

Stable Isotope Analysis of Greenhouse Gases Requires Analyte Preconcentration

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Abstract: Nitrous oxide (N₂O) is an important trace gas contributing to global warming and depletion of ozone in the stratosphere. Its increasing abundance is caused mainly by anthropogenic sources, such as application of fertilizers in agriculture or emissions from industry. To understand the N₂O global budget, its sources and sinks need to be well-described and quantified. In this project, a new method for N₂O source appointment was developed that can help with this task. The method is based on analysis of the eight most abundant isotopic molecules of N₂O, using quantum cascade laser absorption spectroscopy (QCLAS). The applicability of the method towards the N₂O biogeochemical cycle was demonstrated on a prominent N₂O source (bacterial denitrification) and the most important N₂O sink (UV photolysis) on samples prepared in laboratory experiments. An extension of the QCLAS method to natural samples can be achieved by hyphenation with a preconcentration technique that increases concentration of the analyte and standardizes the sample matrix. This article provides an overview of currently applied preconcentration techniques in the field of greenhouse-gas analysis and a description of the preconcentration device TREX that will be employed in future projects with the developed QCLAS method.

Keywords: Clumped isotopes · Isotope analysis · Laser spectroscopy · Nitrous oxide · Preconcentration



Kristýna Kantnerová obtained a master's degree in Analytical Chemistry and Quality Engineering at the University of Chemistry and Technology, Prague. She conducted her master thesis in the Molecular Electrochemistry group at the J. Heyrovsky Institute of Physical Chemistry, Czech Academy of Sciences. She was awarded the METAS Award 2021 for her PhD work on developing a quantum cas-

cade laser based (QCLAS) method for the analysis of doubly substituted ('clumped') isotopic species of nitrous oxide and exploring their biogeochemical applications. The work was performed in the groups of Dr. Joachim Mohn at Empa Dübendorf and Prof. Stefano Bernasconi at ETH Zurich. In addition, her PhD thesis was awarded the ETH Medal, the Chorafas Prize, and the ACP Award 2021. Afterwards, she worked as a postdoctoral researcher on an automated preconcentration unit coupled with a QCLAS instrument for isotope analysis of nitrous oxide in the group of Prof. Johan Six at ETH Zurich. Starting 2022, Kristýna is a postdoctoral fellow at University of Colorado Boulder. Her project on a method development for isotope analysis of the oxyanions nitrate and phosphate by electrospray ionization-Orbitrap mass spectrometry is funded by the Swiss National Science Foundation.

1. Introduction

Greenhouse gases (GHGs) have been present in the atmosphere since the formation of the Earth approx. 4.6 billion years

ago.^[1] The composition of the atmosphere has been changing ever since, first due to geological activity, later through the appearance of living organisms (*e.g.* plant photosynthesis), and nowadays due to anthropogenic activities. While the atmospheric composition evolved slowly in the past thousands of years, the recent human-induced changes have occurred very rapidly.

The most important GHGs are CO₂, CH₄, and N₂O (Fig. 1). The change in their atmospheric abundance can be clearly linked to human-induced emissions, starting in the second half of the eighteenth century (Industrial Revolution), mainly with burning of fossil fuels and later introducing fertilizers in agriculture. These three substances are the main cause of GHG-radiative forcing^[3] causing global warming, due to their ability to absorb infrared radiation exiting the atmosphere and emit it back towards the Earth. This so-called greenhouse effect is a natural process; without any GHGs in the atmosphere, the surface temperature on the Earth would be only around −18 °C.^[4] However, the rising abundances of the GHGs have disrupted the sensitive system of our living environment, causing increasing surface temperatures, thinning of the ozone layer, rising of sea levels, and alterations of natural biogeochemical processes.

