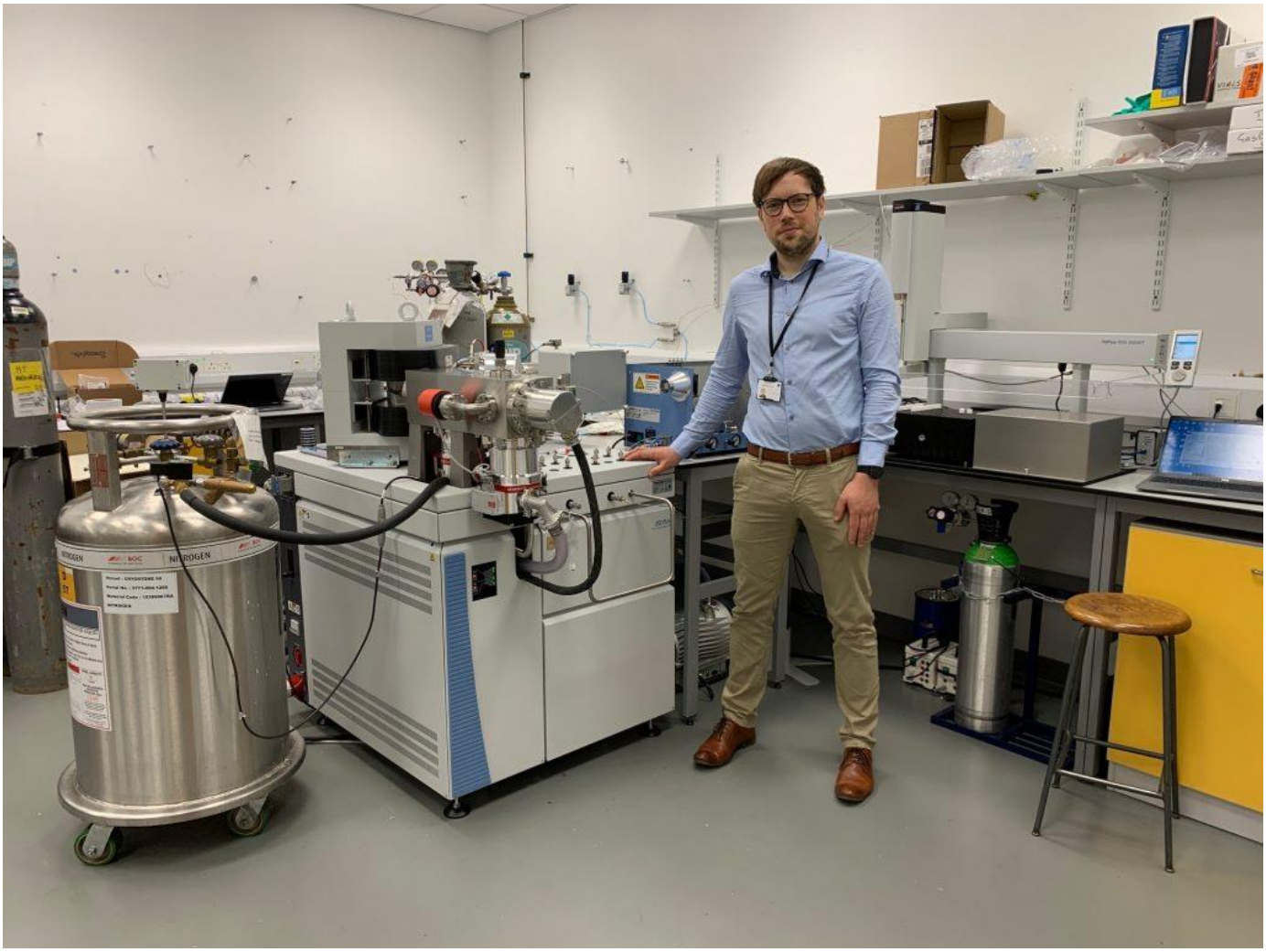
New Thermo Scientific 253 plus 10 kV Isotope Ratio Mass Spectrometer at NPL



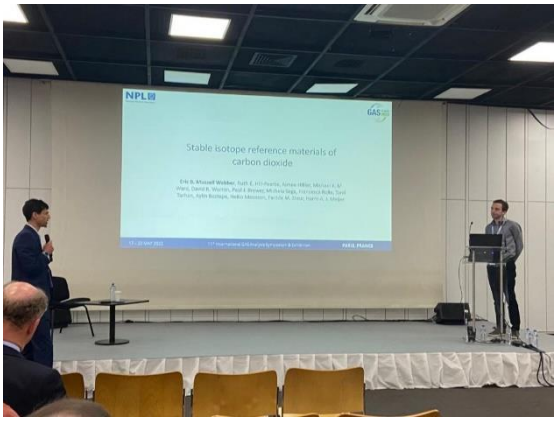
Christoph Nehrbass-Ahles, Senior Research Scientist at NPL with the IRMS

