

$\delta^{15}\text{N-NH}_4^+$ isotopic analysis by the “diffusion” method

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Overview:

A method used to determine the N isotopic composition of dissolved NH_4^+ in water. The procedure involves converting dissolved NH_4^+ into NH_3 gas which is then trapped quantitatively as $(\text{NH}_4)_2\text{SO}_4$ on a specially prepared filter pad and subsequently analyzed in an Elemental Analyzer + Isotope ratio Mass Spectrometer (EA-IRMS) system.

Extraction:

The procedure involves converting dissolved NH_4^+ into NH_3 gas by raising the pH of the sample to above 9 with MgO and subsequently trapping the gas quantitatively as $(\text{NH}_4)_2\text{SO}_4$ on a small strip of quartz filter paper. The amount of sample needed is carefully determined based on the $[\text{NH}_4^+]$ concentration with a target of between 50 and 150ug $[\text{NH}_4^+]$. The trap is prepared by saturating the quartz strip with NaHSO_4 then pressure sealing the strip between two gas-permeable, hydrophobic, polypropylene filters (Maine Manufacturing p/d: 1222102). The filter “sandwich” is then placed on the surface of the water sample in a tightly sealed, 200 ml Schott bottle. Due to the hydrophobic character of the polypropylene filters the “sandwich” will float. The sample is stirred gently using a magnetic stir bar for 7 days. As the NH_3 gas partitions into the headspace of the bottle, it diffuses through the polypropylene filter and reacts with NaHSO_4 , forming $(\text{NH}_4)_2\text{SO}_4$ on the quartz strip. The filter “sandwich” is then removed from the bottle and dried for ~72 hours in an evacuated bell jar containing desiccant. After drying the $(\text{NH}_4)_2\text{SO}_4$ impregnated quartz strip is removed from the “sandwich” and is carefully enclosed in a tin cup (Microelemental Analysis p/n D1008) and combusted in a EA-IRMS system along with a full suite of Reference Materials and QA/QC standards. In the ISL, either a *Costech* 4010[®] or *Elementar* Isotope-CUBE[®] is used. Both are interfaced to a Thermo DeltaVPlus[®] IRMS via a ConFloIV[®] device. The EA converts total nitrogen in a solid sample into N_2 gas. The co-produced SO_2 is removed from the carrier stream by a plug of Ag wool placed at the bottom of the reaction tube. The flash combustion in the EA is quantitative, so no isotope fractionation is involved. The IRMS is capable of detecting ion beams with mass/charge (m/z) 28, 29, 30. The ion beams from N_2 are as follows: m/z 28 = $^{14}\text{N}^{14}\text{N}$, m/z 29 = $^{14}\text{N}^{15}\text{N}$, and m/z 30 = $^{15}\text{N}^{15}\text{N}$. The m/z 30 ion beam also measures NO ($^{14}\text{N}^{16}\text{O}$), which may indicate contamination or incomplete reduction (exhaustion of the copper packing in the reduction tube). $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values are calculated by the instrument software (ISODAT 3.88). Stable isotope ratios are expressed as delta (δ) and are measures of a ‘per mill’ (‰), or parts per thousand difference between the isotope

ratio of a sample and that of a known (International) standard material. Values are reported relative to 'VSMOW' for Oxygen and 'Atmospheric air' for Nitrogen. The analytical instruments are fully automated and computer controlled using ISODAT 3.63. Prior to sample analysis instrument conditions: oven temperatures, carrier gas flows, ion beam background(s), ion source stability and signal linearity are checked and recorded ("Daily check" routine).

Data correction:

Ion currents of masses 28 and 29 are measured simultaneously and the $^{15}/^{14}\text{N}$ ratios of the sample are compared to that of a working-reference N_2 gas (5.0, Praxair Air, Canada). The raw data is corrected to the International N_2 scale by normalization with two reference materials (USGS 40 and USGS 41) during each EA sequence. In addition, two QA/QC standards are prepared with each sample batch to adhere to the "IT" principal described in Werner & Brand, 2001.

Reference materials:

<u>Identifier</u>	<u>$\delta^{15}\text{N}$ (‰)</u>
IAEA N_2 (QC/QC #1)	$+20.3 \pm 0.2$
ISL KNO_3 (QA/QC #2)	-1.32 ± 0.2
USGS 40	-4.50 ± 0.2
USGS 41	$+47.6 \pm 0.2$

- Internal lab standards are used at the beginning and end of each sequence to correct for instrument drift and to normalize the data to internationally accepted standards
- USGS LIMs is used for drift correction, normalization and data management. (<http://water.usgs.gov/software/LIMS/>)

Accuracy and Precision:

Accuracy and precision of $\delta^{15}\text{N-NH}_4^+$ determinations based on a long-term record of analyses of ISL in-house reference (ISL- KNO_3) is: ± 0.5 per mil.

References:

R.A. Werner and W.A. Brand, Referencing strategies and techniques in stable isotope ratio analysis, *Rapid Communications in Mass Spectrometry*, 2001: 15: 501-519

Janet E. Hannon and J.K. Böhlke, Determination of the $\delta(^{15}\text{N}/^{14}\text{N})$ of Ammonium (NH_4^+) in Water: RSIL Lab Code 2898

S. Matheiu et.al., The Use of the 'Ammonium Diffusion' Method for $^{15}\text{N-NH}_4^+$ and $^{15}\text{N-NO}_3^-$ Measurements: Comparison with Other Techniques, *Environ. Chem.* 2004, 1, 99-103