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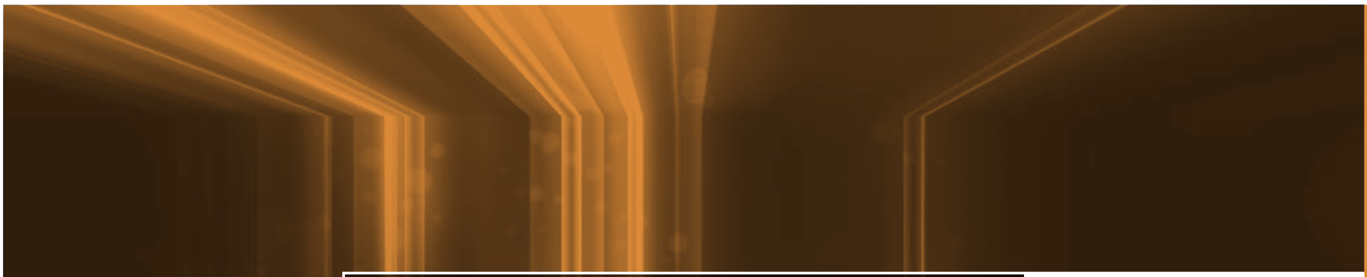

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No. 2066

Measurement of the Stable Carbon Isotope Ratio in Atmospheric CH_4 Using Laser Spectroscopy for CH_4 Source Characterization

MEASUREMENT OF THE STABLE CARBON ISOTOPE RATIO IN ATMOSPHERIC CH_4 USING LASER SPECTROSCOPY FOR CH_4 SOURCE CHARACTERIZATION

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MEASUREMENT OF THE STABLE CARBON ISOTOPE RATIO IN ATMOSPHERIC CH_4 USING LASER SPECTROSCOPY FOR CH_4 SOURCE CHARACTERIZATION

INTERNATIONAL ATOMIC ENERGY AGENCY
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International Atomic Energy Agency
Vienna International Centre
PO Box 100
1400 Vienna, Austria
tel.: +43 1 2600 22529 or 22530
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For further information on this publication, please contact:

Terrestrial Environmental Radiochemistry (TERC) Laboratory
International Atomic Energy Agency
Vienna International Centre
PO Box 100
1400 Vienna, Austria
Email: Official.Mail@iaea.org

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FOREWORD

In 2020 the IAEA launched an interregional technical cooperation project with the support of the World Meteorological Organization (WMO) entitled Developing Capacity Towards the Wider Use of Stable Isotopic Techniques for Source Attribution of Greenhouse Gases in the Atmosphere. The project aims to assist countries in building capacity in stable isotope analysis of atmospheric greenhouse gases and to accurately determine their source.

The project intends to establish regional training and analysis centres which will support laboratories from their respective regions with developing analytical capacities for the collection and interpretation of greenhouse gas data. The trained scientists will be able to inform decision makers, help authorities tailor their climate policies and build support for focused climate action. Training is based on the development and dissemination of good practice publications and training materials and on the organization of regional and interregional training courses.

This publication is the first good practice publication developed as part of the project. It describes the analytical infrastructure, sampling strategies and approaches for measuring the stable carbon isotope ratio in atmospheric methane using laser spectroscopy and the tools for interpretating the data for source characterization.

The IAEA acknowledges the efforts of the contributors listed at the end of this publication, in particular P. Sperlich (New Zealand) as leader of the group of experts. The IAEA officer responsible for this publication was F. Camin of the Division of Physical and Chemical Sciences.

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CONTENTS

1. INTRODUCTION

1.1.BACKGROUND

Atmospheric methane (CH_4) is the second most important anthropogenic greenhouse gas after carbon dioxide (CO_2). It is a major contributor to global climate change as it traps more heat in the earth's atmosphere per weight than carbon dioxide. Therefore, decreasing methane emissions is critical to reduce global warming.

In order to be able to impact methane concentration in the atmosphere, it is important to understand and track its fluxes and changes in sources and sinks. These can be determined by using stable isotope ratio analysis, because the different sources of atmospheric methane have been found to systematically vary in its carbon ($\delta^{13}C$-CH_4, see Chapter 3.1for data expression) and hydrogen ($\delta^{2}H$-CH_4) isotopic composition. For example, CH_4 emissions from biogenic sources are depleted in the "heavier" isotope (^{13}C, ^{2}H), while CH_4 associated with fossil sources is more enriched in these isotopes. The measurements of the isotopic composition of atmospheric CH_4 can therefore allow a better allocation of different natural and anthropogenic CH_4 sources.

Accurately quantifying CH_4 emissions at national and global scales is difficult due to the widespread distribution of many emission sources. To enhance our understanding, it's crucial to collect more isotope data from CH_4 source regions, particularly those that are currently underrepresented.

In addition to the scientific demand for increased number of CH_4 observations, stakeholders in national administrations and economies are urgently seeking information about their CH_4 budgets, including emission amounts and sources. Notably, as of December 5, 2022, 130 countries have signed the 'Global Methane Pledge,' committing to reduce their annual CH_4 emissions by 30% by 2030 compared to 2020 levels.

Nowadays $\delta^{13}C$-CH_4 analysis of atmospheric methane is mainly performed using laser spectroscopy, i.e. optical instruments, which typically measure the isotopic composition of CH_4 in the air matrix directly, without requiring complicated preparation steps. These instruments can monitor temporal changes in CH_4 and $\delta^{13}C$-CH_4 through continuous observations. In situ analysers can be utilized to locate and to isotopically characterize individual CH_4 sources. They can also be used on mobile platforms, such as cars, to detect, map and isotopically characterize previously unknown CH_4 sources in rural or urban regions.

The major problem to be addressed is that developing countries do not have expertise in these techniques and need capacity building to utilize stable isotope analysis methods effectively to measure the carbon stable isotope ratio of atmospheric CH_4.

To enhance our understanding of CH_4 emissions at local, regional, and global scales, we need to provide intensified research efforts and an expanded observational infrastructure. This will not only improve our knowledge of national CH_4 budgets but also allow us to assess progress toward mitigation targets. To achieve this objective, we need to create comprehensive guidelines for laboratories that are new to the use of optical instruments for measuring CH_4 and its carbon stable isotope ratios and for interpretating the measurement results.

1.2.OBJECTIVE

This document seeks to provide high-level guidance to laboratories on sampling, measuring, and interpreting the results of CH_4 and its carbon stable isotope ratios for characterizing the sources of CH_4 emissions. The overall goal is to find and isotopically characterize methane sources on local to regional scales, and to attribute sector-specific CH_4 emissions based on $\delta^{13}C$-CH_4 source values.

1.3.SCOPE

This publication covers analytical infrastructure, sampling strategies, as well as techniques for measurement, calibration, data processing, analysis and interpretation of carbon stable isotope ratio in atmospheric methane. Further emphasis is on technical solutions that ensure that observations are accurate and comparable, as well as on sustainable data management techniques, and quality control procedures, to maximize the impact of newly generated data. While the authors note the importance of $\delta^{2}H$-CH_4 observations, as well as of radiocarbon and clumped isotopes in atmospheric CH_4, to better understand CH_4 processes, these tracers are out of scope for this document.

1.4.STRUCTURE

This publication consists of ten Chapters and two Appendices. Chapter 2 provides the state of the art on stable carbon isotope ratio in atmospheric CH_4 using laser spectroscopy for CH_4 source characterization. Chapter 3 describes the data quality objective of this analysis and Chapter 4 gives a comprehensive description of assessment of performances of the optical analyser. An overview on the laboratory design, infrastructure and supplies is given in Chapter 5. Chapter 6 provides a comprehensive review of the gasses used for calibration. The sampling strategy is described in Chapter 7. Chapter 8 discusses the measurements and data processing protocols. Tools for assessing data quality and for data interpretation are presented in Chapters 9 and 10. Appendix 1 deals with the traceability of $\delta^{13}C$-CH_4 values to the VPDB (Vienna Peedee belemnite) carbon isotope delta scale and Appendix 2 with possible technical problems when performing the measurements.

2. STATE OF THE ART ON STABLE CARBON ISOTOPE RATIO IN ATMOSPHERIC CH_4

This Chapter provides an overview about the carbon stable isotope ratio analysis in atmospheric methane for methane source identification.

2.1.THE VARIATION OF METHANE IN THE GLOBAL ATMOSPHERE

Atmospheric methane (CH_4) is the second most important anthropogenic greenhouse gas after carbon dioxide (CO_2). The present atmospheric burden of CH_4 is unprecedented in the last 800,000 years [1–3] and has almost tripled since the onset of the industrial revolution, mostly due to increased CH_4 emissions based on human activities (Fig. 1). On a 100-year horizon, the global warming potential of CH_4 is ~28 °C [3]. The 6th Assessment Report (AR6) of the Intergovernmental Panel on Climate Change (IPCC) assesses that the average additional warming effect of atmospheric CH_4 between 2010-2019 with respect to 1850-1900 accounts for ~0.5 °C [3] . At the same time, the warming of CO_2 accounts for ~0.75 °C, highlighting the relative importance of CH_4 as a greenhouse gas [3].

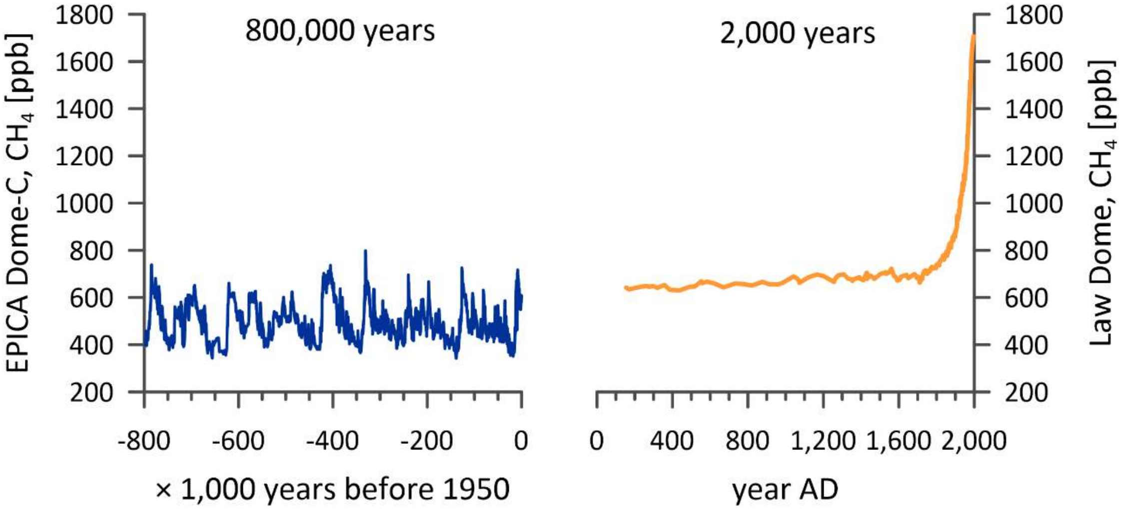

FIG. 1. CH_4 mole fractions reconstructed from Antarctic ice core samples. Left: CH_4 over the last 800,000 years from EPICA Dome-C ice core (data from Ref. [1]) right: Law Dome ice core and firn air samples connect CH_4 reconstructions over the last 2000 years with direct atmospheric CH_4 observations (data from Ref.[2]) .

The amount of CH_4 in the atmosphere depends on the balance of its sources and sinks. Methane that is emitted from different sources has been found to systematically vary in its carbon ($\delta^{13}C$-CH_4, see Chapter 3.1for data expression) and hydrogen ($\delta^{2}H$-CH_4) isotopic composition (e.g., [4]). On average, CH_4 emissions from biogenic sources are most depleted in the “heavier” or “rare” isotope (^{13}C, ^{2}H), while CH_4 derived from fossil sources is more enriched in both ^{13}C and ^{2}H (Fig. 2, Table 1). The isotopic composition of each CH_4 source is thus characteristic of its biogeochemical production pathway. However, the isotopic composition of CH_4 from different source categories may overlap, depending on the sources. Details can be found in a global database of isotope signatures of various, mainly anthropogenic, CH_4 sources, which was presented by [5] and [6], while additional measurements in Europe were reported by [7]. Furthermore, the sink processes that remove CH_4 from the atmosphere preferentially reduce CH_4 molecules carrying the “lighter” isotopes (^{12}C, ^{1}H); therefore, the CH_4 that is remaining in the atmosphere is enriched in the “heavier” isotopes. This “isotopic fractionation” of the sink causes the unpolluted background atmosphere to be isotopically more enriched in ^{13}C and ^{2}H than the emissions-weighted mean of all of its sources (e.g., [8]), (Fig. 2).

