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1 Executive Summary

Introduction

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 (CO_2), carbon monoxide (CO), nitrogen dioxide (N_2O) and methane (CH_4). 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 CO_2, CO, N_2O, CH_4 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.

The Problem

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 Solution

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 CO_2, CO, N_2O and CH_4. 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.

Impact

Greenhouse reference materials developed in the project are already being used in the UK GAUGE network and have been provided to other stakeholders via NPL's measurement service offering.

Novel methods developed in the project for the preparation of high accuracy static and dynamic reference standards will be considered for inclusion in the next draft of the standards ISO 6142 and 6145 for the production and certification of reference materials.

The research will have impact beyond the immediate community of laboratories concerned with monitoring long-term atmospheric trends. Particular examples will be the impact on public health from future improvements in the accuracy and efficiency of the data acquired to meet the EU Air Quality Directives (e.g. 2008/50/EC).

2 Project context, rationale and objectives

Context

Global climate change poses one of the greatest risks to society worldwide. The Intergovernmental Panel on Climate Change (IPCC) has established that the observed rise of temperature is due to increasing greenhouse gases in the atmosphere, driven by man-made emissions overtaking the natural cycles of carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O). 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 of major global concern. These high impact greenhouse gases also govern a family of chemical reactions that determine the oxidising capacity of the atmosphere and influence the formation of tropospheric ozone and aerosols, so are also relevant to both air quality (directive 2008/50/EC) and climate. The significant drivers in this area are national and international legislation aimed at reducing emissions of greenhouse gases and their measurement in the atmosphere. These include the Kyoto protocol, rules for emission inventories developed under the UNFCCC, EC directives, ICOS and the WMO GAW programme. The WMO's Global Atmospheric Watch (GAW) programme plays a central role in coordinating global monitoring of atmospheric composition and addresses the main long-term objectives of the WMO strategic plan 2012-2015. These include the detection of long-term man-made trends in the concentration of greenhouse gases and aerosols related to climate change above natural variability and the corollary impacts of climate change on atmospheric composition. Consequently, there is substantial demand from policy makers to improve our understanding, control the increasing influence of human activity on it and address the effects of climate change. The measurement of greenhouse gases is pivotal to understanding the changes in the Earth's climate. There is a requirement for long-term observations based on accurate and stable standards of the highest impact greenhouse gases to ensure that the data meets the requirements of WMO DQOs, environmental policy makers as well as academic and regulatory users. Consequently there is an urgent requirement to provide a validated and traceable measurement infrastructure to develop our understanding of the increasing influence of human activity on the global atmosphere, address the effects of climate change and provide the basis for stable and comparable measurements of the highest impact greenhouse gases.

While significant progress has been made, the interpretation of data is limited by a lack of traceable calibration resulting in poor comparability of measurement results. The WMO have stated the importance of reference standards, in order to maintain short and long term stable values of greenhouse gases for analysis of trends in the atmosphere with confidence, coherent, comparable and stable reference standards at unprecedented levels of precision and accuracy are essential. The current approach adopted by the atmospheric monitoring community is that all measurements are traceable to a "scale", a collection (family) of artefacts carefully monitored and maintained by the National Oceanic and Atmospheric Administration (NOAA). The GAW programme of the WMO is a partnership involving the members of the WMO, contributing networks and collaborating organisations and bodies which provide reliable scientific data and information on the chemical composition of the atmosphere, it's natural and anthropogenic change, and help to improve the understanding of interactions between the atmosphere, the oceans and the biosphere. The WMO greenhouse gas expert group transferred responsibility for maintaining the WMO Scale for CO_2 from the Scripps Institute of Oceanography (SIO) to the Climate Monitoring and Diagnostics Laboratory (CMDL) at NOAA in 1995. NOAA is now the Central Calibration Laboratory (CCL) for CO_2 and CH_4 to disseminate reference materials and standardise international data. NOAA uses a manometric system to assign absolute CO_2 values to the primary standards and then uses these to transfer the WMO scale to secondary standards using non-dispersive infrared (NDIR) instruments. There are currently 15 primary CO_2/air standards ranging from 250 – 520 µmol/mol. These are calibrated at regular intervals (between 1 and 2 years) with the manometric system. Reference standards of CH4 in air are prepared by gravimetry and cover the nominal range of 300 – 2600 nmol/mol for measurements from air extracted from glacial ice to contemporary background atmospheric conditions. Standards for both components are disseminated in high-pressure gas cylinders and have been the subject of intensive research to determine their accuracy and stabilities. In order to maintain short and long term stable values of greenhouse gases for analysis of trends in the atmosphere with confidence, reference standards at challengingly high levels of precision and accuracy are required (e.g. approximately 0.02 % for CO_2 for the northern hemisphere, which is at least a factor of 5 better than has currently been demonstrated at CCQM). These will need to be prepared by a number of laboratories to demonstrate comparability within these stringent uncertainties.

