



ABB MEASUREMENT & ANALYTICS | APPLICATION NOTE

## AUTOMATED TRIPLE-ISOTOPE NITRATE ANALYSIS USING ABB'S OA-ICOS TECHNOLOGY

ABB's automated rapid triple-isotope ( $\delta^{15}\text{N}$ ,  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$ ) analyzer is an innovative and reliable solution for nitrate pollution source apportionment.

### Introduction

Nitrate ( $\text{NO}_3^-$ ) contamination in water is a growing concern, stemming largely from agricultural runoff, animal manure and wastewater. This pollution leads to serious environmental issues such as lake eutrophication and oceanic dead zones, that impact tourism and fishing. It also poses significant public health risks, due to high nitrate levels in drinking water [1,2].

To combat this, it is crucial to understand and quantify the nitrate sources. The analysis of stable nitrogen and oxygen isotopes in nitrate ( $\delta^{15}\text{N}$ ,  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$ ) is a powerful tool for tracking nitrate origins, movement and transformations. These isotopic fingerprints allow one to:

- Discriminate between pollution sources such as organic waste, synthetic fertilizers and atmospheric deposition
- Identify natural bioremediation processes such as bacterial denitrification

- Reveal changes in agricultural land use and optimize fertilization practices, which is not possible with concentration values alone

By using isotopologue analysis, it is possible to develop targeted strategies to manage nitrogen fertilization and mitigate the harmful effects of nitrate pollution; thus, safeguarding both environment and public health.

Traditional methods for nitrate isotopologue analysis, such as microbial or cadmium reduction followed by gas chromatograph isotope-ratio mass spectrometry (GC-IRMS) often involve use of toxic chemicals and multi-step conversions. Moreover, they do not allow direct measurement of  $\delta^{17}\text{O}$  that can help distinguish atmospheric nitrate sources from nutrient-derived sources.

These limitations have been particularly restrictive in atmospheric chemistry and water quality monitoring, where nitrate isotope signatures need to be analyzed rapidly and repeatedly over time.

The use of ABB's laser-based Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS) analyzers allows to overcome these challenges. ABB's GLA451-N2O13 model is a triple-isotopologue  $N_2O$  analyzer that enables direct and fully automated analysis of  $\delta^{15}N$  (bulk), site specific ( $\delta^{15}N_{\beta}$  and  $\delta^{15}N_{\alpha}$ ),  $\delta^{18}O$ , and  $\delta^{17}O$  in  $N_2O$  gas derived from nitrates with minimal operator intervention. Some of the advantages of using a laser-based analytical technique over IRMS are:

- Direct and simultaneous measurement of  $\delta^{15}N$ ,  $\delta^{17}O$  and  $\delta^{18}O$  with minimal sample preparation
- Integration of a headspace autosampler with the  $N_2O$  triple-isotope laser analyzer to enable unattended analysis of aqueous nitrate from several environmental water samples—this allows high-temporal resolution studies of atmospheric nitrogen pollution research
- Provides direct information about the  $\delta^{17}O$  without requiring any prior sample conversion, unlike IRMS

### Instrumentation

The GLA451-N2O13 laser-based analyzer is optimized for the precise measurement of isotopologues  $\delta^{15}N_{\alpha}$ ,  $\delta^{15}N_{\beta}$ ,  $\delta^{15}N_{bulk}$ ,  $\delta^{17}O$  and  $\delta^{18}O$  in  $N_2O$  gas. Operating across a 0.3–20 ppm  $N_2O$  concentration range, this system is paired with a headspace autosampler fitted with a 5 mL gas-tight syringe.



01. GLA451-N2O13 with autosampler

This setup enables automated injection of up to three 5 mL headspace samples directly into the analyzer. Gas is transferred through a 1-meter PTFE line into a 0.9 L evacuated optical cavity where it is equilibrated and diluted with  $N_2O$ -free zero air to a working pressure of 60 mbar.

The system is equipped with a DHCP-controlled ethernet interface for synchronized autosampler control and uses an external ABB three-head diaphragm pump to evacuate the cavity (<1 mbar) between samples. The autosampler accommodates up to 36 capped vials (40 mL each), allowing fully unattended overnight runs.

### Reference materials and test samples

The samples used in this study were archived rainwater samples. The article demonstrates the benefits of an automated laser-based system for air nitrogen pollution studies [3]. To validate performance, the system was tested using certified nitrate isotope standards

from the US Geological Survey (USGS) and International Atomic Energy Agency (IAEA). These materials have consistent  $\delta^{15}N$ ,  $\delta^{18}O$  and  $\delta^{17}O$  values traceable to AIR (Atmospheric Air) and VSMOW (Vienna Standard Mean Ocean Water) international scales.

The International Atomic Energy Agency (IAEA), in collaboration with the University of Massachusetts, has developed an innovative method for tracing the origin of nitrogen pollution in lakes, seas and rivers. The new method uses a form of titanium chloride to convert the nitrates dissolved in water samples to nitrous oxide gas and is referred to as “Ti method” [5]. This headspace gas can be measured using laser-based absorption techniques.