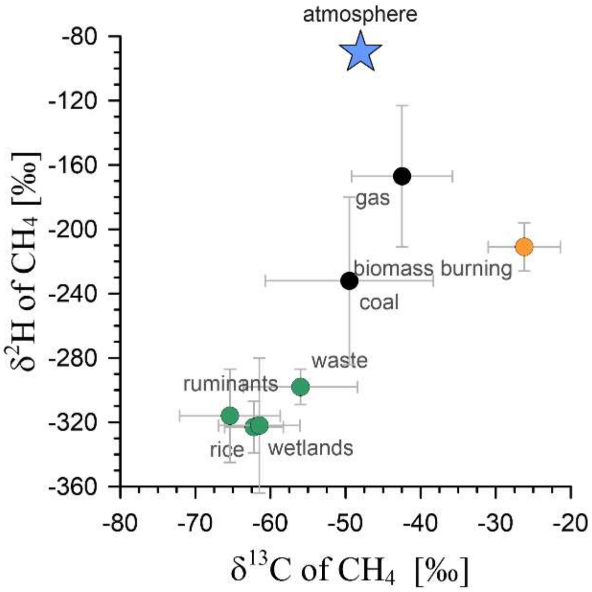

FIG. 2. Dual isotope plot of main CH_4 sources, depending on the biogeochemical production pathway. Green symbols show values for biogenic CH_4, black for fossil CH_4 and orange for CH_4 from biomass burning, respectively. All CH_4 source values are taken from Ref.[9]. Typical atmospheric $\delta^{13}C$-CH_4 and δ^2H-CH_4 values vary around –47.5 ‰ and –90 ‰, respectively, and are indicated by the blue star, in line with [8, 10–12].

The CH_4 amount in the well-mixed atmosphere reflects the balance of its sources and sinks on continental to global scales. Likewise, the balance of these source and sink fluxes defines the isotopic composition of CH_4 in the well-mixed atmosphere (e.g., [8, 9, 13] For example, the stable carbon isotopic composition of CH_4 in marine background air shows small, yet significant variations as a result from changes in global sink and source fluxes (Fig. 3). The analysis of such measurements suggests that the atmospheric CH_4 increase since 2007 is likely due to an increase in biogenic CH_4 emissions (e.g., [8, 14–16]), while an increase in the emissions of fossil CH_4 is plausible, but unlikely to be the main driver of the CH_4 increase [14]. Furthermore, [17] found that a scenario of decreasing CH_4 emissions from biomass burning is able to close the CH_4 isotope budget, while it also aligns with estimates of fossil CH_4 emissions based on methane-ethane ratios. While the exact cause of the CH_4 increase on the global scale is still subject to scientific debate, it clearly highlights the potential of co-located CH_4 and $\delta^{13}C$-CH_4 observations to attribute CH_4 emissions to specific CH_4 sources.

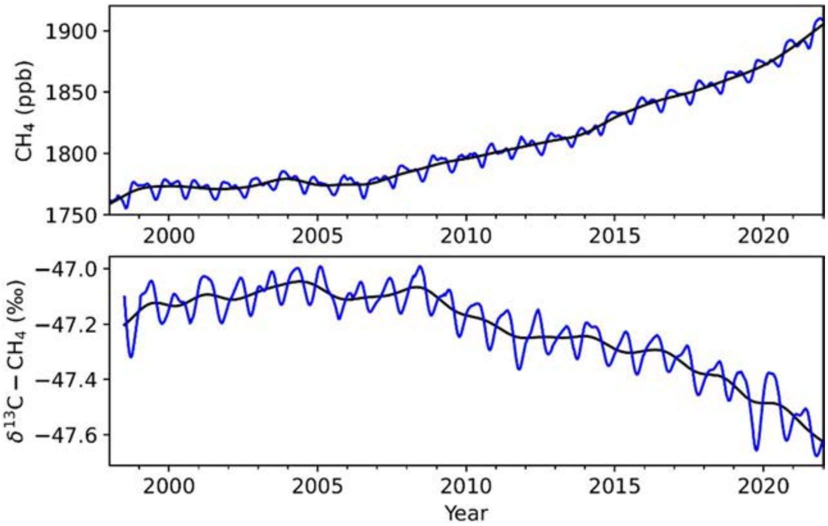

FIG. 3. Globally averaged atmospheric CH_4 (top) and $\delta^{13}C$-CH_4 (bottom) at Earth's surface at weekly resolution (blue). The black line is a deseasonalised trend fitted to the data. Data source: NOAA Global Monitoring Laboratory and INSTAAR (update from the plot in Ref [18], figure provided by Xin Lan pers. comm. 22nd November 2022 (courtesy of X. Lan, NOAA Global Monitoring Laboratory).

The quantification of CH_4 emissions on national to global scales is challenged by the widely dispersed nature of many of these sources [19, 20]. Isotope-enabled CH_4 models are increasingly used to quantify CH_4 fluxes. However, $\delta^{13}C$-CH_4 source signatures for distinct source categories vary geographically and temporally and therefore, the quality of the model results in particular for regional studies relies on the availability of representative data on the isotopic composition of CH_4 sources (e.g., [21]; [6]). Ref. [6] gridded the available $\delta^{13}C$ signatures of fossil CH_4 sources, highlighting the large spatial variability within this source category (Fig. 4). Furthermore, these data also highlight the lack of data from large regions on Earth, in line with [4] and [7]. An improved coverage of isotope data from CH_4 source regions, especially from those regions that are currently underrepresented, is urgently needed to improve isotope-enabled CH_4 global models ([6]) and to better understand the variability of atmospheric CH_4.

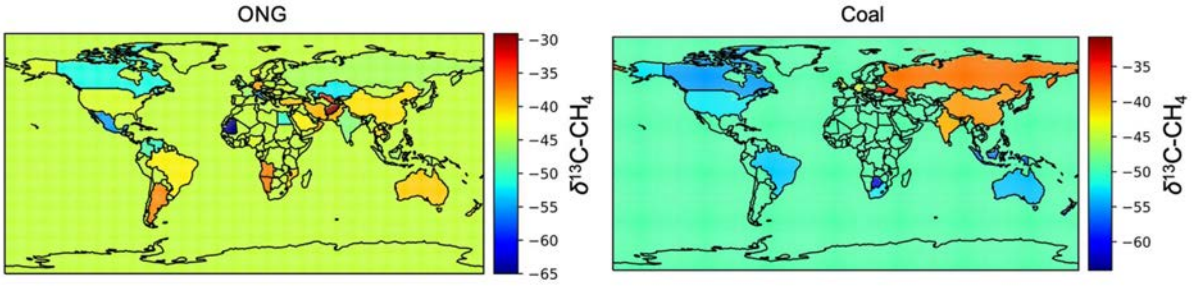

FIG. 4. Country-level $\delta^{13}C$-CH_4 source signatures for oil and natural gas production (ONG) and coal emissions, assumed as time invariant and employed in a global CH_4 model study. For grid cells without data, a global flux weighted mean is used. (Reproduced from Ref. [22], with permission). For regional investigations, emission data with higher geographic and temporal resolution are suggested.

2.2.TECHNIQUES FOR CH_4 AND $\delta^{13}C$-CH_4 OBSERVATIONS

Traditionally, CH_4 stable isotope ($\delta^{13}C$-CH_4, $\delta^{2}H$-CH_4) measurements have been made using Isotope Ratio Mass Spectrometry (IRMS), using offline or online preparation / analysis techniques (e.g., [23–26], for overview see Ref [27]. Common to all techniques is the oxidation of the target gas CH_4 to CO_2 before $\delta^{13}C$-CO_2 analysis or alternatively its reduction to H_2 prior to $\delta^{2}H$-H_2 analysis. IRMS can provide high instrumental precision in routine use and has the capability for quasi-continuous operation at monitoring stations; however, it is mostly limited to measurements of discrete samples in the laboratory, and requires a significant level of expertise, infrastructure, and expense. Accurate measurements of CH_4 mole fractions require additional instrumentation, such as gas chromatography (e.g., Ref. [28]), or optical spectroscopy (e.g., Ref. [29], and need to utilize reference gases linked to the well-established WMO X2004A scale (Section 6.5for definition of reference gases).

The advent of optical instruments opened a new window of opportunity to measure atmospheric CH_4 and its stable isotope ratios in a single instrument that is more affordable, potentially more user-friendly, and field deployable. Laser spectroscopy offers a complementary approach for $\delta^{13}C$-CH_4, $\delta^{2}H$-CH_4 analysis, as it does not require chemical conversion of the analyte, but directly probes selected rotational lines of the CH_4 isotopologues $^{12}CH_4$, $^{13}CH_4$, $^{12}CH_3D$ (e.g., Ref. [30]. Instruments using different detection schemes have been developed and commercialized, such as direct absorption spectroscopy, cavity ring-down spectroscopy and off-axis integrated cavity output spectroscopy. These instruments provide data at high temporal resolution and coverage and are less operationally complex than IRMS; however, achievable precision levels for $\delta^{13}C$-CH_4 generally exceed the compatibility goals of the WMO-GAW [31] , unless samples are measured over extended, e.g. 30 minutes, integration periods or instruments coupled to automated preconcentration devices [32–34].

In cavity ring-down spectroscopy, mole fractions in a gas sample are measured by quantifying the optical decay rate of a highly resonant optical cell into which the sample has been introduced. Likewise, an optical analyser for isotope ratios measures isotopologue mole fractions and then uses this information to calculate isotope ratios (e.g., Ref. [35]). A central feature for its sensitivity is the high reflectivity mirrors of the optical resonator to realise effective pathlengths, which can be on the order of tens of km for some instruments [36]. High selectivity is provided by scanning a single-frequency laser diode across a wavenumber region, in which the target isotopologues display characteristic spectral features.

Optical analysers typically measure the analytes of interest in the air matrix directly, without requiring complicated preparation steps, and are therefore able to monitor temporal changes in CH_4 and $\delta^{13}C$-CH_4 through continuous observations. In comparison to previous IRMS-based techniques, these analysers enable highly versatile studies: in a central laboratory, like IRMS-based systems to make continuous ambient air measurements as well as measurements in flask or bag samples [37], or alternatively at regional observatories [38], or on mobile platforms to identify local CH_4 plumes [39–42]. With that, optical analysers, especially those that are isotope-specific, open a new window of research opportunities.

2.3.FIND AND CHARACTERISE INDIVIDUAL CH_4 SOURCES

In situ analysers for CH_4 and $\delta^{13}C$-CH_4 can be utilized to locate and to isotopically characterize individual CH_4 sources. By sampling across a range of CH_4 enhancements from a single CH_4 source (such as a wetland, landfill, oil facility, feedlot, etc), researchers may utilize Keeling Plot or Miller-Tans analysis (Section 10.1) to characterize the isotopic value of that source, (e.g., Ref. [37]). Several studies used in situ CH_4 analysers on mobile platforms (i.e., cars) to detect CH_4 emission plumes at street level. Air from detected plumes was then sampled in bags for subsequent isotope analysis in the laboratory (e.g., Ref. [39–42]). For example [44] measured methane plumes and $\delta^{13}C$-CH_4 around a proposed shale gas extraction site in a rural area in western Lancashire, England. In addition to measuring sources of methane above background levels, they were able to isotopically characterize these to fossil fuel sources, biogenic sources from agriculture, and waste. These data will allow researchers to distinguish and quantify emissions at the site where gas production takes place. In combination with high-resolution GPS data, these observations were used for isotopic mapping of CH_4 sources (Fig. 5). Permanently deployed CH_4 isotopologue analysers generate time series of high temporal resolution, allowing for the isotopic characterization of CH_4 sources across entire regions, including their variability with time (e.g., Ref. [38]). Optical CH_4 analysers have also been used on mobile platforms, such as cars, to detect, map and isotopically characterize previously unknown CH_4 sources in rural or urban regions (e.g., Ref. [37, 43]). Potential CH_4 sources to be characterized include CH_4 emissions from livestock farming, wastewater treatment plants, landfills as well as emissions associated with fossil fuel exploration and distribution.

More high-quality $\delta^{13}C\text{-}CH_4$ source values are urgently needed to improve source attribution in regional and global CH_4 studies (e.g., Ref. [7, 15, 21, 22]).

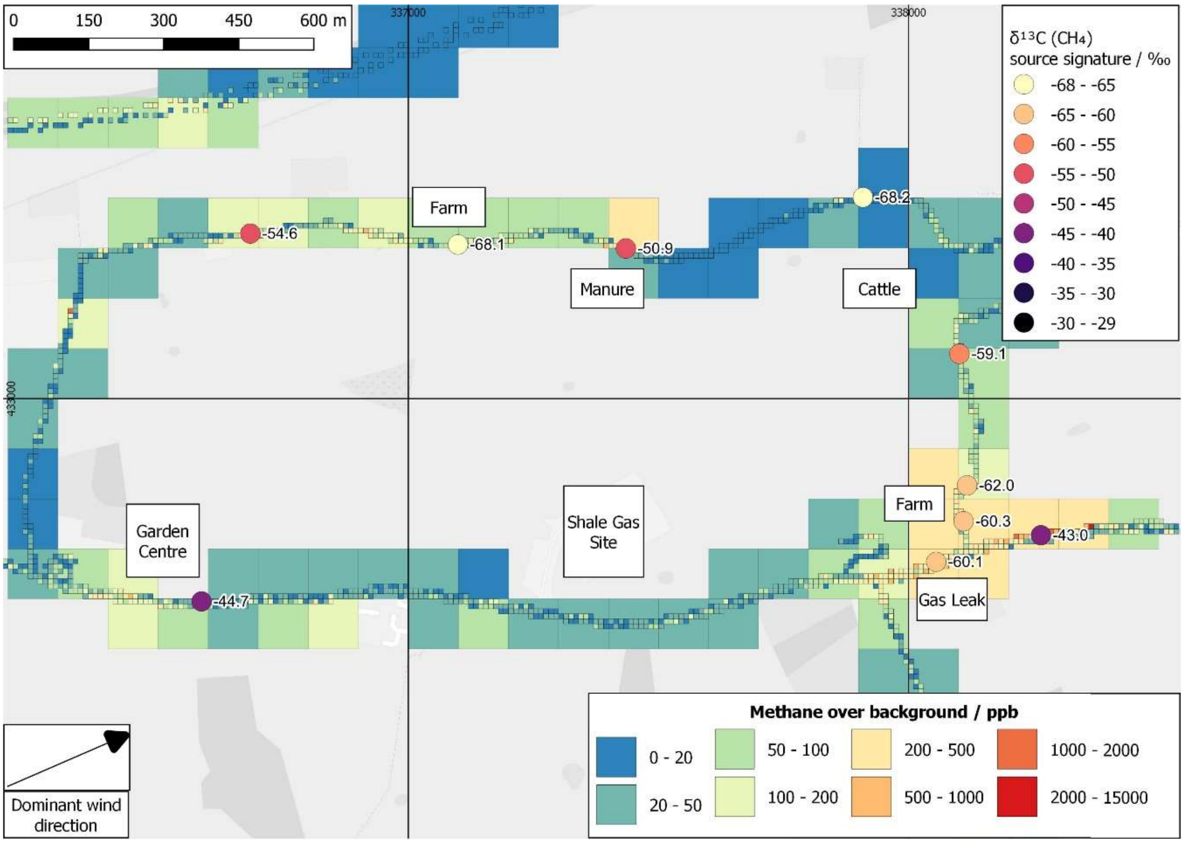

FIG. 5. Example of isotopic mapping of CH_4 sources (reproduced from Ref. [40],with permission).