The scale approach has benefits as it produces highly consistent data, which is ideal for trend analysis. However, the main disadvantages are that the responsibility, cost and maintenance are concentrated at one institute, it is impossible to regenerate or develop the scale independently and it is insensitive to drift in the reference artefact. For these reasons there is a pressing need for reference values to be disseminated that are traceable to the international system of units (SI). Firstly, they provide the possibility for more than one source and promise to overcome the supply issues currently experienced. This would be enabled and supported by the global agreement under the International Committee for Weights and Measures (CIPM) Mutual Recognition Arrangement (MRA). Secondly, it is important that all measurements are made on the same basis and the property of the measurement system that enables this is coherence. This allows different quantities to be combined without the need for scaling factors (e.g. measurements of O_2 and CO_2 from monitoring stations could be directly compared). Values traceable to the SI are coherent and accurate.

Objectives

In order to progress beyond the state of the art, the following challenges were identified that must be addressed to enable robust traceability to the SI for the components of interest at the uncertainties required for global monitoring:

- Chemically passivated high-pressure gas cylinders are available and are presently used to disseminate standards for greenhouse gases. However, with the exception of CO_2, where the NOAA have made manometric calibrations and observed no evidence of overall drift of the primaries from 1996 to 2004, there is a lack of evidence that the passivation chemistry used is adequate to guarantee the stability and accuracy over the timescales required. Furthermore, there is limited experimental work to study the influence of passivation chemistry on concentration losses during transfer.
- Purification systems and methods for quantification of impurities of target components in matrix gases used in static and dynamic standards are currently available; however, they usually struggle to provide the uncertainties required to underpin global monitoring. There are requirements for novel methods to produce high accuracy reference standards at these trace concentrations in order to quantify the levels of target components in the matrix gas and improved purification systems with a specification of < 1 nmol/mol (this is currently a challenge for certain components, e.g. CO).
- Systematic biases are often introduced from instrumentation at monitoring stations when reference gases vary in isotopic composition from the measured environment which significantly increases the measurement challenge (CO_2 in particular). Although some research has been undertaken, a large amount remains to fully resolve these biases. This can be achieved from a detailed study of instrument response to traceable isotope ratio standards in high pressure cylinders which are currently not available. Hence preparation and validation of an appropriate scale is highly significant and valuable.
- Dynamic methods based on dilution from reference standards at higher concentrations are commonplace, however, major challenges exist to achieve the desired accuracy to meet the requirements of the WMO. These methods are required for application in portable calibration devices for dissemination to the field and to address the components that are unstable in high pressure cylinders such as F-gases (e.g. SF_6), at the required pmol/mol level, where reliable standards and a traceable scale are missing.
- There is currently a lack of transfer standards to validate field measurement techniques (including in-situ calibration methodologies). The work in this JRP will address this urgent requirement by developments of optical transfer standards based on laser absorption spectroscopy which will obey metrological principles and address WMO-specified needs for greenhouse gas measurements.
- Different sources and sinks of high impact greenhouse gases fractionate isotopic compositions accordingly to the physical phenomena taking place in the process. The heavier isotopes of molecules having biogenic origin are typically depleted due to the preference of life forms to utilise the lighter isotopes. Anthropogenic sources, such as high temperature combustion, are typically enriched in heavier isotopes. Anthropogenic emissions also carry information of the isotopic composition of the fuels used. Therefore, ratios of stable isotopologues, typically denoted as δ ratio, can be used to trace