Project partner NPL have acquired a new Thermo Scientific 253 plus 10 kV Isotope Ratio Mass Spectrometer (IRMS). The IRMS will be able to measure $d^{13}C\text{-}CO_2$ and $d^{18}O\text{-}CO_2$ on pure CO_2 samples. After a period of method development in 2023, NPL will look to expand their capabilities to measure atmospheric $d^{13}C\text{-}CO_2$ and $d^{18}O\text{-}CO_2$ as well as $d^{13}CH_4$ and $d^{2}H\text{-}CH_4$ in air. For the STELLAR project, the IRMS will be able to further work currently progressing under WP1 and WP2.

The aim of WP1 is to considerably improve gas reference materials of carbon dioxide that were developed as part of the EMPIR funded SIRS project (16ENV06). These reference materials have target uncertainties of 0.1 ‰ for $d^{13}C\text{-}CO_2$ and 0.5 ‰ for $d^{18}O\text{-}CO_2$ measurements and must be strengthened to make them meet requirements for underpinning global monitoring.

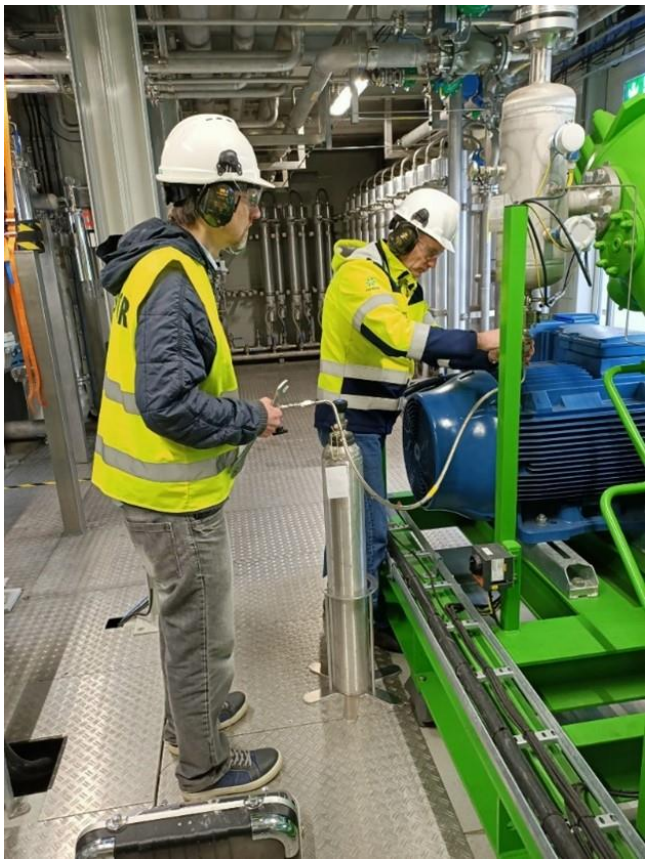
The aim WP2 is to develop first time gas reference materials of pure methane and at 1.85 µmol mol^{-1} in an air matrix on a large scale and with a repeatability in the preparation process of 0.02 ‰ for d^{13}C-CH_4 and of 1 ‰ for d^2H-CH_4 and with target uncertainties of 0.2 ‰ for d^{13}C-CH_4 and 5 ‰ for d^2H-CH_4. The stability of the isotopic composition reference materials should be more than two years. The d^{13}C-CH_4 and d^2H-CH_4 isotope ratio reference materials will be traceable to the VPDB and VSMOW/SLAP scales, respectively.

STELLAR Presented at Gas Analysis 2022



Eric Mussell Webber of project partner NPL recently presented at the Gas Analysis 2022 conference, held in Paris, France. The title was Stable Isotope reference materials of carbon dioxide, presenting progress from WP1 in STELLAR and the results of the SIRS project. The conference was attended by experts from across the gas analysis field, including those from industry, metrological institutes, and research laboratories.