2.4.ATTRIBUTING CH_4 EMISSIONS TO SPECIFIC SECTORS USING $\delta^{13}C\text{-}CH_4$ AND OTHER TRACERS

Analyzing CH_4 and $\delta^{13}C\text{-}CH_4$ measurements in combination with knowledge on the isotopic composition of regionally significant CH_4 sources (e.g., Table 1) enables the attribution of observed CH_4 plumes to specific CH_4 emitting sectors. For example, observations of biogenic CH_4 emissions will increase CH_4 mole fractions and simultaneously lower $\delta^{13}C\text{-}CH_4$, while fossil CH_4 emissions will typically increase both CH_4 mole fractions and $\delta^{13}C\text{-}CH_4$. Researchers use mixing models, e.g., Keeling Plot or Miller-Tans analysis (see Section 10.1), to derive $\delta^{13}C\text{-}CH_4$ values of a source, and in reverse to interpret ambient air measurements by comparison with sector-specific δ^{13}C-CH_4 source values (Table 1). Furthermore, it is beneficial to quantify ethane (C_2H_6), which is co-emitted with fossil CH_4 emissions, but not with biogenic CH_4 emissions. Ethane can be measured by some δ^{13}C-CH_4 analysers (e.g., Ref. [45]). Multiple-tracer methods (e.g., CH_4, δ^{13}C-CH_4 and C_2H_6) provide a powerful analytical tool to attribute CH_4 emissions to specific sectors. Lowry et al. [40]; Maazallahi et al.[39] and Fernandez et al. [42] use a triple-tracer approach to attribute detected plumes to emissions from waste, industry and agriculture, or leaks in the natural gas networks (e.g., Fig. 5). Röckmann et al. [10]; Menoud et al. [11] and [46] use continuous CH_4 and δ^{13}C-CH_4 observations from tower and roof-top measurements to determine changes in the relative contribution from specific sectors across spatial scales of several 10s of kms using atmospheric modelling approaches.

TABLE 1: AVERAGE AND STANDARD DEVIATION OF δ^{13}C-CH_4 SOURCE VALUES FROM [47], (*) FROM [48], AND (#) FROM [49] .

CH4 Source	**δ^{13}C-CH_4 [‰]**	**Simultaneous C_2H_6 Emissions**
Ruminants	–65.4 ± 6.7	no
Rice paddies	–62.2 ± 3.9	no
Wetlands	–61.5 ± 5.4	no
Termites	–63.4 ± 6.4	no
Waste	–56.0 ± 7.6	no
Biomass Burning	–26.6 ± 4.8	yes
Fossil Fuel	–44.8 ± 10.7	yes
Range in Mixed Troposphere	Around –47.5 (*)	Around 200 – 2000 pmol/mol (#)

2.5.URGENT NEED FOR INTENSIFICATION OF CH_4 OBSERVATIONS

Besides the scientific demand for intensified observations of CH_4 to close observational gaps, there is an urgent need from stakeholders in national administrations and economies to know their CH_4 budgets – both with respect to the amount of emissions, and where they are coming from. In 2015, 196 countries adopted the Paris Agreement of the United Nations Framework Convention on Climate Change (UNFCCC), as a legally binding international treaty to limit global warming to 2 °C, and peruse efforts to limit it to less than 1.5 °C [50]. Because of its relatively short atmospheric lifetime (9.1-11.8 years, [51]), and because of its large global warming potential (GWP-100 27-30, [51]), reducing CH_4 emissions can provide a vital consideration to limit global warming below 1.5 °C (Collins et al., 2018; Nisbet et al., 2020). Reductions of anthropogenic CH_4 emissions have been discussed as an attractive opportunity to address climate change [52, 53] and it was estimated that the societal benefits of reducing anthropogenic CH_4 emissions for most, i.e. > 75 % of the identified abatement technologies / policy options, outweighs the implementation costs [54]. Many countries have therefore prioritized the mitigation of CH_4 emissions. By 5th December 2022, 130 countries have signed the “Global Methane Pledge” and committed to cut their annual CH_4 emissions by 30 % until 2030, relative to 2020 levels [55].

Intensified research efforts as well as an expansion of observational infrastructure are urgently required to better understand CH_4 emissions on regional and global scales [56]. This will improve our knowledge of national CH_4 budgets and furthermore provide a way to test achievement of mitigation targets.

3. DATA QUALITY OBJECTIVES (DQOS)

This Chapter provides guidance on DQOs for the carbon stable isotope ratio analysis of atmospheric CH_4.

3.1.UNITS AND QUANTITIES

The quantities intended to be measured, i.e., the measurands [57] are the mole fraction of methane in dry air (which includes all gaseous species except water) and the isotope delta values, the relative difference of isotope ratios, of methane. For expression of stable isotope ratios, the guidelines provided by [58] have been followed. The following definitions and units are used throughout this document:

Methane mole fractions are provided in ppb = nmol mol^{-1} = 10^{-9} mole of CH_4 per mole of dry air (dry air includes all gaseous species except water). The WMO recommends the application of specific mole fraction scale realisations, for example WMO CH_4 X2004A for CH_4 mole fractions [59] (Section 6.2).

Isotope deltas are expressed in multiples of 0.001, designated ‰ or "per mil" and defined by:

$$\delta_{\mathrm{VPDB}}(^{13}C) \text{ or } \delta^{13}\mathrm{C}_{\mathrm{VPDB}} = \frac{\mathrm{R}(^{13}\mathrm{C}/^{12}\mathrm{C})_{\mathrm{sample}} - \mathrm{R}(^{13}\mathrm{C}/^{12}\mathrm{C})_{\mathrm{VPDB}}}{\mathrm{R}(^{13}\mathrm{C}/^{12}\mathrm{C})_{\mathrm{VPDB}}} \qquad (1)$$

$$\delta_{\mathrm{VSMOW\text{-}SLAP}}(^{2}H) \text{ or } \delta^{2}\mathrm{H}_{\mathrm{VSMOW\text{-}SLAP}} = \frac{\mathrm{R}(^{2}\mathrm{H}/^{1}\mathrm{H})_{\mathrm{sample}} - \mathrm{R}(^{2}\mathrm{H}/^{1}\mathrm{H})_{\mathrm{VSMOW\text{-}SLAP}}}{\mathrm{R}(^{2}\mathrm{H}/^{1}\mathrm{H})_{\mathrm{VSMOW\text{-}SLAP}}} \qquad (2)$$

where $R(^{n}X/^{m}X)$ is the isotope ratio of the heavy-to-light isotope of the element (C or H) in the sample or the standard. The international isotope ratio scale for carbon is VPDB (Vienna Pee Dee Belemnite, $\delta^{13}C_{VPDB}$) and for hydrogen is VSMOW-SLAP (Vienna Standard Mean Ocean Water-Standard Light Antarctic Precipitation, $\delta^{2}H_{VSMOW\text{-}SLAP}$).

3.2.COMPARABILITY, COMPATIBILITY, AND REPRESENTATIVENESS

Data quality objectives (DQOs) are qualitative and quantitative statements that clarify the objectives of observations, define the appropriate type of data, and specify tolerable levels of uncertainty. DQOs are used as the basis for establishing the quality and quantity of data needed to support decisions [60]

Target applications within the framework of this guideline are techniques for the sector-specific detection of CH_4 sources by isotopic analysis. The prime focus is on the measurement and interpretation of local CH_4 sources, where isotopic signatures of an unknown source (or a source mixture) are retrieved from temporal variations in ambient air CH_4 mole fractions and $\delta^{13}C$-CH_4 data using a mixing model. Isotopic signatures are then used to disclose the identity or the relative share of source processes. Example studies are methane mapping at street level on city scale, or in plumes of different CH_4 emitters as published by Rella et al. [45], Von Fischer et al. [61] , Hoheisel et al. [37]; Maazallahi et al. [39]; Lowry et al. [40]; Menoud et al. [46]; Fernandez et al. [42] , Saboya et al. [62] , and Defratyka et al. [43]).

Another, technically more challenging topic is the continuous analysis of ambient air CH_4, $\delta^{13}C$-CH_4 and optionally $\delta^{2}H$-CH_4 at remote monitoring stations or tall-towers to investigate CH_4 sources within the atmospheric footprint of the locations. Using atmospheric modelling approaches, this provides sector-specific emissions from regional [10, 11, 63] to global scales [14, 22, 64]. Although there is no clear distinction from the above, applications at remote locations are characterized by smaller trends and gradients in CH_4, $\delta^{13}C\text{-}CH_4$ and measurements are therefore accomplished by high-accuracy IRMS or preconcentration-laser spectroscopy. Nevertheless, the stringent DQOs required for data interpretation are difficult to achieve given current limits in analytical and scale transfer uncertainties.

DQO with respect to this Guideline include measurement uncertainty, repeatability, inter-laboratory or network compatibility and number of data points. A comprehensive overview and discussion of uncertainties and DQOs is provided by the "Guide to the expression of uncertainty in measurement (GUM)"[65] and the WMO-GAW Report #255 [31].

3.3. DQO CRITERION FOR OBSERVATION GOALS

A guidance on how to identify DQOs for the envisaged target applications are here provided. It will focus on *near-source* analyses of CH_4 mole fractions, $\delta^{13}C\text{-}CH_4$ (and $\delta^{2}H\text{-}CH_4$) and subsequent data analysis with Keeling plot [10, 66], or Miller-Tans [67] mixing models but will also give indications for monitoring at *remote* locations and interpretation using larger scale atmospheric modelling approaches. The inter-laboratory compatibility objectives for CH_4 mole fractions and isotope delta values recommended by the expert meeting for the GAW Programme [31] provide an indication on the laboratory agreement that is required within an observation network, which provides guidance when setting DQOs for instrumental measurement uncertainty. Due to the diverse applications envisaged, only characteristic figures are given.

3.4. CONSIDERATIONS

- For regionally focused studies with large local fluxes, or services related to urban air quality, focusing on relatively large measurand variability in space and time, the expert meeting for the GAW Programme recommends extended network compatibility goals of ±5 ppb for CH_4 mole fractions, ±0.2 ‰ for $\delta^{13}C\text{-}CH_4$ and ±5 ‰ for $\delta^{2}H\text{-}CH_4$ (95% confidence level or coverage factor k=2), respectively. Alternatively, the GAW Programme suggests network compatibility of 5 % (or better) of the excess dry air mole fraction over the appropriate local background.
- The very stringent compatibility goals for measurements of well-mixed background air are ±2 ppb for CH_4 mole fractions, ±0.02 ‰ for $\delta^{13}C\text{-}CH_4$ and ±1 ‰ $\delta^{2}H\text{-}CH_4$, (95% confidence level or coverage factor k=2), respectively.
- Laser based spectrometers offer the potential of operators to meet the WMO/GAW compatibility goals for CH_4 mole fractions, for both studies with large local fluxes and measurements of well-mixed, regionally representative air [68].
- The measurement precision achieved within IRMS laboratories for $\delta^{13}C\text{-}CH_4$ (and $\delta^{2}H\text{-}CH_4$) is usually significantly better than the measurement precision that can be achieved with off-the-shelf optical instruments [69]. A currently ongoing laboratory comparison highlights that IRMS laboratories measuring isotopes in atmospheric CH_4 can meet the extended network compatibility goals and potentially also the network compatibility goals for $\delta^{13}C\text{-}CH_4$, if a unique set of reference gases was available [70].
- The uncertainty of $\delta^{13}C\text{-}CH_4$ and $\delta^{2}H\text{-}CH_4$ source signature values, which can be extracted from a dataset by using a Keeling plot or Miller-Tans approach (Section 10.1), is in addition to instrumental measurement uncertainty mainly determined by the enhancement of CH_4 mole fractions above background and the number of data points. The Keeling plot approach, in addition, presumes constant isotopic composition of the local CH_4 source and stable CH_4 mole fractions and isotope ratios in the background air [66]. In contrast, the Miller-Tans approach can be applied under variable background

air conditions, by pairing background air and plume sample for analysis of δ^{13}C-CH_4 source values [67]. Therefore, background air variability needs to be assessed and implemented into the study design. A procedure to estimate requirements for CH_4 peak height and number of data points for a specific analyser with defined analytical uncertainty to reach a target uncertainty for source signatures is provided by Hoheisel et al.[37] (Section 10.1).