the origin or sink of atmospheric CO_2, CH_4 and N_2O. Due to strong dilution of source emission with ambient air, applicability of isotope ratio measurements is limited to techniques, such as Isotope Ratio Mass Spectrometry (IRMS), capable of resolving very small isotopic δ ratio variations with very high precisions ranging for different species around 0.05‰ to 1‰ which require expensive laboratory-based instrumentation and sample preparation. Hence it is essential to develop less costly techniques that can be employed in the field such as Optical Isotopic Ratio Spectroscopy (OIRS). Spectroscopic techniques suitable for OIRS comprise Cavity Enhanced Spectroscopic (CES) techniques such as Cavity Ring Down Spectroscopy (CRDS), Cavity Enhanced Absorption Spectroscopy (CEAS) and Integrated Cavity Output Spectroscopy (ICOS) as well as Tunable Diode Laser Absorption Spectroscopy (TDLAS) and Fourier-Transform Infrared (FTIR) spectroscopy. New concepts linking any of these techniques to metrological principles of traceability will complement current practices in the field.
- Differences in isotope ratios also influence the atomic weights used in the calculation of amount-of-substance fractions, which impact the uncertainty of high-accuracy gas measurement standards. The importance of this work is highlighted in the letter of support from IUPAC.

Traceable standards with long-term stability for high impact greenhouse gases have been identified by the World Meteorological Organisation (WMO) as being critical for long-term global monitoring. Standards for these components are required with challengingly low uncertainties to improve the quality assurance and control processes used for the global networks such as those coordinated by the WMO to better assess climate trends. The availability of these standards to the global monitoring community is of paramount importance. Without these, there is a substantial risk of discontinuity and step changes in global monitoring in the short to medium term, destroying much of the evidence base required to drive the global science consensus for political action. It is therefore vital that we position ourselves with widespread but accurate and low uncertainty measurements of the presence of high impact greenhouse gases in the atmosphere that meet the WMO compatibility goals to inform upcoming legislation and ensure compliance with emission targets. This will only be achieved by developing a robust measurement infrastructure through the development of high accuracy reference standards in high pressure cylinders; novel dynamic methods for generation of reference standards, and the development of spectroscopic methods as transfer standards and to provide measurements of isotopic composition. To achieve this, the broad scientific aims of the project were:

- Development of novel static reference standards of the highest impact greenhouse gases (CO_2, CH_4 and N_2O) and components that have an indirect effect on global warming (carbon monoxide (CO)) at unprecedented levels of precision and accuracy, to meet the challenging WMO data quality objectives for underpinning trend assessment. These are reference standards of CO_2 at 400 µmol/mol, CH_4 at 1.8 µmol/mol, N_2O at 325 nmol/mol, CO at 300 nmol/mol with target uncertainties of 100 nmol/mol, 2 nmol/mol, 0.1 nmol/mol and 2 nmol/mol (all at k=2) respectively.
- New dynamic reference standards will be developed to target other challenging greenhouse gases such as sulphur hexafluoride (SF_6) and other fluorinated gases (F-gases) which are unstable in high pressure cylinders. It will also focus on the development of dynamic generation methods for on-site preparation of these components at trace concentrations with accurate quantification to the level of parts-per-billion and below. Dynamic methods will also be developed for generating reference standards CO and N_2O to access the range of concentrations required for field calibration and to provide validation for the reference standards developed in WP1.
- Development of complementary optical methods as multi-component transfer standards. It also provides the metrology to support isotopic composition measurements of several components (e.g. CO_2 and N_2O) essential for achieving reference standards that meet the stringent DQOs set by the WMO and for supporting measurements to determine the origin of these components.

The specific aim of this project was to develop a European metrological infrastructure to underpin measurements of the highest impact greenhouse gases identified by the WMO and health effects research as critical for global monitoring. The project will provide and disseminate stable, coherent and internationally comparable reference standards that meet the target requirements specified for global monitoring by the WMO expert group. It will also overcome the supply issue, by providing the opportunity for more than one source of reference standards, supported by the global agreement under the CIPM MRA. The development of comparable synthetic reference standards will further enable demand to be met.

It addressed the following scientific and technical objectives:

1. Develop static reference standards of CO_2, CH_4, N_2O 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 N_2O for validation of reference standards and for dissemination to the field.
3. Develop new dynamic reference standards for on-site preparation of sulphur hexafluoride (SF_6) 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. CO_2 and N_2O) 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.

3 Research results

Objective 1: Develop static reference standards of CO_2, CH_4, N_2O and CO at levels of precision and accuracy to meet the challenging WMO DQOs for underpinning trend assessment.