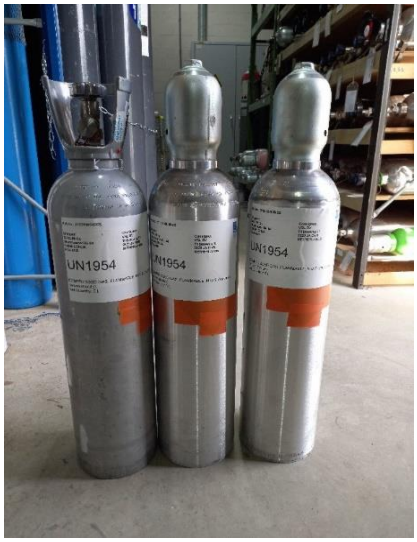
Nordsol and Gasum supply biomethane samples for the Stellar project



Filling of the cylinders with biomethane at the Nordsol bio-LNG installation by Jerom van Roosmalen, CEO of Nordsol.

Global warming is one of the greatest current risks to humanity. Emissions of the major contributing greenhouse gases methane and carbon dioxide must be reduced to prevent even more severe climate changes. Both gases are currently at record high levels in the atmosphere, and this is mainly due to anthropogenic (human) activities. To determine the effectiveness of emission reduction policies it is essential to discriminate between anthropogenic sources and natural contributions. This can be done by measuring the stable isotopic composition of carbon dioxide and methane. The Stellar project will fill the existing traceability gap in the measurement of the isotopic composition of both gases by providing a new infrastructure for delivering gaseous carbon dioxide and methane reference materials and methods. Within the Stellar project, VSL is leading the development of isotopic methane reference materials. To make these reference materials, methane from fossil origin is mixed with methane from biogenic origin. Methane of fossil origin has been supplied by project partner Air Liquide.

Methane from biogenic origin was recently supplied by Nordsol from a newly constructed bio-LNG installation in a partnership with Shell and Renewi. This bio-LNG installation is located in Amsterdam and was officially put into service by the Dutch king Willem-Alexander last October. In this

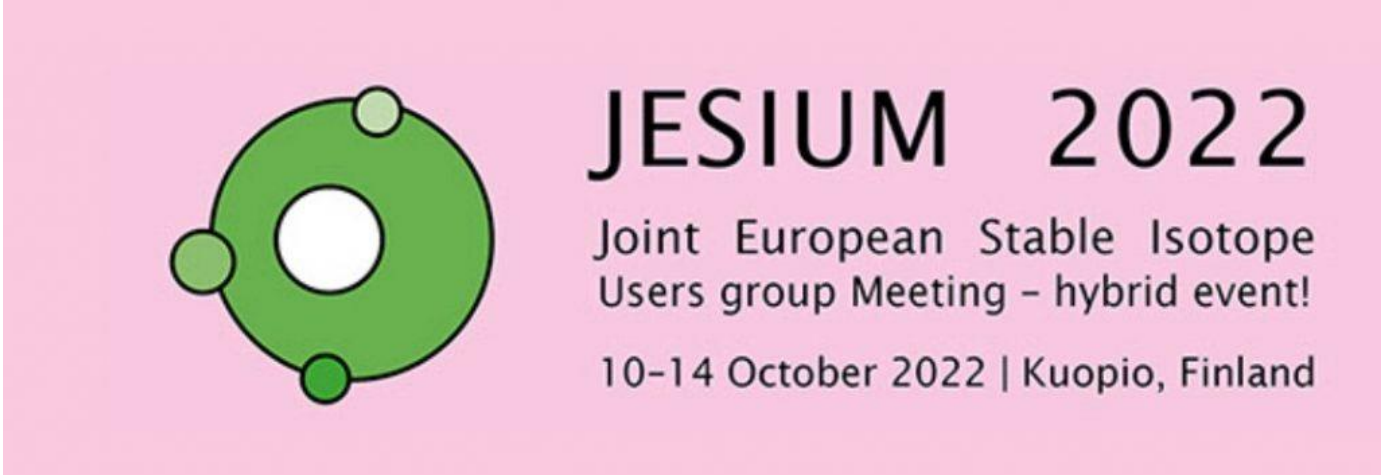


The 3 cylinders filled by Gasum with biomethane from their Lohja plant.

installation, biogas is made from organic waste like out-of-date peanut butter, then purified to obtain biomethane and finally cooled down to obtain bio-LNG. Samples for VSL were taken after purification but before the cooling step.

Another source of biogenic methane was supplied by the Finnish Gas company Gasum. Gasum is the main processer of biodegradable waste and supplier of biogas in the Nordic countries. They kindly supplied biomethane from their Lohja plant by filling 3 cylinders with gas for the Stellar project.