To mitigate anthropogenic GHG emissions, their source and sink processes and magnitudes must be well-understood. Aside from many atmospheric monitoring programs (*e.g.* Global Atmosphere Watch GAW, the European ICOS program, or the American NOAA program), there have been numerous small-scale studies focusing not only on the GHG abundances, but also abundances of their isotopically substituted molecules (isoto-

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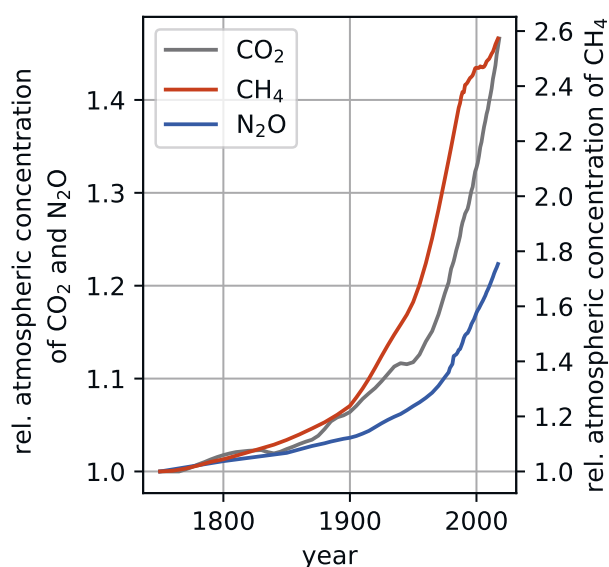


Fig. 1. Atmospheric abundances of the greenhouse gases CO₂, CH₄, and N₂O, shown relative (rel.) to their pre-industrial levels in 1750: CO₂ at 270 ppm, CH₄ at 719.01 ppb, N₂O at 270 ppb. Data provided by the European Environment Agency (EEA).^[2] The current levels are stated in Table 1.

pocules).^[5] It has been shown that GHGs emitted from specific sources possess unique isotopic signatures that can be applied to semi-quantification of sector-specific fluxes and construction of global budgets of the GHGs.^[6]

Isotopic composition of GHGs is commonly analyzed by isotope-ratio mass spectrometry (IRMS).^[7] The technique separates ionized molecules using electric and magnetic fields based on differing mass-to-charge ratios (m/z). Another, less prevalent technique for isotope-ratio analysis of GHGs is laser absorption spectroscopy (LAS). This technique detects rotational-vibrational motions of gaseous or volatile molecules, where frequencies of the internal molecular motions depend on their reduced masses and rotational constants. Therefore, in contrast to IRMS, LAS techniques can directly distinguish isotopocules with the same nominal mass but different molecular position of the isotopic substitution. Such species are called isotopic isomers (isotopomers); an example for N₂O with one ¹⁵N substitution are the isotopomers ¹⁴N¹⁵N¹⁶O and ¹⁵N¹⁴N¹⁶O. In addition, in the last decade, the techniques have been used to develop new methods for analysis of multiply substituted isotopocules (clumped isotopes). More details on this emerging field and the methods can be found in our previous CHIMIA publication^[8] and references therein.

Table 1. Current ambient concentrations of the three most abundant greenhouse gases (after water vapour, H₂O), their global warming potential, and molar amounts required for isotope analysis of their singly substituted isotopocules and clumped isotopes.

greenhouse gas	ambient concentration ^[3]	global warming potential (GWP-100) ^{a [9]}	sample amounts required for analysis of:	
			singly substituted isotopic species	clumped isotopes
CO ₂	413.2 ± 0.2 ppm	1	hundreds of nmol or more ^[10,11]	tens of μmol ^[12] 100 μmol ^[13]
CH ₄	1889 ± 2 ppb	27.9	hundreds of nmol ^[14]	tens of μmol ^[15,16] hundreds of μmol ^[17,18]
N ₂ O	333.2 ± 0.1 ppb	273	tens of nmol ^[19]	4 μmol ^[20] 10 μmol ^[21]

^aGlobal warming potential (GWP-100) is a measure of the heat absorbed by a greenhouse gas after its emission into the atmosphere over the time horizon of 100 years relative to a reference substance, CO₂.^[22]

For both IRMS and LAS techniques, there are specific requirements on sample preparation. First, ambient concentrations of GHGs are too low for direct isotope analysis as the required amount of the analyte is substantially higher (*cf.* Table 1). Second, both techniques are affected by characteristic interference issues. In the case of IRMS, isobaric interferences of species with similar nominal masses can hinder the analysis, unless sufficiently high mass resolution is achieved. For LAS, there can be spectral overlaps when species have rovibrational transitions at nearly the same absorption frequencies. Therefore, an online or offline separation of the target substance from a larger sample amount is usually required to preconcentrate the analyte into a smaller volume and remove potential interferences.

