



Final Publishable JRP Summary for ENV52 HIGHGAS Metrology for High-Impact Greenhouse Gases

Overview

Global climate change poses one of the greatest risks to society worldwide. Increasing amounts of greenhouse gases are the driver behind the observed rise in global temperature. Thus, atmospheric measurements of greenhouse gases are pivotal to understanding the changes in the Earth's climate and the influence of human activity. There is an urgent requirement for a validated and traceable measurement infrastructure to provide the basis for stable and comparable measurements of the highest impact greenhouse gases (i.e. carbon dioxide (CO₂), carbon monoxide (CO), nitrogen dioxide (N₂O) and methane (CH₄)). This will improve the data used to compile national greenhouse gas inventories and help demonstrate compliance with legislation or recommendations, such as the Kyoto protocol, European air quality directives, World Meteorological Organisation Data Quality Objectives (WMO DQO) and COP 21 (i.e. the 2015 United Nations Climate Change Conference). The project developed new accurate reference standards for CO₂, CO, N₂O, CH₄ and fluorinated gases, which reflect the amount fractions typically found in the atmosphere. Methods for the production and storage of the new reference standards were also developed and compared to ensure the stability and quality of the reference standards.

Need for the project

Understanding the chemistry of the atmosphere and the mechanisms that control the levels of the gases involved in radiative forcing (the basic mechanism behind global climate change) are a global priority. These high impact greenhouse gases govern a family of chemical reactions that determine the oxidising capacity of the atmosphere and influence the formation of tropospheric ozone and aerosols. Therefore the gases are relevant to both air quality and climate change. National and international legislation aimed at reducing emissions of greenhouse gases requires accurate measurement with low uncertainty of the high impact greenhouse gases in the atmosphere. This will improve the understanding of these gases, inform upcoming legislation, ensure compliance with emission targets, and potentially control the influence of human activity.

The project will look at developing new accurate reference standards, which are traceable to the mole via the kilogram for the high impact greenhouse gases CO₂, CO, N₂O and CH₄. Existing reference standards for these gases are traceable to artefacts but not with enough accuracy to meet the new legislative requirements. The project will also develop accurate standards for new fluorinated (F) gases which are in the atmosphere in very low concentrations, and for which there are currently no standards.

Current measurements for greenhouse gases are done spectroscopically, observing the adsorption of certain wavelengths of light that indicate the presence and abundance of different elements. However, this means that if a gas has more than one isotopologue, then if the isotopic composition of the synthetic reference standards differs from that of the ambient atmosphere a systematic bias will result reducing the accuracy of the measurements. Therefore, there is a need to produce synthetic standards with the same isotopic composition as ambient atmosphere, and also to investigate the effect of impurities on spectroscopic measurements.

To achieve a robust measurement infrastructure for greenhouse gases, the project will focus on three specific user requirements: (i) the development of high accuracy reference standards that can be stored in high pressure cylinders; (ii) novel dynamic methods for the generation of reference standards in the field, and (iii) the development of spectroscopic methods, both as transfer standards and to provide measurements of isotopic composition.

Report Status: PU Public



Scientific and technical objectives

The scientific and technical objectives for this project are to:

1. Develop static reference standards of CO₂, CH₄, N₂O and CO at levels of precision and accuracy to meet the challenging WMO DQOs for underpinning trend assessment.
2. Develop new approaches and devices for generating accurate standard gas mixtures for CO and N₂O for validation of reference standards and for dissemination to the field.
3. Develop new dynamic reference standards for on-site preparation of sulphur hexafluoride (SF₆) and a selection of other challenging, high impact F-gases at trace concentrations.
4. Develop complementary optical methods as multi-component transfer standards.
5. Use optical methods to provide the metrology to support isotopic composition measurements of several components (e.g. CO₂ and N₂O) to enable gravimetric reference standards that meet the WMO DQOs and to enable studies that determine the origin of these components in the atmosphere.
6. Assess the comparability of traceable reference standards to existing standards and scales used by the atmospheric monitoring community.

Results & Conclusions

Improved stability and accuracy static reference standards of CO₂, CH₄, N₂O and CO

A static reference standard is a cylinder containing the reference gas at the required amount fraction, within the stated uncertainties, and stable within the stated time frame. A dynamic standard is produced as required by diluting a stable higher amount fraction reference standard to the required amount fraction, within the stated uncertainties. A dynamic standard is required when a static reference standard is not stable at the required amount fraction. New SI traceable reference standards of CO₂, CH₄ and CO at ambient amount fractions in high pressure cylinders were developed with uncertainties that meet the WMO DQOs and are now available under ISO 17025 accreditation. An interlaboratory comparison with the National Oceanic and Atmospheric Administration (NOAA) scale (as part of objective 6) demonstrated that these new reference standards meet the WMO DQOs.