JESIUM 2022, Kuopio, Finland 10–14 October 2022



Project partner UEF have organised the Joint European Stable Isotope Users group Meeting (JESIUM) to be held in Kuopio, Finland – and online, on the 10–14 October 2022.

Stable isotopes have become a crucial research tool in a wide range of scientific fields. The purpose of the meeting is to bring together a broad range of stable isotope scientists from all over the world, to encourage communication across disciplines and country boundaries.

The meeting aims to reflect on ideas and technologies through oral and poster presentations, informal discussions and debates, and during great social events.

For more information, please visit the website: https://www.jesium2022-kuopio.org/

NPL illustrate project progress to the CCQM-IRWG

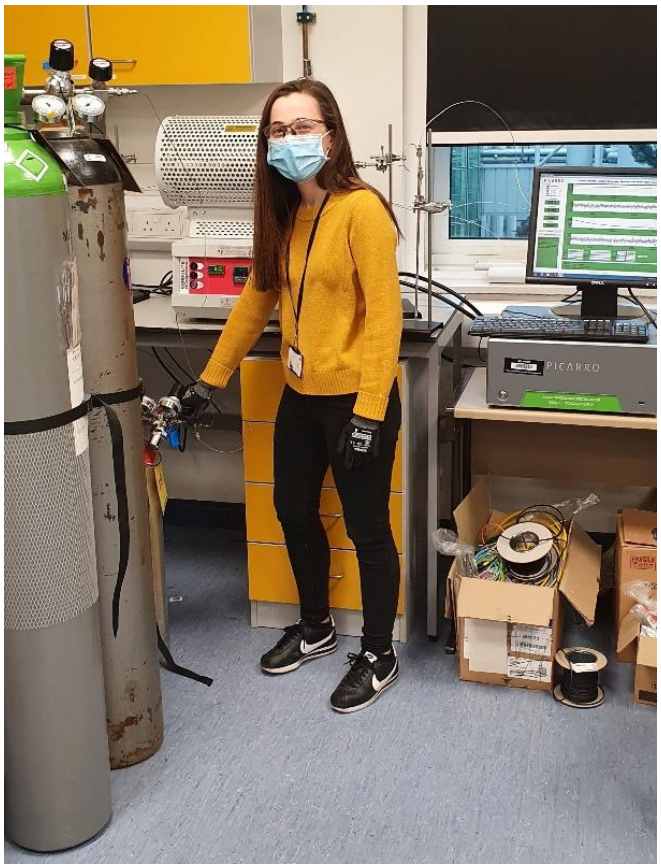
Paul Brewer of project partner NPL recently provided a presentation to the CCQM-IRWG (CCQM Working Group on Isotope Ratios) on work progressed within the 16ENV06 SIRS and 19ENV05 STELLAR projects. *Report from SIRS and STELLAR* can be found here and also on our Documents page.

The overall objective of the SIRS project was to fill a traceability gap by providing a new infrastructure for stable isotopes to deliver international gaseous CO_2 reference materials to meet the increasing demand and international gaseous N_2O reference materials with stated uncertainties to underpin measurements. The STELLAR project builds on this work.

The CCQM (Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology) is responsible for developing, improving and documenting the equivalence of national standards (certified reference materials and reference methods) for chemical and biological measurements. It advises the International Committee for Weights and Measures (CIPM) on matters related to chemical and biological measurements including advice on the BIPM scientific programme activities.

The BIPM is the international organization established by the Metre Convention, through which Member States act together on matters related to measurement science and measurement standards. It is also the home of the International System of Units (SI) and the international reference time scale (UTC).

Testing at NPL



Aimee Hillier of project partner NPL and the testing of the CH_4 to CO_2 combustion system with ppm level CH_4 and measuring the output on the CRDS (Cavity Ring-Down Spectroscopy). This forms part of an activity where NPL will develop a facility to convert the methane reference materials developed to carbon dioxide. In developing the facility, a full assessment of the sensitivities of the conversion process will be made in order to inform the uncertainty budget. Project partners RUG and MPG will also conduct a comparison of the pure carbon dioxide generated by combustion to the pure carbon dioxide reference materials from the 16ENV06 SIRS project using IRMS (Isotope Ratio Mass Spectrometry) and NPL will provide the reference materials.