2. Preconcentration Techniques

Common preconcentration techniques for isotope analysis of GHGs take advantage of different boiling points of the analytes and interferences. Their separation is achieved by trapping analytes in a cold trap (cryofocusing), while non-condensable components such as N₂ or O₂ pass the trap and are removed by evacuation. IRMS preconcentration methods apply trapping of the analyte at liquid-nitrogen temperature (−196 °C) followed by separation of the GHGs by gas chromatography (GC) before entering an IRMS instrument.^[23,24] Purification of CH₄ samples for clumped-isotope IRMS analysis has been done using a helium-cooled cryostat alternating between different temperature settings to remove interferences (from −253.15 °C to −203.15 °C).

Prior to cryofocusing, water vapor is usually removed using chemical adsorbents, *e.g.* magnesium perchlorate (Mg(ClO₄)₂) in an inline trap through which the gas is sampled.^[10] Alternatively, water vapor can be separated cryogenically using a stainless-steel coil immersed into an ethanol-dry ice bath (−78 °C)^[20] or with a Nafion permeation dryer^[25] (a co-polymer membrane with high permeability for water). Such a preconcentration routine before IRMS analysis can be performed offline using a manual procedure, but automated instruments interfaced with water removal, cryofocusing and GC are usually employed.^[10]

Preconcentration before LAS analysis has been mostly achieved with fully automated liquid-N₂-free devices.^[14,26,27] The core part of these devices is a cryogenic refrigeration system or Stirling cooler that actively cools a stainless-steel trap filled with an adsorbent through which dried air or sampled gas are purged. A more detailed description follows in Section 4. The hyphenation of the automatic preconcentration device and a LAS instrument is suitable for unattended field observations, delivering high-precision isotope data in nearly real time.^[28]

3. Applications in the Award-winning Project

N_2O is an isotopically complex molecule that carries a wealth of information, through the abundance of ^{18}O , the site-specific distribution of ^{15}N in the asymmetric N_2O molecule, and the abundance of clumped isotopes.^[29,30] The award-winning PhD work focused on developing a method with quantum cascade LAS (QCLAS) for the analysis of clumped isotopic species of N_2O and exploring isotope signatures of source and sink processes. The developed QCLAS method provides simultaneous high-precision isotope data of eight N_2O isotopocules – the most abundant species $^{14}N^{14}N^{16}O$, four singly substituted species $^{14}N^{15}N^{16}O$, $^{15}N^{14}N^{16}O$, $^{14}N^{14}N^{17}O$, and $^{14}N^{14}N^{18}O$, and so far not accessible doubly substituted (clumped) species $^{14}N^{15}N^{18}O$, $^{15}N^{14}N^{18}O$, and $^{15}N^{15}N^{16}O$.^[20] The method requires samples of N_2O of approx. 1.5% in pure N_2 .

During the PhD project, the QCLAS method, together with a new mole-fraction calibration scheme for quantification of the clumped N_2O species, was applied to explore clumped isotope signatures as potential tracers for the global cycle of N_2O in two projects. In the scope of the first application, Kristýna spent a 3-month research stay in the group of Prof. Naohiro Yoshida at Tokyo Institute of Technology. There, she prepared samples of N_2O from bacterial incubations.

The majority of natural N_2O emissions is generally attributed to bacterial denitrification and nitrification. During the research stay, the denitrifying bacteria *Pseudomonas aureofaciens* and the nitrifying bacteria *Nitrosococcus oceani* were cultivated in nitrogen-containing media and the N_2O produced was purified using a preconcentration line built in-house.^[25] Upstream of the preconcentration, CO_2 and H_2O were removed before N_2O was cryofocused manually in a stainless-steel loop in a liquid- N_2 bath. The purified N_2O samples were collected into stainless-steel cylinders and shipped to Empa for QCLAS analysis. The samples were diluted with N_2 to 1.55% N_2O prior to analysis.