The long term stability of the static reference standard samples in different cylinders was investigated. There was no significant instability in CH₄, CO₂ or N₂O regardless of the cylinder type. CO samples showed a significant improvement in stability using cylinders treated with Air Products' Experis coating, compared with a standard untreated cylinder. For N₂O, the WMO DQOs are still very challenging, however, new measurement capabilities developed by VSL had the potential to reduce the uncertainty.

The project developed the first ever synthetic zero air reference standard with a matrix composition that matches ambient composition (nitrogen, oxygen and argon) and with an accurate fraction of impurities of CO₂, CH₄, N₂O and CO. This synthetic zero air reference standard allows accurate baseline calibration of spectroscopic instrumentation or analyser.

The isotopic composition of the static CO₂ reference standards were blended to match atmospheric isotopic composition to minimise any biases resulting from spectroscopic instrumentation that only detect a single isotopologue.

Develop improved approaches for generating accurate standard gas mixtures for CO and N₂O

High accuracy dynamic generation facilities for CO and N₂O reference standards were developed and validated. The dynamic generation facilities for CO reference standards have smaller uncertainties of 1.03 nmol/mol than the WMO compatibility goals of 2 nmol/mol. For N₂O, the WMO DQOs are still very challenging (0.1 nmol/mol) and dynamic reference standards of N₂O with uncertainties of 0.9 nmol/mol demonstrated that the state of the art is still not good enough although substantial progress has been made. These dynamic generation devices have the potential to be used in the field as portable reference standards and have

delivered repeatability better than the WMO DQOs providing accessible and highly repeatable propagation of the calibration scale from one artefact to another.

Develop dynamic reference standards of high impact F-gases at trace amount fractions.

A new method to generate accurate SI-traceable reference gas mixtures of high impact fluorinated gases (SF₆, pentafluoroethane (HFC-125) and 2,3,3,3-tetrafluoropropene (HFC-1234yf) at ambient molar fractions in synthetic air was developed and validated. The newly produced reference gas mixtures were in agreement, within the uncertainties, within the existing calibration scales developed by Scripps Institute of Oceanography (SIO) as part of the Advanced Global Atmospheric Gases Experiment (AGAGE).

When newly emitted compounds, such as HFO-1234yf which is a refrigerant, are detected in the atmosphere, dynamic generation methods have proved to be an excellent means to produce the necessary reference gas mixtures rapidly, and with SI-traceability. This means that the dynamic reference standards can be used to demonstrate compliance with international agreements and requirements such as WMO DQOs.

A portable generator to make on-site instrument calibration and linearity tests of fluorinated gases was developed and validated. METAS developed a multi-component suite of reference gas mixtures for SF₆, HFC-125, HFO-1234yf, (1,1-difluoro-1,2-dichloroethane) HCFC-132b and (chlorotrifluoromethane) CFC-13 at atmospheric molar fractions. This is the first ever primary calibration scale for HCFC-132b. In addition the project produced an improved calibration scales for CFC-13 and HFO-1234yf and which can now be compared with existing scales for SF₆ and HFC-125.

Develop complementary optical methods as multi-component transfer standards

Existing spectroscopic methods including Cavity Ring-Down Spectroscopy, Tunable Diode Laser Absorption Spectroscopy (TDLAS) and Quantum Cascade Laser Absorption Spectroscopy were reviewed by the project partners in the international community responsible for the measurement of greenhouse gases. The suitability of spectral line data, for use in optical transfer standards for CO and CO₂ was defined in terms of uncertainty levels and traceability to the SI.

A method for the development of optical transfer standards for CO and CO₂ was developed. A new OTS based on TDLAS was developed for atmospheric CO and CO₂ measurements. TDLAS means that the laser wavelength can be varied to detect certain elements. An optical transfer standard (OTS) system based on TDLAS for CO and CO₂ was developed and validated against gravimetric standards. This new OTS system provides direct traceability for the amount fraction results to the SI. The OTS systems also provides an alternative to static and dynamic calibration gas standards, but is able to complement their use for on-site calibration. Field measurements are integral to the whole traceability chain for measurements of greenhouse gases. Therefore this new OTS system will support the link between reference standards and measurements at monitoring stations and will improve future greenhouse gas measurements in terms of lower uncertainties, reduced matrix gas effects, and the potential to reduce the total calibration cost of field gas analysers.

Use optical methods to provide metrology to support isotopic composition measurements

Methods and procedures for four different measurement spectroscopy systems, including Optical Isotope Ratio Spectroscopy (OIRS), were developed and validated. The precision of OIRS measurements, which distinguish between isotopes, was sufficient for the analysis of atmospheric isotope ratios of CO, N₂O and CH₄, and is now available for use within the extended compatibility goals stated by WMO DQOs.