This work falls under WP2 of the project. The aim of WP2 is to develop first time gas reference materials of pure methane and at 1.85 µmol mol^{-1} in an air matrix on a large scale and with a repeatability in the preparation process of 0.02 ‰ for $d^{13}C\text{-}CH_4$ and of 1 ‰ for $d^{2}H\text{-}CH_4$ and with target uncertainties of 0.2 ‰ for $d^{13}C\text{-}CH_4$ and 5 ‰ for $d^{2}H\text{-}CH_4$.

Optical Isotope Ratio Spectroscopy – Complementing Isotope Ratio Mass Spectrometry

Project partners from PTB, VSL, Empa, INRIM, RUG and DFM have collaborated together on the following paper, *Optical Isotope Ratio Spectroscopy – Complementing Isotope Ratio Mass Spectrometry*.

Isotope ratio measurements and scale definitions are typically related to mass specectroscopy. This work discusses the challenges of optical isotope ratio spectroscopy and its prospects to significantly complement isotope ratio mass spectrometry. The paper was part of the OSA Optical Sensors and Sensing Congress 2021 and forms part of the session Isotopes and Metrology (EW5D) that occurred online and in Washington, DC United States 19–23 July 2021. You can find the paper here and over on our Documents page.

Boreas: A Sample Preparation-Coupled Laser Spectrometer System for Simultaneous High-Precision in Situ Analysis of $\delta^{13}C$ and $\delta^{2}H$ from Ambient Air Methane

Project partner NPL have collaborated with the Department of Earth Sciences, Royal Holloway, University of London on the following paper for *Analytical Chemistry* (Anal. Chem. 2021, 93, 29, 10141–10151). *Boreas: A Sample Preparation-Coupled Laser Spectrometer System for Simultaneous High-Precision in Situ Analysis of $\delta^{13}C$ and $\delta^{2}H$ from Ambient Air Methane* .

The paper presents a new instrument, “Boreas”, a cryogen-free methane (CH_4) preconcentration system coupled to a dual-laser spectrometer for making simultaneous measurements of $\delta^{13}C(CH_4)$ and $\delta^{2}H(CH_4)$ in ambient air. Excluding isotope ratio scale uncertainty, we estimate a typical standard measurement uncertainty for an ambient air sample of 0.07‰ for $\delta^{13}C(CH_4)$ and 0.9‰ for $\delta^{2}H(CH_4)$, which are the lowest reported for a laser spectroscopy-based system and comparable to isotope ratio mass spectrometry. We trap CH_4 (~1.9 μmol mol^{-1}) from ~5 L of air onto the front end of a packed column, subsequently separating CH_4 from interferences using a controlled temperature ramp with nitrogen (N_2) as the carrier gas, before eluting CH_4 at ~550 μmol mol^{-1}. This processed sample is then delivered to an infrared laser spectrometer for measuring the amount fractions of $^{12}CH_4$, $^{13}CH_4$, and $^{12}CH_3D$ isotopologues. We calibrate the instrument using a set of gravimetrically prepared amount fraction primary reference materials directly into the laser spectrometer that span a range of 500–626 μmol mol^{-1} (CH_4 in N_2) made from a single pure CH_4 source that has been isotopically characterized for $\delta^{13}C(CH_4)$ by IRMS. Under the principle of identical treatment, a compressed ambient air sample is used as a working standard and measured between air samples, from which a final calibrated isotope ratio is calculated. Finally, we make automated measurements of both $\delta^{13}C(CH_4)$ and $\delta^{2}H(CH_4)$ in over 200 ambient air samples and demonstrate the application of Boreas for deployment to atmospheric monitoring sites.

Papers

- *Boreas: A Sample Preparation-Coupled Laser Spectrometer System for Simultaneous High-Precision in Situ Analysis of $\delta^{13}C$ and $\delta^{2}H$ from Ambient Air Methane*
  Chris Rennick, Tim Arnold, Emmal Safi, Alice Drinkwater, Caroline Dylag, Eric Mussell Webber, Ruth Hill-Pearce, David R. Worton, Francesco Bausi, and Dave Lowry

- *Optical Isotope Ratio Spectroscopy – Complementing Isotope Ratio Mass Spectrometry*
  Jelka Braden-Behrens, Heleen Meuzelaar, Joachim Mohn, Javis A. Nwaboh, Stefan Persijn, Francesca Rolle, Michela Sega, Pharahilda M. Steur, Lars Wacker, Kerstin Zeyer, Olav Werhahn and Volker Ebert

Acknowledgements

The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

This project has received funding from the EMPIR programme co-financed by the Participating States and from the European Union's Horizon 2020 research and innovation programme.