Incubations of the denitrifying bacteria in a nitrate (NO_3^-) medium provided large amounts of N_2O , as N_2O is the final product of NO_3^- reduction for the cultivated bacterial strain of *Pseudomonas aureofaciens* (Fig. 2). N_2O was sampled one day, three days, and seven days after the incubation started, to obtain temporal trends of isotopic composition of the produced gas. From the temporal trends, isotope enrichment factors during NO_3^- reduction to N_2O were obtained. Isotopic signatures of the singly substituted species and the clumped isotopocules suggest a *trans*-isomeric structure of a reaction intermediate that is involved in the enzymatically catalyzed NO reduction, where two N atoms coming from two different NO_3^- species combine and the N–N bond in the final N_2O is formed. A more detailed interpretation of the obtained data requires theoretical models, which have not been developed yet; for more details see ref. [25].

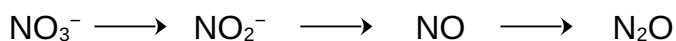


Fig. 2. Reaction sequence occurring during denitrification by *Pseudomonas aureofaciens*: nitrate (NO_3^-) is reduced through nitrite (NO_2^-) and nitric oxide (NO) to N_2O .

In the nitrification process, N_2O is produced only as a side product during oxidation of hydroxylamine (NH_2OH ; Fig. 3).^[31] For several repetitions of the QCLAS analysis and purging of gas lines, around 50 – 100 μmol of pure N_2O are required. However, due to relatively short lifetimes of the cultivated nitrifying bacteria *Nitrosococcus oceani* and low N_2O yields, data from the QCLAS analysis of the nitrification-derived N_2O could not be evaluated in this project.

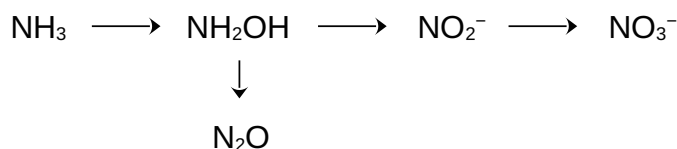


Fig. 3. Reaction sequence occurring during nitrification by *Nitrosococcus oceani*: ammonia (NH_3) is oxidized through hydroxylamine (NH_2OH) and nitrite (NO_2^-) to nitrate (NO_3^-). N_2O is produced in a side reaction by both biotic and abiotic oxidations of NH_2OH .

In the second application, the QCLAS method was employed to study the most important N_2O sink that occurs in the stratosphere – photolysis by UV light. Aliquots of 1.70% N_2O in N_2 were gradually photolyzed by UV light in a custom-made photoreactor at two wavelengths, 200 nm and 214 nm, as UV light in this spectral region has the largest contribution to N_2O photolysis. The gas was directly sampled every 12 hours from the photoreactor to the QCLAS instrument using an automated gas inlet system.^[32] Unique isotope fractionation constants for the N_2O isotopocules were retrieved from the obtained temporally resolved data and compared with theoretical fractionation constants that were calculated based on previously published absorption cross sections derived from first principles.

The experiments showed that stratospheric photolysis has a low impact on the clumped isotope signatures of atmospheric N_2O . Therefore, variations in the N_2O isotopic composition are expected to be mostly affected by sources and not by photolysis. More details on the results and their discussion can be found in ref. [32].

4. TREX – A Preconcentration Device for N_2O Analysis

Sufficiently high N_2O concentrations for direct QCLAS analysis can be obtained under laboratory settings, as was shown in the two previous applications. However, in most natural samples, N_2O concentrations are too low for direct analysis. Therefore, as described in Section 2, a preconcentration technique must be employed to study singly substituted molecules and also the more rare clumped isotopes with sufficient accuracy.