Introduction

Research is required to develop traceable standards with long-term stability for high impact greenhouse gases (CO_2, CH_4, N_2O and CO) identified by the World Meteorological Organisation (WMO) as critical for global monitoring. Standards for these components are required with challengingly low uncertainties to improve the quality assurance and control processes used for global networks such as those coordinated by the WMO to better assess climate trends and satisfy the unmet need for traceability to the SI. The availability of these standards to the global monitoring community is of paramount importance. Without these, there is a substantial risk of discontinuity and step changes in global monitoring in the short to medium term, destroying much of the evidence base required to drive the global science consensus for political action.

Research Undertaken

High accuracy static reference standards of CO_2 at 400 µmol/mol (NPL, VSL, TUBITAK), CH_4 at 1.8 µmol/mol (NPL, VSL), CO at 300 nmol/mol (NPL, LNE) and N_2O at 325 nmol/mol (VSL, LNE) were prepared in both synthetic and whole air. These were studied to investigate the effect of different cylinder passivation chemistries on the long term stability of the reference mixtures at a range of cylinder pressures. Target impurities in the matrix gases used were accurately quantified. Synthetic standards were developed that compared closely to those made from whole air in order to facilitate production to meet the demand from monitoring stations. A full understanding of all major contributors to the uncertainty budget including atomic weights of components and a strategy to reduce uncertainty in gravimetric preparation and the influence of isotopic composition on the analytical technique used for measurement and validation.

Key research outputs and conclusions

A detailed uncertainty budget for the preparation of CO_2, CO, N_2O and CH_4 reference standards has been defined by NPL and VSL. The calculations provided essential information on the main contributors to the uncertainty which the research targeted providing reference standards with the desired accuracy required to underpin global measurements. These were the determination of the composition of the matrix gas, measuring the background level of target components in the matrix and gravimetry of added components to the mixture. New facilities have been made available at NPL and VSL for high accuracy quantification of trace CO_2, CH_4, N_2O and CO in the matrix gas. NPL has also developed the first synthetic zero air standard with a matrix of N_2, O_2 and Ar closely matching ambient composition with gravimetrically assigned values and with accurate quantification of the CO, CO_2, and CH_4 impurities aiming towards the WMO DQOs for each impurity. These standard provides a more accurate approach to zero spectroscopic (e.g., CRDS) instrumentation. For CO_2, CH_4 and CO the uncertainty on the quantification is near or below the WMO DQOs, which was successfully demonstrated by a comparison to the NOAA scale, organised by REG(EMPA). For N_2O the DQOs are still very challenging, however, the new measurement capabilities with OPO-CRDA in the 5 µm wavelength region, developed by VSL, have the potential to further reduce the uncertainty.

NPL, VSL, LNE and CMI have investigated the short term (10 weeks) and long term (two years) stabilities of CO_2, CH_4, CO and N_2O for a range of cylinder passivation chemistries and cylinder pressures. These stability studies are required to ensure that the mixtures meet the WMO DQO's over the lifetime of their usage. The long term stability studies showed no significant instability in CH_4, CO_2 or N_2O regardless of cylinder type. For CO significant differences in the stability of the standards in the untreated and Experis treated aluminium cylinders are observed, which have become more pronounced with increasing time. For static standards repeatability is an issue with a larger spread in results than expected regardless of preparation lab or measurement technique. LNE have shown that dynamic preparation of reference standards gave a more repeatable result than static standards made at NPL.

An Isotope Ratio Mass Spectrometry (IRMS) facility at TUBITAK has been developed and used to characterise the isotopic composition of the CO_2 reference standards developed by NPL. A suite of CO_2 mixtures with varying isotopic composition has been characterised at this new facility. These IRMS measurements have enabled the calibration of NPL isotopic measurement capabilities and provide a well characterised suite of standards with a known delta^{13}C value, an important step in resolving commutability issues when using CO_2 reference standards prepared from industrial sources in the field. They have also facilitated the quantification of the measurement bias in CRDS arising from calibration using reference standards with isotopic CO_2 compositions different to ambient.

Objective 2: Develop new approaches and devices for generating accurate standard gas mixtures for CO and N_2O for validation of reference standards and for dissemination to the field.

