

## Development of new N<sub>2</sub>O reference materials for $\delta^{15}\text{N}$ , $\delta^{18}\text{O}$ and $^{15}\text{N}$ site preference within the EMPIR project SIRS

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In recent years, research on nitrous oxide (N<sub>2</sub>O) stable isotopes has significantly advanced, addressing an increasing number of research questions in biogeochemical and atmospheric sciences [1]. An important milestone was the development of optical isotope ratio spectroscopy (OIRS), which is inherently specific for structural isomers ( $^{15}\text{N}^{14}\text{N}^{16}\text{O}$  vs.  $^{14}\text{N}^{15}\text{N}^{16}\text{O}$ ) and capable to collect real-time data with high temporal resolution, complementary to the well-established isotope-ratio mass-spectrometry (IRMS) method.

The compatibility between different IRMS and OIRS laboratories, however, was shown to be limited, in particular for  $^{15}\text{N}$  site preference, i.e. the difference between  $^{15}\text{N}$  abundance in central (N\*NO) and end (\*NNO) position [2]. This was attributed to two reasons, first no WMO-GAW Central Calibration Laboratory (CCL) for N<sub>2</sub>O stable isotopes currently exists and second no international reference material in the form of gaseous N<sub>2</sub>O with stated uncertainty is available. In addition, the accuracy of the NH<sub>4</sub>NO<sub>3</sub> decomposition reaction, which provides the link between  $^{15}\text{N}$  site preference and the international  $^{15}\text{N}/^{14}\text{N}$  scale, was recently found to be limited by non-quantitative NH<sub>4</sub>NO<sub>3</sub> decomposition in combination with substantially different isotope enrichment factors for both nitrogen atoms [3].

The above tasks will be addressed in the upcoming European Metrology Programme for Innovation and Research (EMPIR) project “Metrology for Stable Isotope Reference Standards (SIRS)” 2017-2020. With respect to N<sub>2</sub>O reference materials the SIRS project will focus on the following subjects:

- 1) Develop improved techniques to characterise N<sub>2</sub>O gases for  $\delta^{15}\text{N}$ ,  $\delta^{18}\text{O}$  and the  $^{15}\text{N}$  site preference with reference to the respective international isotope ratio scales including an uncertainty assessment.
- 2) Develop at least three new international gaseous N<sub>2</sub>O reference materials for  $\delta^{15}\text{N}^{\alpha}$ ,  $\delta^{15}\text{N}^{\beta}$ ,  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$ , available both as pure substance and diluted in whole air.

### References

[1] S. Toyoda et al., Isotopocule analysis of biologically produced nitrous oxide in various environments, *Mass Spectrom. Rev.*, 30, 135-160, 2017.

[2] J. Mohn et al., Interlaboratory assessment of nitrous oxide isotopomer analysis by isotope ratio mass spectrometry and laser spectroscopy: current status and perspectives, *Rapid Commun. Mass Spectrom.*, 28, 1995–2007, 2014.

[3] J. Mohn et al. Reassessment of the NH<sub>4</sub>NO<sub>3</sub> thermal decomposition technique for calibration of the N<sub>2</sub>O isotopic composition, *Rapid Commun. Mass Spectrom.*, 30, 2487–2496, 2016.