The methods developed by this project for accurate isotope ratio measurements, addressed basic metrological principles such as traceability and reduced uncertainties, and will support the preparation of static and dynamic calibration gas standards of high impact greenhouse gases. They will also have a direct impact on the practices used by isotope ratio measurement communities.

Assessment of the comparability of traceable reference standards to existing standards and scales

The reference standards of high impact greenhouse gases developed by the project in previous objectives were successfully shown to be comparable with the existing scales being used by the atmospheric monitoring community through a comparison against NOAA and SIO standards. These results provide an essential link for the project's newly developed measurement infrastructure to existing datasets.

Actual and potential impact

Dissemination of results

The project generated 11 publications in high quality journals and the project outputs have been presented in 13 posters and 21 presentations, including four invited talks at 20 different international conferences. NPL, a Researcher Excellence Grant at EMPA (REG(EMPA)) and METAS jointly convened a dedicated metrology session 'Climate and atmospherically important trace gases: metrology, quality control and measurement comparability' at the European Geoscience Union (EGU) General Assembly and the project was also presented to approximately 165 experts at the specialised 18th WMO/International Atomic Energy Agency (IAEA) Meeting on Carbon Dioxide, Other Greenhouse Gases, and Related Measurement Techniques (GGMT).

Two articles were also published in the popular press journals e.g. 'Gefahrstoffe - Reinhaltung der Luft' and 'MET Info'. In addition, project outputs were presented at the BIPM Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology (CCQM) annual meetings in 2015 and 2016.

Two stakeholder workshops were held to understand stakeholder requirements and included attendees from the speciality gas industry, instrument manufacturers, atmospheric monitoring networks, standardisation committees and NMIs. A webinar focused on the technical outputs of the project and was attended by 20 stakeholders, and is now available on the [project website](#). Two open training courses were also held: (1) on internal training on spectroscopic gas analysis and its potentials and (2) on Isotope-selective gas analysis. Furthermore, the results of the project were communicated to the communities closely connected to global long-term measurements of greenhouse gases, through presentations at the BIPM Carbon Workshop.

Impact on standards

The work from the project provided input to draft documentary standard ISO TC158 standard *Analysis of gases* WG2 Quality assurance of gas analysis, WG3 Gravimetric methods, WG4 Comparison methods and certificates and WG5 Static and dynamic methods) and DIN NA062 -05-73AA.

The results were also presented to the BIPM's CCQM working group on gas analysis (GAWG) and at an IAEA K4-TM-45739 technical meeting on stable isotope reference materials.

Actual impact

There is clear evidence that the project results are already feeding through and informing gas metrology at the global level. Examples of uptake of the project outputs include:

- The UK GAUGE network is a measurement network of 4 tall towers that are used to determine the emissions of greenhouse gases from the UK and are fundamental to demonstrate commitment to the Kyoto and COP21 international treaties/agreements. Greenhouse gas mixtures have been sold to the University of Bristol for use in the UK GAUGE network and discussions are underway for further sales to the University of Bristol, including higher fraction gas mixtures for work in urban network monitoring.
- Static Greenhouse gas mixtures have been sold to the BIPM in Paris.
- Greenhouse gas reference standards, as a result of NPL's improved calibration and measurement capabilities for methane, have been sold to the University of East Anglia.
- METAS and REG(EMPA) have prepared a reference gas mixture for SF₆ that was used as primary reference standard to measure two circulating cylinders as part of the World Climate Change SF₆ [intercomparison exercise](#). This compared METAS's primary standard to other references and scales

at an international level (i.e., NOAA scale, SIO scale) and demonstrated METAS's capabilities to prepare SI-traceable standards at atmospheric concentration for F-gases.

- The feasibility study on OIRS to support gravimetric preparation of CO₂ reference standards demonstrated accurate characterisation of isotopic composition. This is essential to meet the uncertainty targets for CO₂ reference standards. A specific example is a key comparison on CO₂ where reference standards and knowledge developed within the project are being used that will provide improved CMCs of the participating NMIs.

Potential impact

The project has significantly contributed to a European measurement infrastructure that directly addresses the need for traceability to the SI for measurements of high impact greenhouse gases for global monitoring. The project has provided reference materials at unprecedented levels of accuracy and stability, developed dynamic reference materials for unstable components and developed spectroscopic methods for dissemination to the field as OTS systems.

The metrology underpins scientific data collected from atmospheric monitoring stations to inform policy and provide the means to demonstrate compliance with legislation. The project will also have a direct impact on the environment and quality of life by providing a greater understanding of the increasing influence of human activity on the global atmosphere, and thereby helping to inform decisions on policy which could save the EU billions of euros with the cost of climate change projected to reach almost 4 % of GDP by the end of the century (*Horizon – EU research and innovation magazine*).