3.5. ONGOING RESEARCH

In contrast to CH_4 mole fractions, compatibility goals for δ^{13}C-CH_4 and δ^{2}H-CH_4 measurements are more challenging. Inter-comparison measurements between IRMS laboratories revealed differences in measurement results, around 0.5 ‰ (δ^{13}C-CH_4) and 13 ‰ (δ^{2}H-CH_4), which is significantly larger than the WMO / GAW extended network compatibility goals [69].
A currently ongoing round robin exercise shows that many of the laboratory offsets have been consistent over several years (unpublished data), demonstrating the stability of local scale realisations; this suggest that discrepancies can therefore be attributed to inconsistencies in calibration approaches (see Section 6.3).

4. ASSESSMENT OF ANALYSER PERFORMANCE

In principle, laser spectroscopic measurements of CH_4 mole fractions and $\delta^{13}C$-CH_4 values have the potential to be intrinsically accurate (SI-traceable) provided that the intensity of the analyzed $^{12}CH_4$ and $^{13}CH_4$ absorption lines are known and the pressure-broadening mechanism is well understood [30]. However, the factory calibration of an analyser only provides a first indication of results but may not be trusted as an accurate measurement. Consequently, a sufficient level of accuracy can only be achieved by calibration against gas standards, which is described in detail in Section 6.

This calibration is valid for a particular set of conditions, e.g., spectrometer configuration, pressure, temperature and the composition of measured gases. As changes in the instrument's status occur due to variations in cavity temperature, pressure, or laser wavelength, calibrations need to be repeated in regular time intervals. Sections 4.1 and 4.2provide guidance how to evaluate instrument stability / drift and derive optimal averaging times for sample analyses and frequency of calibrations. The extent to which an analyser drifts depends on the instrument type, model or even single device, and might not be constant over time as well as depend on the range of CH_4 mole fraction or isotopic composition [45].

Users need to adapt the composition of calibration gases to their sample as the analyser reading might be affected by differences in mole fractions of main air constituents (for ambient measurements: N_2, O_2, Ar), trace gases with spectral interferences and CH_4. Section 4.3 provides a procedure to assess the stabilization time of a setup, an important characteristic to decide on the timing of measurements. Note that test gases need to be used for these assessments to minimize the consumption of valuable calibration gases (Table 3). Sections 4.4 and 4.5 give advice, how to characterize these effects, formulate correction functions and estimate threshold values for post-measurement correction.

4.1. ALLAN VARIANCE

In general, the variability of measurement results includes both frequency independent "white" noise, and frequency dependent noise, considered as instrument drift. Averaging the analyser output over time reduces random variations (white noise), while instrument drift increases. The optimal averaging time and achievable precision before instrumental drift deteriorates results can be estimated with the Allan variance technique [71, 72]. The Allan variance technique provides information on optimal averaging times and associated precision targets for analyses of samples of constant composition (cylinders, glass flasks, or sample bags). It also informs how frequently calibration cylinders need to be measured. This information can be utilized when building analytical sequences for sample measurements and calibrations. As analysers from the same manufacturer series can achieve different performance levels, the Allan Variance needs to be determined for each individual analyser [73]. Researchers create Allan plots by plotting the Allan variance $\sigma^2(X)$ or its square root, the Allan standard deviation ($\sigma(\tau)$), over the averaging interval τ on a log-log plot. The main steps in Allan variance experiments include:

- Analyze a test gas for an extended period of time, typically between 24 and 48 hours. The gas needs to be of constant composition and representative of the CH_4 mole fraction of the target application. In addition, Allan variance tests need to be repeated using a gas mixture with enhanced CH_4 mole fractions (e.g., 10 ppm CH_4) to assess the changing instrument performance with varying CH_4 mole fractions. Use test gases such as T-1 to T-4 (Table 3) for these experiments, valuable reference gases may not be used for this purpose.

- Implementing the Allan variance technique requires applying an appropriate software package or customized programming. Thereby, for a given averaging interval τ, sequential block averages $y(\tau)_i$ are calculated by dividing the measurement data into N time intervals. The Allan variance σ^2 is then determined by summation of the squared differences of consecutive sequential averages $y(\tau)_i$ and $y(\tau)_{i+1}$.

$$\sigma^2(\tau) = \frac{1}{2N}\sum_{i=1}^{N}\left[y(\tau)_{i+1} - y(\tau)_i\right]^2 \tag{3}$$

- Create the Allan plot and determine the averaging time where the Allan Variance or the Allan standard deviation shows its minimum before it rises again ($\tau_{AV\text{-}min}$ in Fig. 6). This time interval needs to be applied to future instrument calibrations and sample measurements to reach maximum precision.
- The minimum averaging time (τ_{min}) to reach DQO's can also be determined from the Allan plot. An example is provided on the top panel in Fig. 6, which shows a schematic Allan plot for an arbitrary tracer using arbitrary mole fraction units on the y-axis. The black line represents the Allan standard deviation, and the horizontal red line indicates the DQO. The first intersection of DQO and Allan standard deviation indicates the minimum averaging time (τ_{min}), where measurements at the given mole fraction achieve DQOs.
- The Allan plot also provides an indication of τ_{max} as the upper time limit, after which the precision, due to instrumental drift, exceeds DQOs (Fig. 6). τ_{max} needs to be applied as the time interval between instrument calibrations, to ensure that long-term drift does not deteriorate the optimal instrument performance and therefore fail DQOs.

The lower plot in Fig. 6 presents a practical example for a typical Allan plot from a CRDS analyser [45]. Averaging the high frequency data over longer time intervals (several minutes to hours) reduces the influence of instrument noise and increases the precision of the measurement. For the presented example, integration of measurement results over 1000 s (16.7 min) provides a precision for δ^{13}C-CH_4 at 1.78 ppm CH_4 in the range of 0.2 ‰. With further averaging δ^{13}C-CH_4 precision improves below 0.1 ‰ ($\tau > 10'000$ s). To avoid detrimental effects of drift on data quality, sample and calibration gas measurements need to be completed before the Allan standard deviation increases above the DQO limit (not shown on the plot).

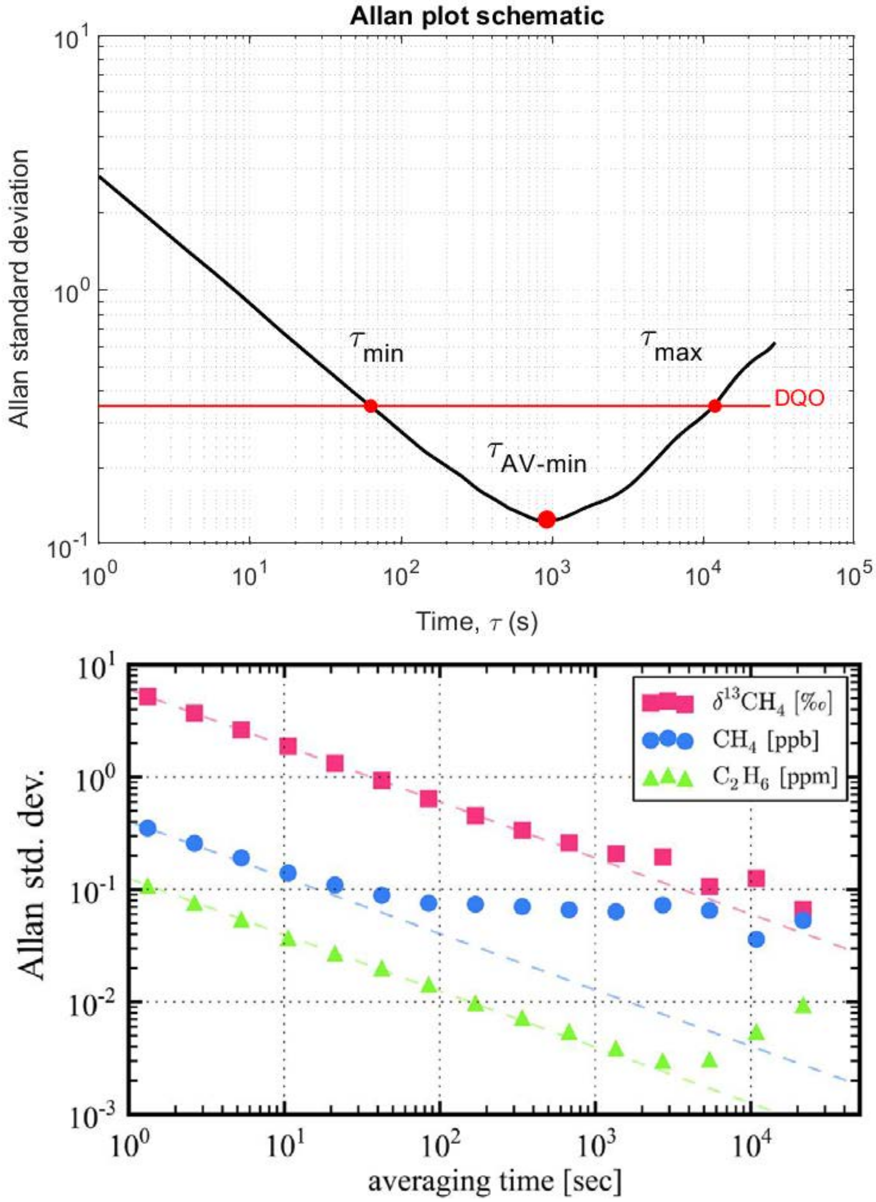

FIG. 6. Top: Schematic to show principal information that can be derived from an Allan plot. Intercepts of Allan standard deviation (black line) and DQO (red line) provide τ_{min} and τ_{max}. $\tau_{AV\text{-}min}$ is the averaging time to achieve maximum precision. Bottom: Example Allan plot for CH_4 and C_2H_6 mole fractions and $\delta^{13}C$-CH_4 analyzed by a CRDS analyser (Picarro G2132-i). Improved precision with averaging time, resulting in Allan standard deviations below 1 ‰ and 25 ppb for $\delta^{13}C$-CH_4 and C_2H_6 for 1 minute of averaging. (Reproduced from Ref. [45], with permission).

4.2. LONG-TERM DRIFT EFFECTS

For timescales of several days or months, considerably larger drift effects might occur than those observed with the Allan variance technique. The main steps to analyse long-term drift effects include:

- Analyse sample gas (or multiple sample gases) – with a constant composition that is representative for the target application for several days or even weeks. Measurements can be done continuously or repeatedly for time intervals corresponding to the Allan minimum. Optionally, alternate measurements between several gases with ambient air or ambient air at enhanced CH_4 mole fractions provided in high pressure cylinders. Note that valuable reference gases may not be used for this purpose.

- Plot temporal trends of CH_4 mole fractions and delta values and evaluate the data.

The example in Fig. 7 indicates that when analysing sample gas from high pressure cylinders at constant composition on a CRDS analyser over several days, apparent $\delta^{13}C$-CH_4 values can vary considerably for ambient or sub-ambient CH_4 mole fractions. In contrast, variations in $\delta^{13}C$-CH_4 are much smaller for enhanced CH_4 mole fraction of 10 ppm. Selection of an appropriate calibration and drift correction strategy will depend on the analyser performance for representative sample gases and the target data quality. The frequency of calibrations needs to be adjusted to resolve the observed instrument drift, relevant with respect to DQOs, so that instrument drift can be monitored and corrected for. The calibration strategy will be discussed in more detail in Section 6.

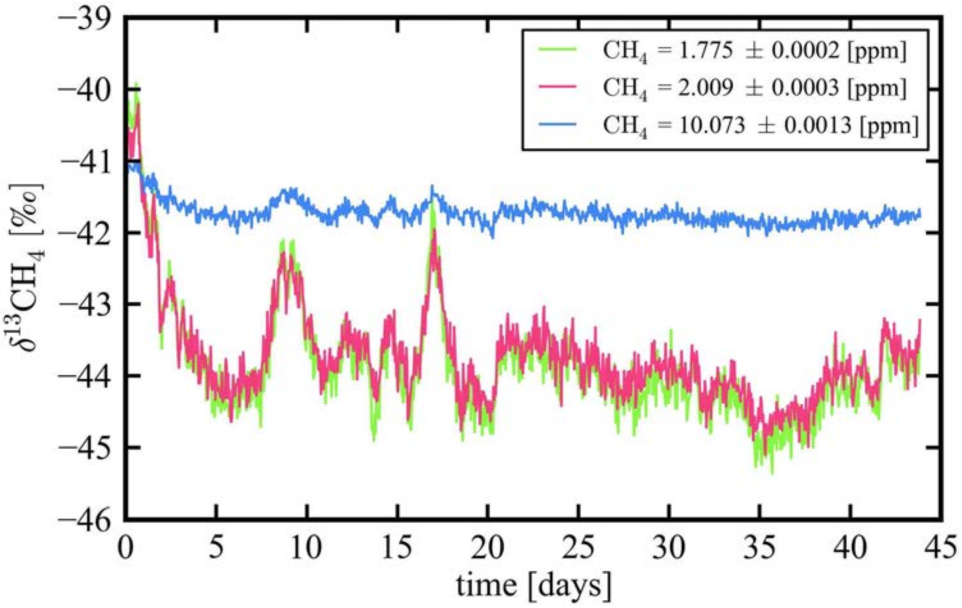

FIG. 7. Example of apparent $\delta^{13}C$-CH_4 values analysed by a CRDS analyser (Picarro G2132-i) in sample gas from three cylinders at sub-ambient, ambient and enhanced CH_4 mole fraction levels without intermittent drift correction. The plot indicates enhanced drift at ambient and sub-ambient compared to higher CH_4 mole fractions (reproduced from Ref. [45], with permission). Offset in $\delta^{13}C$-CH_4 between individual cylinders are due to different isotopic compositions of the applied gases.