Introduction

Research is required to develop novel dynamic generation methods and devices for on-site preparation of reference standards of CO (50 - 500 nmol/mol) and N_2O (50 - 500 nmol/mol), with uncertainties that meet the WMO targets of 2 nmol/mol (CO) and 0.1 nmol/mol (N_2O). Dynamic reference standards of these components are already generated by dynamic methods in laboratories often based on permeation of gases through semi-permeable membranes or dilution from higher concentration reference standards. However international comparisons have shown that they do not have the necessary accuracy to meet the uncertainty requirements for global monitoring, so significant research is needed to lead to a new generation of methods for providing these standards at lower concentrations and uncertainties.

Research Undertaken

High accuracy dilution systems were constructed for generating dynamic reference standards of CO (LNE, TUBITAK) and N_2O (LNE, IL) from gravimetrically prepared high amount fraction standards. These dilution devices were validated and compared to static reference standards generated in the project as part of an inter-laboratory comparison. Accurate quantification of target impurities in matrix gases were also determined.

Key research outputs and conclusions

High accuracy dynamic and fully validated facilities were developed by LNE, TUBITAK and IL for generating reference standards of CO and N_2O based on the dilution of high concentration gas mixtures with Molbloc/Molbox flowmeters. A dynamic facility has also been developed at IL based on a commercial dilution device (Sonimix 6000 A1 from LN-Industries with sonic nozzles) for N_2O. The facilities generate reference standards of CO with smaller uncertainties than the WMO compatibility goals (1.03 nmol/mol compared to 2 nmol/mol). Reference standards for N_2O are generated with uncertainties of 0.9 nmol/mol. These devices have potential impact for use in the field as portable reference standards and have delivered repeatability better than the WMO DQOs providing accessible and highly repeatable propagation of scale from one artefact to another.

Objective 3: Develop new dynamic reference standards for on-site preparation of sulphur hexafluoride (SF_6) and a selection of other challenging, high impact F-gases at trace concentrations.

Introduction

Research is required to develop dynamic generation methods for preparing reliable European-based calibration scales for the measurements of high-impact F-gases in the atmosphere. F-gases include not only HFCs, perfluorocarbons (PFCs) and SF_6 which are part of the Kyoto Protocol, but also contain chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) which due to their additional ozone depleting properties, have been globally banned from use in the Montreal Protocol, but still have large emissions from reservoir sources. The developed standards will define the first European calibration scale for F-gases at the parts-per-trillion level (e.g. SF_6 at 100 pmol/mol). They will be used for atmospheric measurements to determine and track clean background air and their temporal trends and for atmospheric measurements of regional pollution in Europe, thereby providing an independent tool to estimate fluorinated greenhouse gas emissions in Europe. Moreover, they will also help to verify the industry-based bottom-up emission estimates used under the regulations of the Kyoto Protocol.

Research Undertaken
METAS and REG(EMPA) developed a method to purify synthetic air to remove target F-gases and to accurate quantify the remaining level of F-gases in the diluent gas. Development of novel high accuracy dynamic dilution systems by METAS and CMI. VSL provided a gravimetrically prepared static mixture of SF6 that was dynamically diluted used this device. METAS and CMI (SF_6 only) prepared dynamic reference standards of three key identified F-gases (SF_6, HFC-125 and HFO-1234yf) in the pmol/mol range.

Key research outputs and conclusions
METAS, EMPA, VSL and CMI have developed and validated a method to produce SI-traceable reference gas mixtures at near atmospheric molar fraction, in synthetic air, for SF_6, HFC-125 and HFC-1234yf ha. This method applied a gravimetric and dynamic method (permeation), combined with dynamic dilution using thermal mass flow controllers. Furthermore, methods to cryo-fill the generated standard in a cylinder to be delivered to the end-user has also be developed by METAS and CMI and validated by REG(EMPA). This has been done for SF_6 (generated at 7, 8 and 10 pmol/mol), HFC-125 (generated at 17 pmol/mol) and HFO-1234yf (detected in the atmosphere at sub-pmol/mol levels and generated at 2 pmol/mol). The expanded uncertainty (k=2) of the final mixtures ranges from 1.1% to 2.4%. The newly produced reference gas mixtures were in agreement with existing scales (AGAGE) within the uncertainties. As a result, the stated objectives of the HIGHGAS project have been surpassed by 1) targeting atmospheric molar fraction (up to 50 times lower than the HIGHGAS target of 100 pmol/mol) and 2) reaching expanded uncertainties up to twice lower than the HIGHGAS objective of < 3%.