All samples were prepared to yield headspace  $N_2O$  concentrations of 4 to 5 ppm, which is the optimal range determined by the scientists for precise isotope ratio determination.

### Automated measurement workflow

Before initiating a batch measurement of nitrate-derived  $N_2O$  samples, the GLA451-N2O13 analyzer is powered on and stabilized at 45°C. The spectral alignment is verified by measuring gas mixture of 10 ppm  $N_2O$  in air in continuous mode before switching to the autosampler mode. Once stabilized, the system was switched to autosampler mode to establish connection with the headspace autosampler.

Pre-run checks involved analyzing several 40 mL septum vials containing 10 ppm  $N_2O$  to confirm system functionality and measurement reproducibility. The pre-run checks enabled the correction of instrumental drift and blank offsets during post-processing.

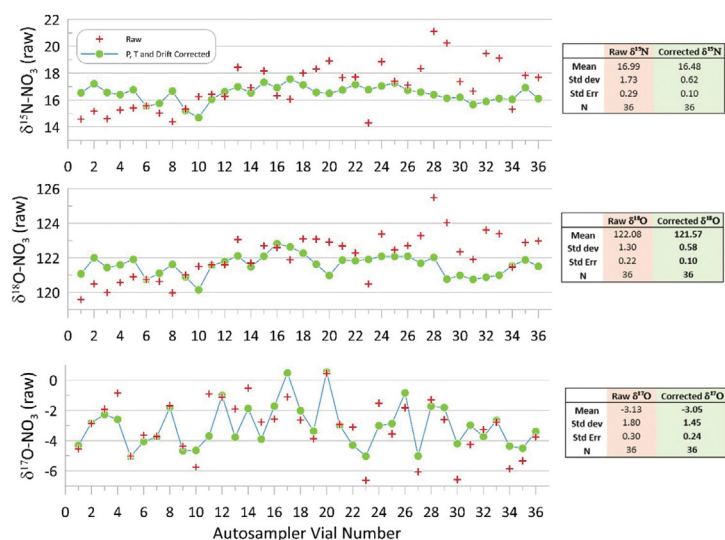
A syringe with a volume of 5 mL is used to inject the sample. User can inject the sample up to 3 times to ensure sufficient  $N_2O$  concentration for accurate measurement. The analysis sequence per sample vial was as follows:

1. The analyzer measurement cell is flushed with zero air and evacuated down to < 0.5 mbar.
2. The headspace  $N_2O$  gas is injected into the analyser's sample tank by the autosampler. Up to 15 mL samples can be injected in the tank.
3. Three- 5 mL samples are injected into the sample.
4. The sample is expanded into the measurement cell and diluted with zero air to reach operational pressure of 60 mbar.
5. Absorption spectrum is measured for 300 seconds at a 1 Hz rate and the isotopologue values are calculated using spectral information—then the averaged value is reported and saved in the output file.
6. The system is evacuated post-analysis to prepare for the next sample. Each sample requires approximately 10-12 minutes for full analysis, including all replicates. An entire tray containing 36 samples takes 7.5 hours to measure and report.

### Results

A stability test using a nitrate reference (1 mg/L as N) was performed to evaluate the complete system performance, including chemical conversion via the Ti method, autosampler and  $N_2O$  analyzer. In a single session, 36 consecutive measurements demonstrated that raw values for  $\delta^{15}N$ ,  $\delta^{18}O$  and  $\delta^{17}O$  showed significant scatter and uncertainty prior to correction.

However, after applying corrections for pressure, N<sub>2</sub>O and H<sub>2</sub>O effects, the system delivered stable and consistent results, highlighting the importance of automated correction protocols for reliable high-precision isotope analysis (Figure 02).



02 Isotope stability results of raw instrumental values (crosses) compared to pressure, N<sub>2</sub>O, H<sub>2</sub>O and drift-corrected results (circles)

## Conclusion

This study illustrates the simplicity, precision and accuracy of ABB's OA-ICOS technology, offering a robust and user-friendly solution for demanding isotope applications. ABB's OA-ICOS technology for triple-isotope analysis of nitrates has proven to be an authoritative solution that combines analytical precision with operational ease of use. This approach, featuring a one-step Ti(III) nitrate conversion coupled with a headspace autosampler and OA-ICOS laser-based analyzer, sets a new standard for nitrate isotope analysis and supports high-frequency monitoring, which was impractical with traditional methods. It offers fully automated, high-throughput analysis, enabling rapid and unattended processing. The high precision and data quality of the GLA451-N2O13 platform ensure accurate and reproducible δ-values, resolving even subtle isotopic variations.

Crucially, its unique direct δ<sup>17</sup>O measurement capability provides the full triple-isotope fingerprint, including Δ17O-excess, which is critical for distinguishing atmospheric nitrate sources. Collectively, these advancements make the GLA451-N2O13 an invaluable tool for environmental and analytical scientists, empowering high-resolution monitoring, atmospheric nitrogen research and water quality assessments with unprecedented confidence and efficiency.

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