4.3. STABILIZATION TIME (MEMORY EFFECT)

The stabilization time, i.e., time required to read out a representative result after switching between different gas samples is an important characteristic to design an experiment or a sampling strategy. The instrument response is a function of the volumes and geometry of the complete analytical setup, including its inlet system, e.g., dehumidification etc., at a given sample flow rate. The stabilization time is the sum of lag time and response time (e.g., t90, 90 % of final signal, see below for definitions) and can be determined with the following experiment:

- Establish the experimental setup, comprising of inlet system and analyser and set typical gas flows, pressures etc. Sequentially provide two different sample gases for 30 minutes each and repeat cycles at least 3 times. Sample gases "A" and "B" need to be sufficiently different, for example in CH_4 mole fraction, to detect gradual changes in analyte composition.

- Plot temporal trends of CH_4 mole fractions and delta values and evaluate the data for lag time and response time (e.g., t90). The lag time is the time interval between gas switch from "A" to "B" and the point in time, when the first instrument response can be detected. The response time is the time interval between the first instrument response and the point in time, when 90% of final signal ("B") is reached.
- The sum of lag, response and analysis time define the minimum measurement time and the minimum gas volume required per sample. This minimum requirement needs to be considered in the instrument tests in Sections 4.4 and 4.5.

4.4. AMOUNT DEPENDENCE

If the CH_4 mole fraction changes in the sample gas, this may affect measured delta values, as has been observed for different isotope systems ($\delta^{13}C$-CH_4, δ^2H-CH_4, $\delta^{15}N$-N_2O, $\delta^{18}O$-N_2O, etc.) and laser spectroscopic detection schemes (e.g., CRDS, OA-ICOS and direct absorption spectroscopy) [32, 38, 45, 74]. This effect can introduce large deviations of the apparent from the true delta values; therefore, dependencies need to be characterized as part of an initial evaluation period for individual analysers and eventually for calibration schemes. The main steps of the experiment are:

- Dynamically dilute a high mole fraction CH_4 standard in an ambient air matrix with a CH_4-free air to different CH_4 mole fractions relevant for the desired application and analyse the gas mixture (Fig. 8). The minimal measurement time needs to comply with the sum of stabilization time of the instrumentation (4.3) and the sample analysis time (4.1). In-between each CH_4 mole fraction step-change, set the dilution ratio to ambient CH_4 mole fractions to perform a reference measurement. Ensure that potential changes in $\delta^{13}C$-CH_4 values during this characterization are only due to changes in CH_4 mole fractions, and not to other effects such as instrument drift.
- Plot the $\delta^{13}C$-CH_4 instrument response versus CH_4 mole fractions and inverse CH_4 mole fractions to characterize the relationship and to assess whether effects are significant.
- Derive a mathematical correction function for the effect of variable CH_4 mole fractions on the $\delta^{13}C$-CH_4 instrument response. This function can then be used for data post correction, if required (Section 8.5.2).

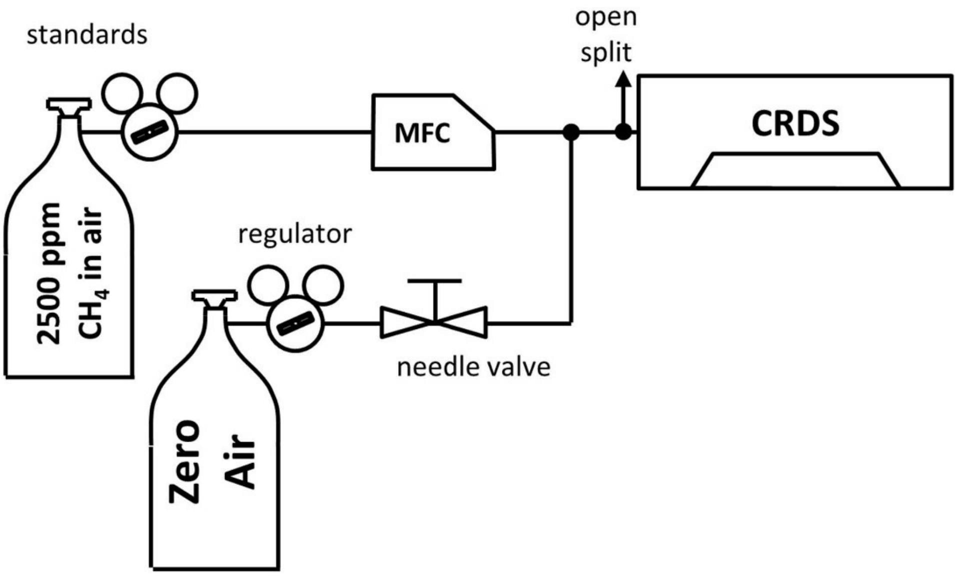

FIG. 8. Example setup to characterize the amount dependence of a CRDS analyser (reproduced from Ref. [45] with permission).

4.5. GAS MATRIX EFFECTS AND SPECTRAL INTERFERENCES

If mole fractions of atmospheric trace gases (H_2O, CO_2, CO, C_2H_6 etc.) or main constituents (e.g., N_2, O_2, Ar) differ considerably between sample and reference gas, this may result in an offset of the reading of the optical analyser for CH_4 mole fractions and $\delta^{13}C$-CH_4 [32, 37, 45, 75]. These effects introduce a measurement bias if the reference gas composition does not reflect the sample gas, or if the sample gas composition changes over time (e.g., close to source measurements or laboratory incubation studies). The required level of consistency between sample and reference gas composition in an interfering compound depends on its effect on the specific analyser and the acceptable level of deviation. If the effects exceed DQOs, a correction may need to be applied.

Similar care needs to be taken when diluting samples prior to analysis, to make use of synthetic air with appropriate N_2, O_2, and Ar and trace gas composition. The physical basis behind these phenomena are spectral interferences for trace gases with absorption lines in the operating range of the analyser (Fig. 9) and differences in pressure broadening by main atmospheric constituents [76]. For standard applications, trace gas effects might be reported in manufacturer's technical specifications and published instrument tests. Table 2 provides an overview of gas matrix effects and spectral interferences reported for example commercial CRDS analysers for $\delta^{13}C$-CH_4. The numeric value of a cross interferences for other devices of the same model may deviate and therefore needs to be experimentally determined. Note that optical instruments from other manufacturers are sensitive to gas matrix variation as well [32]. To our knowledge, these are less well documented in the literature and would need to be defined by the operators.

TABLE 2: EXAMPLES FOR GAS MATRIX EFFECTS AND SPECTRAL INTERFERENCES OF EXAMPLE CRDS ANALYSERS[37, 38, 45, 75].

Instrument	Gas species (formula)	Estimated effect on δ^{13}C-CH_4	Notes	References
Picarro G2132-i1	Oxygen (O_2)	+0.173 ± 0.023 ‰ %$^{-1}$ O_2	Independent of CH_4 mole fraction	[45]
	Argon (Ar)	≈ +0.4 ‰ %-1 Ar	Independent of CH_4 mole fraction; estimated from O_2 dependence	[45]
	Water vapour (H_2O)	< ± 1 ‰	0–2.5 % H_2O and 1–15 ppm CH_4	[45]
	Carbon dioxide (CO_2)	< ± 0.5 ‰	200–1800 ppm CO_2 and 1–15 ppm CH_4	[45]
	Ethane (C_2H_6)	+35 ‰ ppm CH_4 (ppm C_2H_6)$^{-1}$	Inversely proportional to CH_4 mole fraction	[45]
		+58.56 ‰ ppm CH_4 (ppm C_2H_6)$^{-1}$	Inversely proportional to CH_4 mole fraction	[38]
	Ammonia (NH_3)	-7.0 ‰ ppm CH_4 (ppm NH_3)$^{-1}$	Inversely proportional to CH_4 mole fraction	[45]
Picarro G2201-i	Water vapour (H_2O)	-0.54 ± 0.29 ‰ %$^{-1}$ H_2O	Tested range: 0.16 to 1.5 % H_2O	[37]
	Ethane (C_2H_6)	+40.87 ± 0.49 ‰ ppm CH_4 (ppm C_2H_6)$^{-1}$	Tested range: up to 0.7 ppm C_2H_6 (ppm CH_4)$^{-1}$	[37]
	Carbon dioxide (CO_2)	(1.25 ± 0.94) x 10^{-4} ppm C_2H_6 (ppm CO_2)$^{-1}$	Interference on C_2H_6; tested range up to 600 ppm CO_2	[37]
	Methane (CH_4)	0.0077 ± 0.0007 ppm C_2H_6 (ppm CH_4)$^{-1}$	Interference on C_2H_6; tested range up to 10 ppm CH4	[37]

Some previous studies indicate comparable correction factors for different CRDS analysers of the same model type, and no temporal changes [74, 75], while other manuscripts indicate differences (see Table 2: G2201-i C_2H_6 interference on δ^{13}C-CH_4). Consistency of interferences are plausible for instruments scanning the same spectral range and applying identical quantification algorithms; however, this may not be generalized without further testing. For novel applications with nonstandard or highly variable non-analyte trace gas mole fractions, researchers might consult spectral databases [76] or perform specific tests to investigate interferences. The following procedure can be applied to test the effect of interferants and develop correction functions:

4.5.1. Make measurements

- Dynamically mix a high mole fraction CH_4 standard (test gas T-6, Table 3c) and the interferant gas (e.g., C_2H_6, T-7), both in an ambient air matrix with CH_4-free air (T-5) with mass flow controllers to make up sample gas with different interferant mole fractions but constant CH_4 mole fractions and delta values.
- In-between each interferant mole fraction step-change, perform a reference measurement, i.e., analyse a gas sample with similar CH_4 mole fractions and δ^{13}C-CH_4 but without interferant (or at ambient mole fractions).
- Repeat tests at different relevant CH_4 mole fractions. For non-reactive interferant gases, static gas mixtures, prepared in gas bags, might be analysed alternatively.
- Similar to the above, interferences of trace gases (e.g., CO_2, CH_4) on analyte mole fractions (e.g., C_2H_6) have to be considered and if necessary characterized and corrected. These effects are listed in Table 2 and described in literature (e.g., Ref. [37]). An exemplary set of cylinders applied for these tasks are T5-T8 in Table 3. The analysis of results and limits/procedures is done in accordance with points given below.

4.5.2. Analyse results

- Plot apparent CH_4 mole fractions and δ^{13}C-CH_4 values versus interferant mole fractions for all measured CH_4 mole fractions.
- Characterize the mathematical relationship to identify whether effects are significant for interferant mole fractions expected in the sample. In general, the deviation of the analyser output from the true (undisturbed) signal for δ^{13}C-CH_4 for spectral interferences has been found to depend linearly on the mole fraction of the interferant and on the inverse of the CH_4 mole fraction. Consequently, correction factors are reported as ‰ per [interferant] / [CH_4]. For the gas matrix effect, the correction factors are reported as ‰ per [interferant]. No effect of CH_4 mole fraction changes on apparent gas matrix effects has been observed by [45].

4.5.3. Set limits/procedures

Define a maximum acceptable level of deviation of apparent δ^{13}C-CH_4 from true values due to a spectral interference, considering DQOs. Calculate the mole fraction of the interferant, using the above correction factor, at which the deviation exceeds the maximum acceptable level at an anticipated CH_4 mole fraction. Use this interferant mole fraction as a threshold value to decide whether or not a correction needs to be applied. In subsequent sample gas measurements, mole fractions of interferant gases need to be known or analysed for sample and reference gases. Whenever interferant effects are above acceptable levels, correction functions need to be applied to minimize measurement biases. Estimate the uncertainty of corrections in accordance with Section 6.8.

Alternative to mathematical corrections, trace gas effects can be minimized by either removal of the interferant, which is generally applied for water vapour, or balancing of trace gas mole fractions in the reference to the sample gas. Special attention needs to be paid to cross-interferences of laser spectroscopic measurements with H_2O vapour, as this might cause three different effects on the analyser response. These include: i) a dilution effect, as CH_4 mole fraction is reported relative to dry air; ii) a gas matrix effect on CH_4 mole fraction and isotope delta values; iii) and spectral interferences, if water lines exist in the analysed spectral range. Most commercial laser spectrometers account for cross-interferences with an implemented water vapour correction. However, the influence of water vapour is instrument-specific and can vary with time. Both aspects are usually not covered by the internal water correction of the instrument. Therefore, it is suggested to reduce the influence of H_2O by drying the air sample prior to analysis. Rella et al. [45] recommend mole fractions of water vapour below 0.1%, which can be achieved by using a counter-flow membrane dryer or cryogenic H_2O trapping [77]. For details on the setup see Section 7.6.4.