For QCLAS analysis of the singly substituted N_2O species, automated preconcentration systems have been implemented, e.g. in field studies of ecosystem-^[33] or soil-emitted^[28] N_2O . Advantages of using such an automated preconcentration device include higher temporal data resolution and better data quality (no sampling effects) with less manual work, less coordination effort, and long-term unattended operation. In addition, the preconcentration procedure automatically removes gas matrix effects (changes in the bulk gas composition) and spectral interferences that would otherwise interfere with the QCLAS analysis. These effects occur whenever concentration of N_2 , O_2 , argon, or an IR-active compound deviate between sample and reference gases.^[34]

Fig. 4 shows an automated preconcentration device developed at Empa, called TRace gas EXtractor (TREX). The device can cryogenically adsorb N_2O (or another trace gas) from sampled gas or air, separate co-adsorbed species applying stepwise temperature-controlled heating (e.g. CO), and finally desorb the purified N_2O into the optical cell of a QCLAS instrument. The core part of the device is a stainless-steel trap filled with HayeSep D adsorbent. The trap is attached to a linear driver and thus can be pressed against a copper base plate that is cooled down by a Stirling cooler to -210 °C. Upon thermal contact with the base plate, the trap is cooled down to approx. -150 °C and N_2O is adsorbed. After sufficient trapping time, the trap is moved away from the base plate and heated by active resistive heating. In the final heating step, N_2O is desorbed, transferred to the QCLAS optical cell and diluted with a defined matrix gas prior to the QCLAS analysis. A more detailed description of the operation

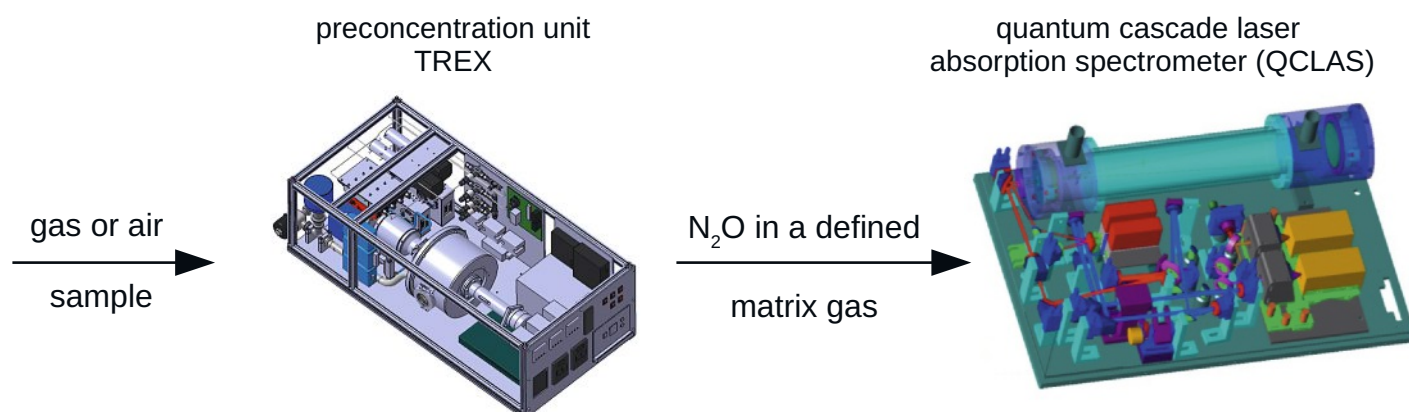


Fig. 4. Scheme of the TREX-QCLAS system. In the first step, the analyte (in this case N_2O) is cryofocused in an adsorbent-filled trap cooled by a Stirling cooler in the preconcentration unit TREX and the target substance is separated from potential interferences. In the second step, the analyte is purged out of the trap by a matrix gas to the optical cell of a QCLAS instrument, where the isotopic composition of the analyte is measured.

can be found in our previous CHIMIA publication^[8] or in the publications cited in this section.