To make on-site instrument calibration and linearity tests more straightforward, METAS have developed a transportable reference gas generator (ReGaS3), based on permeation and dynamic dilution, able to generate multi-component reference gas mixtures at µmol/mol to pmol/mol levels. This generator has been used by RE(EMPA) at the Dübendorf monitoring site (Switzerland) to test the linearity of the system measuring fluorinated gases. METAS and CMI have demonstrated the capabilities to apply a dynamic generation method (permeation, dynamic dilution) to generate reference gas mixtures from the µmol/mol level supplied by VSL to the pmol/mol level with competitive uncertainties (by comparison to static methods) of 1.1% to less than 3%. Finally, while newly emitted compounds are detected in the atmosphere, dynamic generation methods are an excellent means to produce with a limited delay the needed reference gas mixtures to insure SI-traceability of these measurements and therefore comparability to inventories, and compliance with international agreements.

Objective 4: Develop complementary optical methods as multi-component transfer standards.

Introduction
Research is required to provide experimental evidence, concepts and guidance on spectroscopic methods for underpinning high accuracy measurements of atmospheric concentrations of key greenhouse gases and addressing aspects of field measurements. The main objectives are to develop optical transfer standards of greenhouse gas components and optical isotopic ratio measurements to complement and where possible improve on existing calibration methodologies such as the use of high pressure gas mixtures. Spectroscopic methods are widely used for atmospheric measurements either for concentration or for isotope ratio analysis. Optical spectroscopic transfer standards not only offer an alternative calibration route for challenging components, but also allow independent comparisons to be made to static gaseous reference standards, providing further confidence in the reference values. Transfer standards offer a solution for replacing the use of static and dynamic standards in the field and promise to reduce the burden on gas standard producers and reduce calibration times at monitoring stations.

Research Undertaken
PTB, MIKES and DFM identified appropriate spectroscopic techniques and wavelength ranges with DFM

and MIKES focussing on CO_2 and PTB on CO. PTB, MIKES and DFM revised spectral line data ensuring it to be fit for purpose for use in an optical transfer standard. PTB, MIKES and DFM validated the developed optical transfer standards for CO (PTB) and CO_2 (DFM, MIKES) and characterized the influence of changes in the composition of nitrogen, oxygen and argon in the air matrix on the spectroscopy. The developed optical transfer standards were compared against the developed CO and CO_2 reference standards.

Key research outputs and conclusions

A feasibility study has been completed by reviewing existing spectroscopic methods used by the atmospheric community for the measurement of greenhouse gases. The suitability of spectral line data, in terms of uncertainties and traceability to the SI, for use in optical transfer standards for CO and CO_2 was defined and a first spectral line data set for use towards the development of the optical transfer standards for CO and CO_2 has been documented. New optical transfer standards (OTS) based on tunable diode laser absorption spectroscopy (TDLAS) have been developed for atmospheric CO and CO_2 measurements and validated against gravimetric standards, addressing direct traceability of the amount of substance fraction results to the SI. The potential of the OTS systems was demonstrated by comparing OTS results to gravimetric values of gas standards prepared within the project, resulting to very good agreement between the two standards. The precision of amount of substance fraction measurement results delivered by the CO OTS is below the compatibility goal stated by WMO for atmospheric measurements. Field measurements are integral to the whole traceability chain for measurements of greenhouse gases. The expected impact from this work is to link the reference standards to measurements at monitoring stations. Also to provide new calibration strategies which reduce the dependence of reference standards at site. Laboratory tests of atmospheric background measurements were done demonstrating the capability of an OTS system. The availability of OTS systems provides an alternative to static and dynamic calibration gas standards complementing them especially in the field for in-situ calibration to improve future greenhouse gas measurements in terms of lower uncertainties, reduced matrix gas effects, and potentially reduce the total calibration cost of field gas analyzers. The development of OTS systems in this project opens up the possibility to develop such systems for sticky and reactive atmospheric trace gases such as NO_2 and H_2O that are difficult for gas cylinders.

Objective 5: Use optical methods to provide the metrology to support isotopic composition measurements of several components (e.g. CO_2 and N_2O) to enable gravimetric reference standards that meet the WMO DQOs and to enable studies that determine the origin of these components in the atmosphere.