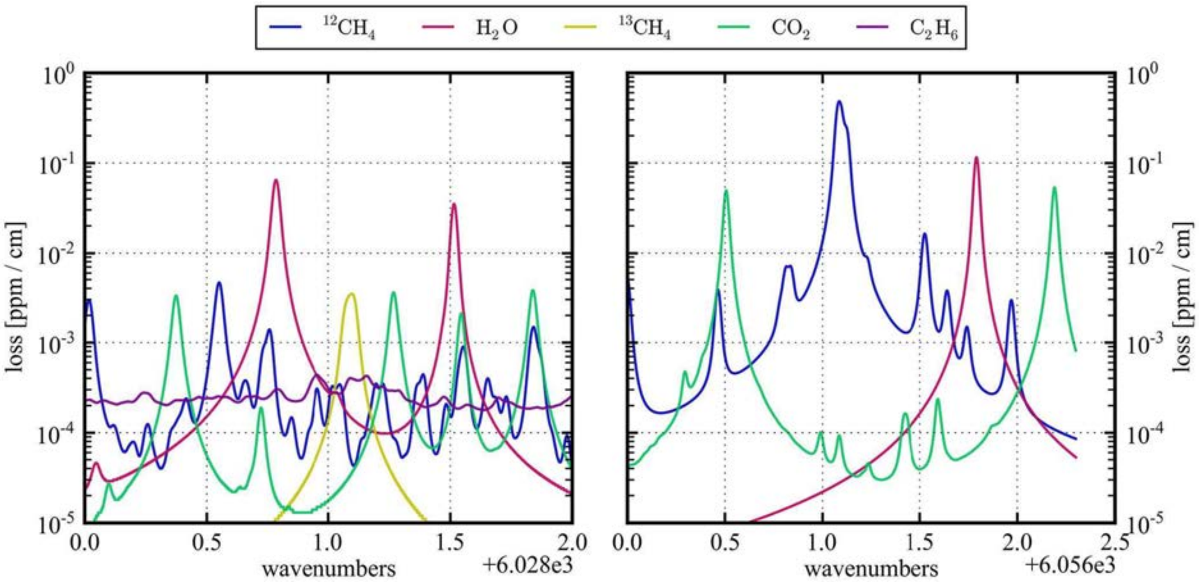

FIG. 9. Spectra within the frequency range at 6028 cm^{-1} (left) and 6056 cm^{-1} (right) covered by an example CRDS analyser (Picarro G2132-I). Spectra for methane isotopic species, water vapour and carbon dioxide were simulated from HITRAN (T = 45°C, p = 197 mbar), while the ethane spectrum was obtained experimentally by analysis of an ethane reference gas using CRDS (reproduced from Ref. [45]),with permission).

5. LABORATORY

5.1. LABORATORY DESIGN AND INFRASTRUCTURE

The requirements for a laboratory space are quite simple. Laboratory spaces need to be clean and dry for assembling and repairing instrumentation and inlet systems.

Most important is that the power supply meets the needs of the analyser and is stable. Power outages are not only disruptive to measurement, but they can also be damaging to the instrumentation. Ideally, Uninterruptable Power Supply (UPS) systems need to be in place to safeguard instrumentation and data.

Variation in laboratory temperatures can strongly impact isotope delta measurements. While optical analysers may include sophisticated internal temperature control around the analytical cell, instrument peripherals, such as pressure regulators on reference gas cylinders and gas inlet systems may be sensitive to strong temperature gradients. Therefore, laboratories need to be temperature stabilized. Also, direct sunlight on any parts of the analytical setup needs to be avoided, as this can introduce measurement biases that scale with daily sunshine hours. Instrument manufacturers need to be consulted as to the sensitivity of their instruments to temperature changes in the laboratories, and this needs to be thoroughly tested in the laboratory. Deployment of instruments in mobile platforms needs also to consider temperature control, like air conditioning in cars. Especially when running instruments in parked vehicles, or in boxes, which are exposed to increased solar radiation, overheating of the instrumentation and thus data loss or even damage to the instrument can easily occur. Analysts need to be aware of additional environmental factors that potentially impact the instrument and apply mitigation measures, for example to account for vibrations.

Other laboratory infrastructure to consider include oil-free compressed air for pneumatic valves (if used), tools for cutting and cleaning clean tubing for sample inlets, and drying systems for humid air such as counter-flow membrane driers or cryogenic chillers. More details about inlet design will be provided in Section 7.

5.2. LABORATORY SUPPLIES/CONSUMABLES

Unlike other instrumentation for stable isotopes, optical analysers use relatively few consumables:

5.2.1. Gases and gas supply

The most important material needed for methane isotope measurement is calibration gases, discussed in Section 6. These take time to prepare, so researchers need to consider their calibration needs and have cylinders filled and measured well before they are required for the measurements. Most analysers also require carrier or standby gases such as nitrogen or dry air. Samples that need dilutions might require methane-free air. All cylinders will need two-stage pressure regulators for high-purity applications with pressure settings appropriate for their use. Sample preparation may require liquid nitrogen, trapping materials, etc. These consumable need to be taken into consideration well before they are required, i.e., before the measurements, especially when instruments are deployed into remote regions. Further precautions will need to be taken when transporting compressed or liquified gases.

5.2.2. Plumbing components

Tubing made of high-purity stainless steel or other high-purity materials with leak-tight compression fittings need to be on hand to connect gases to the analyser. Avoid tubing made from polymers or metals that are not cleaned after manufacturing processes and that are not certified for high-purity applications. Mass flow controllers (MFC) or needle valves are useful for regulating gas flows to the instrumentation. For field campaigns in remote regions, researchers need to consider having spares, as well as the required tools to implement any repairs. High quality valves with the lowest certified leak rate need to be used, as leakage has potential to cause isotope fractionation and/or cause contamination from laboratory air that may contaminate the sample.

5.2.3. Tools

Tools dedicated for laboratory use, clean, and good quality. Tools for tubing applications need to include metric and imperial wrenches, screw drivers, tube cutters suitable for 1/16" to 1/4" tubing, and tube benders for 1/8" and 1/4". An accurate gas flow meter in appropriate range (e.g., 0-500 mL/min) is essential to measure and adjust flow rates.

5.2.4. Chemicals

Molecular sieves and magnesium perchlorate can be used as desiccants. Molecular sieve is the best choice to dry the drying air in a counter-flow dryer (Section 7.6.4, Figure 11) to avoid disintegration during water saturation. Magnesium perchlorate is a good choice as desiccant for example when taking flask or bag samples. Experimental verification is required to ensure the use of desiccants does not introduce measurement bias. A counter-flow membrane drying unit or cryogenic chiller is suggested for dehumidification under continuous operation. To achieve low water vapour contents a counter-flow membrane drying unit / cryogenic chiller in combination with desiccants can be used, which increases the stand-time of the chemical traps (more details in Section 7.6.4).

5.2.5. Extra

A soldering station for electrical repair is very helpful. Other helpful resources include capabilities for glass blowing, stainless steel welding, and stainless-steel milling.

5.2.6. General on components and consumables

The measurement of isotope ratios in CH_4 can be impacted by contamination with non-suitable materials, such as outgassing from polymers or contamination with hydrocarbons, such as oils and grease from manufacturing processes. Materials and components that are in contact with the air sample (wetted components) need to be certified for high-purity research applications. Non-compliant components may degrade the quality of the measurements at best, or contaminate the entire analytical system, including the analyser at worst. To prevent contamination, all materials need to be certified for high-purity applications.

6. CALIBRATION GASES

The following calibration approach follows GAW recommendations for the most accurate and compatible observations [31]. Data generated using this approach maintain high accuracy over long periods of time and can therefore be directly compared to data from other laboratories following the same approach. For the isotopic characterization of local $\delta^{13}C\text{-}CH_4$ source values, however, the GAW approach may exceed practical needs, especially for the mole fractions of the measured gases. For instance, CH_4 mole fractions in an isotopic source study (e.g., inside a barn or at a wastewater plant) may well be outside the range covered by the respective WMO scale and are mainly determined by the ventilation rate. However, accurate knowledge of mole fraction and isotope ranges is critical, for example for the correction of spectral interferences in optical analysers (Section 4.5). Accurate assignments of mole fractions and isotope ratios of samples through comparison against certified reference materials including their uncertainties, is critical to achieve internationally compatible results.

6.1. INSTRUCTIONS FOR CALIBRATION GASES

To achieve high-quality measurements, the system operator needs to apply a suitable instrument calibration and quality control strategy. This is typically accomplished by using a well-designed suite of calibration gases that allows assessing systematic instrument effects and that is matched to the composition of sample gases in important aspects (e.g., air matrix composition, amount effects, interfering substances). A successful calibration system includes an optimized, system-specific calibration schedule. Fundamentals on calibration gases for mole fraction measurements (Section 6.2) and isotope analyses (Section 6.3) are discussed separately, because they are based on separate traceability chains and fundamentally different principles. It is important for the operator to develop a thorough understanding of the principles of instrument calibrations and the method of linking measurements to established scales.

6.2. CALIBRATION GASES FOR MOLE FRACTIONS

Central Calibration Laboratories (CCL) have been established to provide suites of gravimetrically prepared reference gases for CH_4, CO_2 and C_2H_6 mole fractions that are traceable to the SI system (Fig. 10, WMO-GAW, [31] and Brewer et al. [30]). For the target species of interest, the list below provides the names of the most recent WMO mole fraction scales, as well as the website to the respective CCLs and the associated publication.

- For CH_4: WMO X2004A scale, last updated on July 7, 2015, [59], provided by the Global Monitoring Laboratory at the National Oceanic and Atmospheric Administration (NOAA-GML), USA. The CH_4 mole fractions currently covered by the WMO X2004A scale range from 300 to 5000 ppb. Further details and updates on the WMO X2004A scale can be found on the website.[1]
- For CO_2: WMO X2019 scale, last updated on 8 Feb 2021 [53], provided by the Global Monitoring Laboratory at the National Oceanic and Atmospheric Administration (NOAA-GML), USA. WMO X2019 covers a mole fraction range of 250-800 ppm CO_2. Details and updates are published on the website.[2]
- For C_2H_6**:** use reference gases for volatile organic compounds provided by the National Physical Laboratory [78].[3]

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[1] https://gml.noaa.gov/ccl/ch4_scale.html

[2] https://gml.noaa.gov/ccl/co2_scale.html

[3] https://www.npl.co.uk/products-services/gas/volatile-organic-compounds-vocs

- For non WMO-recommended scale realisations**:** Compatibility to the WMO scales needs to be demonstrated if scale realisations from other gas providers are used, such as national metrological institutes [79].

It is strongly advised to follow [31] and consecutive reports, as such scales are updated as needed.

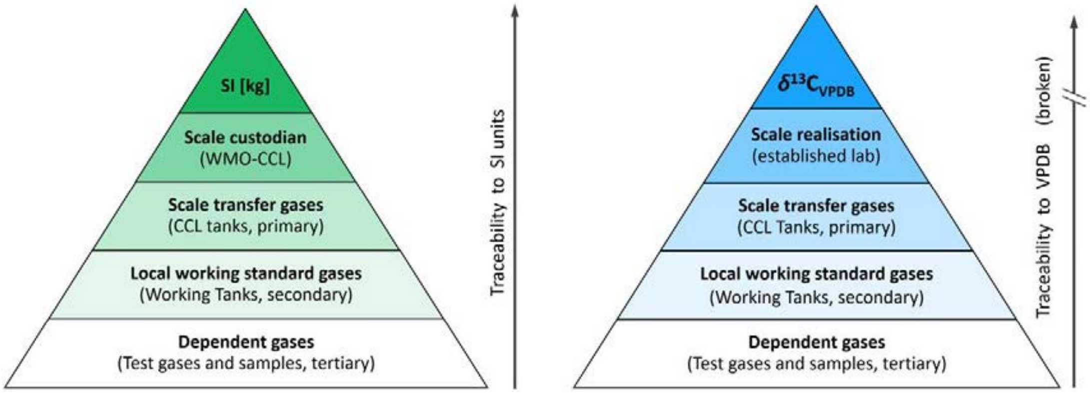


FIG. 10. Unbroken traceability chain from SI-units to samples for mole fractions (left). The $\delta^{13}C_{VPDB}$ scale is not traceable to the SI system but to artefacts (e.g., $CaCO_3$) representing $\delta^{13}C_{VPDB}$ (right). This lack of SI traceability created challenges in the traceability chain for $\delta^{13}C\text{-}CH_4$ to $\delta^{13}C_{VPDB}$ even for established labs. Propagation of $\delta^{13}C\text{-}CH_4$ values from scale realisation (established lab) to a local laboratory and further to local samples needs to be accompanied by a thorough propagation of uncertainties (Eq. 4).

6.3. CALIBRATION GASES FOR ISOTOPES IN ATMOSPHERIC CH_4

A CCL for isotope ratios in atmospheric CH_4 does currently not exist. Therefore, it is important to propagate a $\delta^{13}C_{VPDB}$ scale realisation for $\delta^{13}C\text{-}CH_4$ in air from a well-established, expert laboratory [31]. For that, a set of cylinders holding CH_4 in air mixtures with a suitable range in $\delta^{13}C\text{-}CH_4$ is carefully prepared and measured at an external laboratory. These cylinders can then be used to transfer the $\delta^{13}C\text{-}CH_4$ scale realisation of that external laboratory to the receiving laboratory. All going well, future measurements made by these laboratories need to be in good agreement, i.e., Umezawa et al. [69] . Potential expert laboratories need to have a demonstrated track record for reproducibility in $\delta^{13}C\text{-}CH_4$ in air measurement, as well as participation in round robin and other comparisons. It is of utmost importance to thoroughly document the propagation of the local scale realisation, including exact information on

- Laboratory name, scale name and version of the propagated calibration scale, identity of the reference materials, that the isotope calibration is based on, e.g. cylinder number, with associated isotope values;
- Cylinder numbers;
- Cylinder filling identifiers;
- Operator name;
- Calibration date;
- Measured values;
- Applied ^{17}O-correction (IRMS);
- Measurement uncertainty;
- Calibration uncertainty.