List of Publications

- [1]. Interlaboratory assessment of nitrous oxide isotopomer analysis by isotope ratio mass spectrometry and laser spectroscopy: current status and perspectives. Joachim Mohn, Benjamin Wolf, Sakae Toyoda, Cheng-Ting Lin, Mao-Chang Liang, Nicolas Brüggemann, Holger Wissel, Amy E. Steiker, Jens Dyckmans, Lars Swec, Nathaniel E. Ostrom, Karen L. Casciotti, Matthew Forbes, Anette Giesemann, Reinhard Well, Richard R. Doucett, Chris T. Yarnes, Anna R. Ridley, Jan Kaiser, Naohiro Yoshida *Rapid Commun. Mass Spectrom*, 28 (18), 1995–2007, 2014. DOI: 10.1002/rcm.6982
- [2]. Modern inhalation anesthetics – potent greenhouse gases in the global atmosphere. Vollmer, M.K., T.S. Rhee, M. Rigby, D. Hostetter, M. Hill, F. Schoenenberger, and S. Reimann *Geophys. Res. Lett*, 42, 1606–1611, 2015. DOI: 10.1002/2014GL062785
- [3]. First observation of 4th generation synthetic halocarbons in the atmosphere: HFC-1234yf (CF₃CF=CH₂), HFC-1234ze(E) (trans-CF₃CH=CHF), and HCFC-1233zd(E) (trans-CF₃CH=CHCl). Vollmer, M.K., S. Reimann, M. Hill, and D. Brunner *Environ. Sci&Technol*, 49 (5), 2703–2708, 2015. DOI: 10.1021/es505123x
- [4]. First on-line isotopic characterization of N₂O above intensively managed grassland. Benjamin Wolf, Lutz Merbold, Charlotte Decock, Bela Tuzson, Eliza Harris, Johan Six, Lukas Emmenegger, and Joachim Mohn *Biogeosciences*, 12, 2517-2531, 2015. DOI: 10.5194/bg-12-2517-2015
- [5]. Inter-comparison of halocarbons in an atmospheric dry whole air sample. George C. Rhoderick, Bradley D. Hall, Christina M. Harth, Jin Seog Kim, Jeongsoon Lee, Stephen A. Montzka, Jens Mühle, Stefan Reimann, Martin K. Vollmer, and Ray F. Weiss *Elementa*, 3: 000075, 2015, doi: 10.12952/journal.elementa.000075
- [6]. Tunable Diode Laser Absorption Spectroscopy Sensor for Calibration Free Humidity Measurements in Pure Methane and Low CO₂ Natural Gas. *Applied Spectroscopy*, DOI: 10.1177/0003702816658672
- [7]. ICL-based CO dTDLAS Sensor for Atmospheric Applications. J. Nwaboh, Z. Qu, O. Werhahn, V. Ebert *Imaging and Applied Optics*, DOI:10.1364/LACSEA.2016.LM3G.4
- [8]. Reassessment of the NH₄NO₃ thermal decomposition technique for calibration of the N₂O isotopic composition. Joachim Mohn, Wilhelm Gutjahr, Sakae Toyoda, Eliza Harris, Erkan Ibraim,

Heike Geilmann, Patrick Schleppe, Thomas Kuhn, Moritz F. Lehmann, Charlotte Decock, Roland A. Werner, Naohiro Yoshida and Willi A. Brand *Rapid Communications in Mass Spectrometry*, 30, 2487–2496, 2016. DOI: 10.1002/rcm.7736

- [9]. ICL-based optical transfer standard for atmospheric CO measurements. J. Nwaboh, Z. Qu, O. Werhahn, V. Ebert *Applied Optics*, Vol. 56, Issue 11, pp. E84-E93 (2017), DOI: 10.1364/AO.56.000E84
- [10]. Tracking nitrous oxide emission processes at a suburban site with semicontinuous, in situ measurements of isotopic composition. Eliza Harris, Stephan Henne, Christoph Hüglin, Christoph Zellweger, Béla Tuzson, Erkan Ibraim, Lukas Emmenegger, and Joachim Mohn *Journal of Geophysical Research: Atmospheres*, Vol. 122, pp. 1850–1870, 2017, DOI:10.1002/2016JD025906
- [11]. Rückführbare Referenzen für fluorierte Treibhausgase (Traceable references for fluorinated greenhouse gases). David Lehmann *METinfo*, Vol. 23, No.1/2016
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- [12]. Referenzgase für fluorierte Treibhausgase (Reference gases for fluorinated greenhouse gases). David Lehmann *Gefahrstoffe - Reinhaltung der Luft* (Hazardous substances - Keeping the air clean), 1-2/2017, pp. 25-26 http://www.gefahrstoffe.de/gest/article.php?data%5barticle_id%5d=86993
- [13]. ReGaS: Reactive Gas Standard. Céline Pascale *METinfo*, Vol. 24, No.1/2017
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