The design of such an automatic preconcentration device was first applied for analysis of ambient N_2O by Mohn *et al.*^[26] Based on that, Eyer *et al.*^[14] developed a more compact device with higher cooling power, capable of extracting CH_4 from ambient air. Currently, the Sustainable Agroecosystems group of Prof. Six at ETH Zurich is the first group outside of Empa running a TREX-QCLAS system (a postdoctoral project of the main author). The instrument is based on a replicate of the TREX device that was used in the work of Ibraim *et al.* for field experiments.^[35] The new TREX device was constructed at ETH Zurich by E. Ibraim, and finalized and tested by the main author of this contribution.

An important parameter of a preconcentration device is the capacity of the trap for the trace gas adsorption. The capacity of the ETH TREX device was tested by continuous adsorption of N_2O from a mixture of N_2O in synthetic air (N_2 and O_2 in 70:30 ratio) while analyzing the gas at the outlet of the trap by the QCLAS instrument. In this so-called breakthrough experiment, the TREX device trapped approx. 14 μmol of N_2O , corresponding to the amount of N_2O in more than 1,000 L of ambient air, and no breakthrough was observed in the experimental timeframe. In a breakthrough experiment performed at Empa on the TREX device that was originally employed for CH_4 adsorption,^[14] the breakthrough of the trap capacity was observed after adsorbing 8.2 mmol of N_2O (2,170 L of gas at 90.9 ppm N_2O ; 45.3 hours).

The trap capacity is therefore large enough to preconcentrate sufficient amounts of N_2O even for clumped isotope analysis, provided that interfering CO_2 is removed from the sampled gas prior to adsorption (*e.g.* using an Ascarite trap).^[35] In this application, approx. 360 L of ambient air would be processed (approx. 5 μmol of pure N_2O per analysis). To achieve high output concentration, the current design of the TREX device requires certain modifications, mainly introducing a second, smaller trap to focus the N_2O gas into smaller volume after desorption from the first trap. This also holds advantages with respect to separating gases with similar boiling points, *e.g.* O_2 and CH_4 .^[16]

5. Conclusions

Within the award-winning PhD project, a new analytical method based on the QCLAS technique was developed. Together with a new calibration scheme, it can be directly employed for simultaneous analysis of the eight most abundant N_2O isotopocules, including the three most abundant clumped isotopic species $^{14}N^{15}N^{18}O$, $^{15}N^{14}N^{18}O$, and $^{15}N^{15}N^{16}O$. With this analytical method,

we have opened unexplored possibilities for research in the N_2O biogeochemical cycle, demonstrated in laboratory settings on microbial production and UV photolysis.

For future projects targeting time-resolved data of clumped N_2O isotopes, the developed QCLAS method is to be connected with an automated preconcentration unit of the described TREX design. This will be a part of a follow-up project funded by the Swiss National Science Foundation (SNF; a collaboration between Empa and University of Basel) that is going to start in summer 2022. The aim of the project is to extend the database of prominent N_2O microbial and abiotic production pathways in pure culture and develop a theoretical framework for data interpretation. In addition, under a new SNF project at the Sustainable Agroecosystems group at ETH Zurich, automated gas chambers will be coupled to their TREX-QCLAS system. The analysis setup will be used to obtain the first online measurements of N_2O fluxes and its isotopic composition from tropical agricultural soils in the Eldoret region of Kenya. The isotopic measurements will be used to infer N_2O production and consumption rates for different pathways to advance our understanding of the major drivers of variability in tropical N_2O fluxes.

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CRedit Author Statement

Kristýna Kantnerová: Validation, Formal analysis, Investigation, Writing - Original Draft, Visualization, Funding acquisition. Matti Barthel: Conceptualization, Resources, Writing - Review & Editing. Johan Six: Conceptualization, Writing - Review & Editing, Supervision, Project administration, Funding acquisition. Lukas Emmenegger: Writing - Review & Editing, Supervision, Project administration, Funding acquisition. Stefano M. Bernasconi: Conceptualization, Writing - Review & Editing, Supervision, Project administration, Funding acquisition. Joachim Mohn: Conceptualization, Resources, Writing - Review & Editing, Supervision, Project administration, Funding acquisition

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