This applies to both, the cylinders used for calibration received from an external laboratory, as well as for reference gases made in-house to propagate local scale realisations to working standard gases. This information will enable tracing of all future measurements to the scale realisation of the propagating laboratory, as well as future scale updates.

6.4. THE PRINCIPLE OF IDENTICAL TREATMENT

Where possible, researchers measuring isotope ratios need to apply the `Principle of Identical Treatment` (PIT) during calibration and sample analysis [80]. As a simple rule, what applies to the analysis of samples needs to be applied for the analysis of calibration gases as well. This goes for i) the adequate composition of samples and reference gases, ii) the treatment of samples and reference gases within the analytical system, and iii) the data processing. As a result, potential errors in the analysis of samples and reference gases cancel, leading to higher measurement accuracy. In contrast, if the PIT is violated at any link within the calibration hierarchy (Fig. 10) this violation may result in a significant measurement artefact. The measurement error resulting from this violation will impact on all dependent measurements down the traceability chain (Fig. 10), and therefore cause inaccurate sample measurements. Operators are strongly advised to design the entire instrumentation and calibration strategy around the PIT and to scrutinise every possible link in the calibration hierarchy for potential violations of this principle.

6.5. CALIBRATION GAS CATEGORIES

Calibration gas categories are shown in Fig. 10. Note that this document refers to “reference gases” and “calibration gases” in a general sense when gases of known composition are referred to. This document uses the term “scale transfer gases” when it is specifically referring to a suite of gases that has the unique purpose to establish isotope or mole fraction scales at the receiving laboratory. Likewise, the term “working standard gases” refers to a specific suite of gases that is calibrated to the established isotope and mole fraction scales using the “scale transfer gases” and is used to assign isotope and mole fraction values to unknown gases. Gases used to define the scale realisation are highly valuable and need to be used carefully with view to maximize their lifetime. Therefore, “test gases” with target compositions need to be used by operators to understand and characterize instrument responses (Table 3 c) in experiments that don’t require valuable gases, such as Allan Deviation experiments (Section 4.1). There are a range of points and instrument specific details to consider when planning both, i) the composition and ii) the application of calibration gases for both mole fractions of CH_4, CO_2 and C_2H_6, as well as stable carbon isotope ratios in CH_4:

6.5.1. Overview on calibration gas categories

Operating an in situ analyser for greenhouse gas observations requires a suite of cylinders with gases for calibration and quality control. Four categories of gases are needed: i) scale transfer gases, ii) working standard gases, iii) quality control gases, iv) test gases (Table 3 a-c).

6.5.2. Scale transfer gases

Scale transfer gases are the critical link to relate local measurements to international measurements via internationally recognised scales. Scale transfer gases represent the highest possible calibration level a laboratory can acquire from a Central Calibration Laboratory (CCL, see WMO-GAW, [31]). These gases, named CCL-n in Table 3, has only to be used for the calibration and regular verification of the working standards, to preserve these scale transfer gases long-term, e.g., a decade. It would be most practical if one suite of scale transfer gases can be applied for all measured species, e.g., CH_4, CO_2, C_2H_6, and δ^{13}C-CH_4 in air. As there is not one CCL for all of the above parameters, this needs to be arranged with the respective CCLs. An example is given in Table 3. A minimum suite of scale transfer gases needs to include at least 8 cylinders with compositions shown in Table 3. It is important that the scale transfer suite includes two gases with ambient CH_4 mole fractions and wide range in δ^{13}C-CH_4 (CCL-1 and CCL-2) and two with 10 ppm CH_4 and a wide δ^{13}C-CH_4 range (CCL-3 and CCL-4) to account for the potential CH_4-amount dependence of δ^{13}C-CH_4. Additional gases need to cover the expected sample range for mole fractions as well as isotope ratios in regular intervals (CCL-7 and CCL-8). CCL-5 and CCL6 offer enhanced mole fractions of C_2H_6 and CO_2, but ambient levels in other parameters to enable the mole fraction calibration of C_2H_6 and CO_2 without interferences from CH_4. Note, that the CH_4 mole fractions in CCL-3 and CCL-4 are outside the CCL range [59]. However, these CH_4 levels were suggested by several users of CRDS instruments (e.g., Ref. [37, 38] for most accurate measurements in isotopic source studies. For C_2H_6, the upper mole fraction of 500 ppb was calculated as the C_2H_6 enhancement that would correspond to a CH_4 mole fraction of 5000 ppb under the assumption that all excess CH_4 was derived from fossil sources with 10 % C_2H_6, including a small safety margin from values in Hoheisel et al. [37] . Scale transfer gases need to be re-measured in frequent intervals by the CCL. Community experience shows that CH_4 and CO_2 in aluminium cylinders are stable for decades as long as the pressure remains above 20 bar and decanting flow rates are below 300 mL/min [81]. The WMO currently recommends re-calibrations every three years, but at least at the end of life. Note that CO_2 mole fractions will increase with decreasing pressure in the cylinder following Langmuir's adsorption–desorption model [81]. The use of cylinders with scale transfer gases needs to be terminated as the pressure falls to 20 bar and the cylinders need to be sent to the CCL for end of life calibration. Note that the lead time for scale transfer gases from CCLs can be around one year.

6.5.3. Working standard gases.

Working standard gases are applied in the daily operation of the instrument within each measurement sequence (indicated as WT-n in Table 3 and in the following). Working standards are used to define the instrument response and account for instrument drift and appropriate representation of the isotope scale. The application of three working standard gases (at least two for calibration and one for quality control) is suggested as a minimum in each measurement sequence. A larger number of working standards is suggested for the initial period (e.g., Section 8.1.1). The range of the target tracers in the working standards needs to match the range in the samples for both mole fractions and isotope ratios, to enable the definition of robust data correction and data calibration functions. The values in Table 3 can be used as guidance for studies in ambient air and diluted source gases. Working standard consumption needs to be closely monitored over time. As gas consumption of working standards is high and preparation requires a lot of time, laboratories need to have a replacement strategy in place in case they are fully consumed or accidentally vented. For continuous observations over long-term, laboratories might want to assess a scenario of using two working standard suites on a rotational basis.

TABLE 3 A. SCALE TRANSFER GASES. EXAMPLE FOR CALIBRATION GASES FOR AN OPTICAL ANALYSER, CAPABLE TO MONITOR CH_4, CO_2 AND C_2H_6 MOLE FRACTIONS, AS WELL AS $\delta^{13}C$-CH_4 RANGE WITH FOCUS ON AMBIENT AIR BUT ALSO STUDIES OF (DILUTED) CH_4 SOURCE SAMPLES. THE SPECIFICATIONS OF GASES MIGHT HAVE TO BE ADAPTED FOR ANALYSERS OR APPLICATIONS.

CCL Tanks, Scale Transfer Gases, Highest Level, used to Calibrate Working Standards

tracer	CCL-1	CCL-2	CCL-3	CCL-4	CCL-5	CCL-6	CCL-7	CCL-8
CH_4	ambient	ambient	10 ppm	10 ppm	ambient	ambient	3 ppm	5 ppm
$\delta^{13}C$-CH_4	ambient	–70 ‰	ambient	–70 ‰	ambient	ambient	–60 ‰	–70 ‰
CO_2	ambient	ambient	ambient	ambient	ambient	800 ppm	500 ppm	600 ppm
C_2H_6	ambient	ambient	ambient	ambient	0.5 ppm	ambient	0.2 ppm	0.4 ppm

TABLE 3 B. EXAMPLE FOR WORKING STANDARD GASES FOR AN OPTICAL ANALYSER TO MONITOR CH_4, CO_2, C_2H_6 AND $\delta^{13}C$-CH_4 IN AMBIENT AIR. THE TARGET RANGES NEED TO MATCH THE RANGES OF THE SCALE TRANSFER GASES (TABLE 3 A). THE SPECIFICATIONS OF GASES MIGHT HAVE TO BE ADAPTED FOR ANALYSERS OR APPLICATIONS AND CONSIDER HOW THE AMBIENT ATMOSPHERE CHANGES OVER THE COMING DECADES.

Working Tanks and Quality Control - Measured on Daily Basis, Checked against Primaries

tracer	WT-1	WT-2	WT-3	WT-4	WT-5	WT-6	QC-1
CH_4	ambient	ambient	10 ppm	10 ppm	3 ppm	5 ppm	3 ppm
$\delta^{13}C$-CH_4	ambient	–70 ‰	ambient	–70 ‰	–60 ‰	–70 ‰	–50 ‰
CO_2	ambient	ambient	ambient	ambient	500 ppm	600 ppm	450 ppm
C_2H_6	ambient	ambient	ambient	ambient	0.2 ppm	0.4 ppm	0.2 ppm

TABLE 3 C. EXAMPLE FOR TEST GASES USED TO CHARACTERIZE AN OPTICAL ANALYSER TO MONITOR CH_4, CO_2, C_2H_6 AND $\delta^{13}C$-CH_4 IN AIR. TEST GAS COMPOSITIONS MIGHT HAVE TO BE ADAPTED FOR ANALYSERS OR APPLICATIONS.

Test Gases

tracer	T-1	T-2	T-3	T-4	T-5	T-6	T-7	T-8
CH_4	ambient	ambient	5 ppm	10 ppm	0	100 ppm	0	0
$\delta^{13}C$-CH_4	ambient	ambient	n.d.	n.d.	–	n.d.	–	–
CO_2	ambient	ambient	ambient	ambient	0	0	0	4%
C_2H_6	ambient	ambient	ambient	ambient	0	0	5 ppm	0

6.5.4. Quality control standard gases

One cylinder with air of a similar composition as the samples needs to be used as quality control standard (QC-1 in Table 3). The quality control standard needs precisely known mole fraction and isotope values of the target gases, i.e., by measurements against the working standards. The quality control standard will subsequently be measured in each measurement sequence and be treated in the measurements and data processing as an unknown sample. The results of the quality control standards provide invaluable diagnostic data. Time series of quality control standard measurement results need to be collected in performance charts (Section 9.2). Deviations from the long-term average may indicate an analytical problem. The consumption of the quality control standard needs to be closely monitored, and a replacement strategy has to be in place.

6.5.5. Test gases

A suite of test gases (T-n in Table 3) is needed to perform fundamental experiments, e.g., Allan deviation tests, defining the CH_4 amount dependence of reported $\delta^{13}C\text{-}CH_4$ values and to assess measurement interferences. A high-quality CH_4-free air with the lowest possible CH_4 blank and natural composition of the main air components is required for these experiments. Test gases need to be used instead of working standards or gases of higher level where possible.

6.6. SPECIFICATION OF CALIBRATION GASES

The preparation of the gases used for instrument calibration is critical to making high quality measurements. The following aspects need to be considered.

6.6.1. Cylinder type and volume

Aluminium cylinders with pack-less brass valve for high-purity applications have been reported as reliable and stable for CH_4, CO_2 and CO [81, 82]. For safety, these cylinders require re-testing by an authorized entity every 10 years. When preparing a new cylinder, it is important to ensure it has a recent test date. Volume and filling pressure determine the lifetime of a cylinder filling. Experts recommend aluminium cylinders with a volume of 30 L (Table 4) that can be filled to approximately 2000 PSI or 135 bar, for laboratory-based work. These cylinders are a good compromise between movability within a laboratory and lifetime of the filling (4,000 L of air). Air stored in these cylinders will last several years if used carefully. Note that CO_2 mole fractions start to increase as the cylinder pressure falls below 20 bar [81]. Therefore, smaller cylinder sizes are not advisable. Note that this effect has not yet been observed for CH_4 mole fractions. While fillings of 50 L cylinders last longer, they are significantly heavier and more difficult to manage. When using the analyser on a mobile platform such as a car, experts recommend using cylinders with lower volumes and pressures for the working standards and follow local security recommendations.

TABLE 4: KEY CHARACTERISTICS OF CYLINDERS.

Cylinder Material	**Cylinder Volume**	**Valve Type**	**Valve Connector**	**H_2o Level**	**Air Capacity**	**Maximum Pressure**	**Minimum Pressure**
aluminium	30 L	brass, UHP application	CGA-590	dry	4,000 L	135 bar / 2000 PSI	20 bar / 300 PSI

6.6.2. Number of reference gases

Analytical systems have to include a sufficient number of reference gases to account for all expected instrumental effects. Reported isotope values are likely to show a non-linear dependence on the mole fractions of the same gas, while the instrument response for mole fractions might be linear (e.g., Section 4.4). Furthermore, reference gases need to enable researchers to develop correction schemes for potential measurement interferences. Researchers also need to allow for redundancy, for the unlikely case that a reference gas cylinders becomes unstable. The objective of these guidelines is to formulate a comprehensive reference gas suite that can be maintained over many years and that covers all aforementioned effects for a very broad range of applications. Table 3 suggests a suite of 8 cylinders for scale transfer, 6 working standards and one quality control, and 8 test gases. Note that the suggested suite of reference gases allows a broad range of applications. Therefore, the cylinder number exceeds the minimum requirement for a single application. To account for effects unknown at the time of writing, operators need to critically assess their application and have the capability to expand the reference gas suite as needed.