Introduction

The aim of this task is to develop experimental evidence, concepts and metrological statements on Optical Isotopic Ratio Spectroscopy (OIRS) for underpinning greenhouse gas measurements. OIRS will be reviewed and evaluated as a potential complement to other methodologies already in place. This task will furthermore address specific benefits of OIRS compared to other techniques and provide metrological feedback on traceability issues of existing commercial OIRS instrumentation. Information on isotopic ratios of gas components are known to impact on climate change research as they give insight into sources and sinks of greenhouse gas components. Furthermore, isotopic ratio variations are also affecting the response of spectroscopic analysers and the gravimetric preparation of primary reference gas mixtures. PTB will focus its contribution to this task on $^{13}C/^{12}C$-ratios in CO, REG(EMPA) will work on $^{15}N/^{14}N$ ratios in N O, and DFM will address $^{13}C/^{12}C$-ratios in CH . MIKES will work on $^{2}H/^{1}H$ ratios in CH and O/O ratios in CO .

Research Undertaken

DFM, MIKES, PTB and REG(EMPA) investigated the feasibility of using OIRS to support measurements of CO_2 isotopologues in gravimetric reference standards as a complementary technique to IRMS. REG(EMPA) provided the link to the international isotope ratio scales with an existing suite of reference standards for which comparisons were made to the OIRS techniques. MIKES, DFM, PTB and REG(EMPA) performed a validation of the OIRS measurement procedure.

Key research outputs and conclusions

Four measurement systems in the NIR and mid-IR based on TDLAS, QCLAS and CRDS, methods and procedures for Optical Isotope Ratio Spectroscopy (OIRS) for $^{13}C/^{12}C$ and $^{18}O/^{16}O$ ratios in CO_2, $^{15}N/^{14}N$ ratios in N_2O, and $^{13}C/^{12}C$ and $^{2}H/^{1}H$ ratios in CH_4, have been developed and validated, matching metrological principles. The precision (for instance 0.05 ‰ $\delta^{18}O$ in CO_2, 0.09 ‰ for $\delta^{15}N^{\alpha}$ in N_2O) of the OIRS measurement results are sufficient for the analysis of atmospheric isotope ratios of the indicated gas species and where available are within the extended compatibility goals stated by WMO. Strategies to use the developed OIRS measurement techniques to link existing scales to the SI have been identified. The feasibility of absolute isotope ratio measurements using laser spectroscopic techniques was investigated, and the measurement results showed that this approach is limited by the quality (large uncertainties) of currently available absorption line data.

4 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 an 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 SF_6 that was used as primary reference standard to measure two circulating cylinders as part of the World Climate Change SF_6 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 CO_2 reference standards demonstrated accurate characterisation of isotopic composition. This is essential to meet the uncertainty targets for CO_2 reference standards. A specific example is a key comparison on CO_2 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*).

5 Website address and contact details

A project website has been set up, which details information about the project, including its objectives, publications, events and presentations. The website address is: http://projects.npl.co.uk/highgas/.

A project SharePoint site has also been set up for the partners to exchange and store project information and deliverables: https://shared.npl.co.uk/landing/ (a password is available on request).

The contact person for general questions about the project is Dr. Paul Brewer, NPL (paul.brewer@npl.co.uk).

The contact person for high accuracy primary reference gas mixtures is Mr. Gerard Nieuwenkamp, VSL (gnieuwenkamp@vsl.nl).

The contact person for dynamic methods for trace concentrations and dissemination to the filed is Dr. Tatiana Macé (Tatiana.Mace@lne.fr).

The contact person for spectroscopic methods for isotopic composition measurements and transfer standards is Dr. Javis Nwaboh (Javis.Nwaboh@ptb.de).

6 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 Szwec, 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, HeikeGeilmann, Patrick Schleppi, ThomasKuhn, Moritz F. Lehmann,CharlotteDecock, 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 http://www.metas.ch/dam/data/metas/Dokumentation/METASPublikationen/metinfo/METinfo2016/R%C3%BCckf%C3%BChrbare%20Referneze%20f%C3%BCr%20fluorierte%20Treibhausgase%20.pdf

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[13]. ReGaS: Reactive Gas Standard. Céline Pascale *METinfo*, Vol. 24, No.1/2017 https://www.metas.ch/dam/data/metas/Dokumentation/METASPublikationen/metinfo/METinfo2017/regas.pdf