over elemental copper at 650 $^\circ$C is carried out to convert nitrogen oxides to N\textsubscript{2}. Water is removed in three steps: an air-cooled condenser, a counter-flow membrane dryer and a chemical dryer. Hydrogen halides and halogens are removed by silver wool. After the purification steps the carrier gas enters the nondispersive infrared (NDIR) detector for quantification of the evolved CO\textsubscript{2} (giving the DOC concentration of a pre-acidified sample). The sample is then directed to the interface containing the thermoelectric cooled aluminosilicate trap for $\delta^{15}N$ prior to the IRMS analysis, or is sent directly to the IRMS for determination of $\delta^{13}C$. An additional trap for CO\textsubscript{2} is also included for trace/difficult sample analysis. The IRMS used is an Isoprime 100 (Isoprime, Ltd. Manchester, UK), without any modifications.

Figure 1. Schematic of the isoTOC IRMS system described. (a) Degassing; (b) combustion/reduction; (c) condenser; (d) scrubber; (e) purge and trap
1.2. Results

The degassing unit effectively removes dissolved N₂ from the sample, decreasing the amount from ~30 ppm to <10 ppm. In many cases, this drop is sufficient to nullify the impact of dissolved N₂ on the measurement, allowing for a fully automated process. Memory of the instrument is impacted only by the injection port. Carry-over at the injection port impacts the first two injections for up to an 80 ‰ step. A strategic rinsing protocol can be employed to minimize sample waste and analysis time in dealing with this effect. The total analysis time is under 15 minutes, and the N₂ from the aluminosilicate focussing trap is symmetrical with a peak width of ~45 seconds (Figure 2).

![Figure 2. Total ion chromatogram (m/z = 28) of a 10 - 80 ppm N caffeine solution with trapping an focussing of N₂ evolved from the isoTOC.](image)

δ¹⁵N of nine reference (USGS 25, USGS 26, USGS 41, IAEA-N-2, IAEA-600) and in-house soluble EA standard compounds (caffeine, urea, acetanilide, glutamic acid, sodium nitrate, ammonium chloride) covering a range of 84 ‰ on the N AIR scale result in an average precision of <0.2 ‰ and excellent agreement with consensus or EA-determined values (Figure 3).

![Figure 3. Excellent agreement between measured and true values for 11 reference or standard compounds. Solutions contained 100 ppm of total dissolved nitrogen.](image)
Coupled with the previously demonstrated performance of this system for $\delta^{13}C$ measurement of DOC, this holds great promise for the simultaneous measurement of DOC and TDN in a single run. This coupled measurement presents a significant advance in helping researchers delineate the coupled carbon and nitrogen cycles in aquatic systems.

References