6.6.3. Mole fraction and isotope ranges in reference gases

A suite of suitable calibration gases need to bracket the expected analyte range. i.e. most, if not all sample measurements need to fall in the range covered by the reference gases (Section 6).

6.6.4. Main air components

Natural air comprises around 78.08 % N_2, 20.95 % O_2 and 0.93 % Ar. Deviations in the composition of the main air components causes differences in the so-called pressure-broadening, which has the potential to significantly bias the measurement results of optical analysers (e.g., Ref. [74, 83, 84]). A difference in the composition of main air components between samples and reference gases will generate inaccurate measurement results (Section 6.4). As a practical solution, operators need to follow the PIT [80] and apply reference gases with a gas matrix that is identical to that of the measured samples. For applications on ambient air all gases used in the calibration hierarchy therefore need to comprise natural N_2, O_2 and Ar levels with an uncertainty of 0.1 % absolute (Section 4.5). For specific other application, e.g., incubation studies, the gas matrix in sample may deviate. If this deviation causes a variation in δ^{13}C-CH_4 that exceeds DQOs, reference gases need to be applied that mirror this deviation or a correction scheme to account for this effect needs to be applied.

6.6.5. Effect of the δ^2H-CH_4 on CH_4 mole fraction measurements

Optical analysers for δ^{13}C-CH_4 measurements only quantify the main carbon isotopologues (e.g., $^{12}CH_4$ and $^{13}CH_4$ mole fractions), while the amount of the minor hydrogen isotopologues (e.g., $^{12}CH_3D$) remains unconsidered. If δ^2H-CH_4 in sample and reference gases is sufficiently different, this can introduce an error in the mole fraction measurement, as a δ^{13}C-CH_4 analyser doesn't measure that isotopologue at all. Chen et al. [83] assessed the magnitude of this effect for CO_2. They investigated this effect in synthetic air mixtures that was mixed from CO_2-free air and pure CO_2, where the latter was derived from combusted fossil sources. This pure CO_2 had δ^{13}C-CO_2 and δ^{18}O-CO_2 values that were differed from that of natural air by –29 ‰ and –16 ‰, respectively. When measured with an optical analyser, the isotope difference caused a difference in CO_2 of ~0.15 ppm. Although the effect is much smaller for CH_4/δ^2H-CH_4, operators need to be aware of the origin of CH_4 in their reference gases and assess if corrections are required to achieve DQOs.

6.6.6. H_2O content

Any condensation or liquid water in the sample line, which might be transferred into the analyser needs to be prevented by all means, as this may severely damage the instrument. For high data quality, it is a useful rule to minimize the water vapor content of measured gases as much as possible. Measurement interferences with water vapour are significant and were described previously (e.g., Ref. [45, 83, 85] Reference gases are most commonly prepared as compressed, dried air (Dlugokencky et al., 2005), while natural air has a variable content of H_2O. This results in systematic H_2O differences between reference and sample gas, which needs to be accounted for to prevent measurement bias (Section 6.4). Rella et al. [45] describe interference effects of water vapour on $\delta^{13}C\text{-}CH_4$, which are implemented in spectral analysis, but states that for most accurate results drying < 0.1 % H_2O is required. Welp et al. [86] recommend using a counter-flow membrane dryer to continuously remove H_2O from the sample air stream, which Hoheisel et al. [37] adopted to minimize the correction required for $\delta^{13}C\text{-}CH_4$ measurements.

6.6.7. Non-target gases and interferences

Section 4.5 provides details on measurement interferences for specific optical analysers. For example, Hoheisel et al. [37] report interferences of C_2H_6 on $\delta^{13}C\text{-}CH_4$ measurements in a CRDS analyser. For another CRDS analyser model, Rella et al.[45] provide a more extensive list of interferants (O_2, Ar, H_2O, CO_2, C_2H_6, NH_3, H_2S, CH_3SH, C_3H_8, C_4H_{10}, C_2H_4 and CO). If mole fraction differences for interferants between calibration gases and sample exceed a threshold value (Section 4.5), suitable calibration gases need to be adapted (Section 6.4) or operators have to apply an interference correction. Specific interferants, e.g., H_2S may be removed using a CuO filter [87], which also protects the analyser from corrosion.

6.7. PRACTICAL CONSIDERATIONS

Measurements of isotope ratios in air samples can be severely compromised by small changes in the composition of calibration and reference gases during storage and / or analysis. For example, a small leak may cause isotope fractionation and thereby measurement errors, even though it might not cause a measurable effect on the analysis of mole fractions, or a significant loss of gas, or contamination from laboratory air. Similarly, the use of undesirable material in the experimental setup (e.g., polymer tubing) may result in isotope data of poor quality, even though this is not noticeable in mole fraction measurements.

6.7.1. Pressure regulators

Use two-stage regulators designed for high purity applications, with a narrow supply pressure range for most precise control, i.e., up to 2-3 bar. Acceptable wetted materials include brass, stainless steel, Viton, nickel plated brass, PTFE and PCTFE. Other materials, especially other polymers need to be avoided, as they may potentially cause contamination and thereby measurement artefacts. When pressure regulators are not mounted, the pressure adjustment needs to be set to zero (no pressure on outlet) to relax the internal spring.

6.7.2. Mounting pressure regulators on calibration gas cylinders

Mount the pressure regulator on the cylinder with the pressure adjustment set to zero. Depending on the state of the bullnose on the regulator and the seal inside the cylinder valve, a layer of clean PTFE tape might be needed to ensure a leak-tight seal. While mounting, carefully ensure the integrity of the PTFE tape to prevent fragments of it being blown into the regulator. Apply a thorough leak check protocol to each cylinder.

6.7.3. Leak-check pressure regulators

After the pressure regulator is mounted, open the cylinder valve to pressurize the pressure regulator while the pressure adjustment is set to zero. Once the pressure regulator shows full pressure, close the cylinder valve. This will hold the air inside the pressure regulator. Flush the pressure regulator by opening and closing the cylinder valve, followed by venting of the gas inside the regulator. Repeat 10 times to flush residual air out of the regulator. Close the pressure regulator and open the cylinder valve to pressurize the pressure regulator and then close the cylinder valve. Record the inlet pressure reading and let the system sit for at least one day or ideally a week and compare the inlet pressure values before/after. A reduced pressure indicates a leak. No significant leak needs to be apparent, as this will cause loss of reference gas and likely also isotope fractionation.

6.7.4. Connecting cylinders to analyser

All cylinders need to be connected to the sample inlet using the same materials. The inlet pressure to use is indicated in the instrument specifications. Use of stainless-steel tubing and fittings has proven successful for target components considered in this guideline (CH_4, CO_2, C_2H_6). The type of applied fittings needs to be carefully planned to minimize the number of connections, thereby minimizing the number of potential leaks. The dimension of the plumbing needs to be chosen to minimize the residence time of calibration and sample gases inside the plumbing system, i.e., give preference to small tubing and fitting diameter where possible. The use of 1/16” tubing to connect reference gases to sample inlet systems has proven sufficient for many applications. Use 1/8” if 1/16” is impractical. Small dimension plumbing also reduces system memory effects after switching between different calibration and sample gases. Ensure all lines connected to a cylinder or valve are thoroughly flushed when the respective line is in use. Prevent “dead ends”, i.e., branches of tubing that are not flushed while the gas flows from cylinder to the analyser, as this may result in system memory and contamination.

6.7.5. Test pressure regulators for contamination effects

If a pressure regulator is mounted and thoroughly flushed, the composition of the air inside the regulator needs to be identical to the composition of the air inside the cylinder. Because some pressure regulators have been found to cause contamination for CH_4, the integrity of each pressure regulator needs to be thoroughly verified. Pressure regulators can be assessed by the following protocol: mount a pressure regulator on a gas cylinder filled with pressurized air. Fill the regulator and hold the gas inside the pressure regulator for several days while the cylinder valve is closed. Next, measure the air inside the pressure regulator with an in situ analyser while the cylinder valve is closed. Thereby the air that was held inside the pressure regulator gets measured without dilution from air from the inside of the cylinder. Open the cylinder valve when the inlet pressure approaches low overpressure values, i.e., 10 bar. Contamination from the pressure regulator would show up as excess CH_4 in the initial phase, with the cylinder valve closed. Faulty regulators have to be replaced immediately.

6.7.6. Identical method to supply calibration gases and samples to the analyser

The method of supply for samples and reference gases needs to be as similar as possible (Section 6.4). That is, supplying gas from reference gas cylinders needs to not produce a systematically different instrument response compared to sample gas. This includes, but is not limited to, plumbing and valving components, wetted materials, passage of dryer, and pressure in the analytical cell. The use of identical plumbing components will prevent systematic differences due to use of different materials. Users need to have knowledge about the response of their analyser to sample gas pressure: some instruments are capable to precisely maintain a constant cell pressure over a large range in supply pressure at the sample inlet, whereas other analysers do not have that capability and require an additional pressure correction step in the data processing.

6.7.7. Minimize consumption of reference gases

It is of utmost importance to design the reference gas approach and the calibration schedule strategically, so that the calibration gases last a long time. The lead time for scale transfer gases from CCLs can be on the order of one year, while the lead time for cylinders from manufacturers can be on the order of half a year alone. To preserve these valuable gases, valves of reference gas cylinders need to be closed if gases will not be used for some time.

6.7.8. Storing calibration gas cylinders

All cylinders used for calibration gases need to be thoroughly restrained, following local health and safety regulations. For high quality measurements, it is furthermore important to minimize any impacts on cylinders that may affect their performance and longevity. It is crucial that the cylinders are stored at constant temperatures while in use. Temperature gradients across the cylinder, periodic exposure to direct sunlight or air-outlets from air conditioning systems have to be avoided, as this will imbalance gas adsorption-desorption processes on internal surfaces. Even though the effect is likely to be small, gas adsorption-desorption processes may alter the composition of the gases and therefore cause measurement artefacts (e.g. this has been documented quantitatively for CO_2 by [81]. Cylinders that are not in use need to be properly capped and especially the valves need to be always dry and clean. Long-term storage might require sealing the valve with a plastic cover to avoid impact from humidity, sea salt aerosols etc.

6.8. MEASUREMENTS TRACEABILITY AND UNCERTAINTY

An uncertainty estimation (Table 5) needs to be performed for each specific analyser and measurement task compliant with GUM, the Guide to the expression of uncertainty in measurement [88]. This approach differentiates statistical uncertainty components as observed by the analyst (type A) from all other uncertainty components (type B). An example for a type A uncertainty component is the variance of repeated measurements of a known quantity, such as δ^{13}C-$CH_{4,\ VPDB}$ in a quality control standard. On the other hand, an example for a type B uncertainty component could be the uncertainty of certified reference materials, provided by reference material providers (Table 5). For δ^{13}C-$CH_{4,VPDB}$ the experimental variance of the mean $\sigma^2_c(\delta^{13}$C-$CH_{4,\ VPDB})$ is calculated by applying the law of uncertainty propagation [31, 88]. This needs to include all uncertainties that contribute to the isotope measurements, representing the uncertainty of the traceability chain to the VPDB isotope delta scale following:

$$\sigma_C^2(\delta^{13}C - CH_{4,VPD}\ ) = \sum_{i=1}^{N} \left(\frac{\delta f}{\delta x_i}\right)^2 u^2(xi) \quad (4)$$

In this example, f is the functional dependence of δ^{13}C-$CH_{4,\ VPDB}$ on the quantities x_i. The combined standard uncertainty ($\sigma_c(\delta^{13}$C-$CH_{4,\ VPDB})$) is then calculated as the positive square root of the combined variance (Eq. 4). Uncertainties of all contributing quantities need to be clearly identified with the reported standard uncertainty. This above procedure is appropriate, when input quantities are uncorrelated, while for correlated input quantities the formalism has to be adapted in accordance with GUM [88]. The expanded uncertainty is obtained by multiplying the combined standard uncertainty by a coverage factor k, which is typically in the range 2 to 3 [88].

As a first step a mathematical model that transforms delta observations of the analyser (δ^{13}C-$CH_{4,obs}$) into calibrated measurement results (δ^{13}C-$CH_{4,\ VPDB}$) has to be established (Eq. 5). A two-point calibration system is advisable as the minimum [89].

$$\delta^{13}\text{C-CH}_{4,\ \text{VPDB}} = y_2 \times \delta^{13}\text{C-CH}_{4,\text{obs}} + y_1 \quad (5)$$

y_1, y_2 are the intercept (Eq. 6) and slope (Eq. 7) of the linear calibration function, respectively (Paul et al., 2007), defined as:

$$y_1 = (\delta^{13}\text{C-CH}_{4,\text{cal1}} \times \delta^{13}\text{C-CH}_{4,\text{obs,cal2}} - \delta^{13}\text{C-CH}_{4,\text{cal2}} \times \delta^{13}\text{C-CH}_{4,\text{obs,cal1}}) / (\delta^{13}\text{C-CH}_{4,\text{obs,cal2}} - \delta^{13}\text{C-CH}_{4,\text{obs,cal1}}) \quad (6)$$

$$y_2 = (\delta^{13}\text{C-CH}_{4,\text{cal2}} - \delta^{13}\text{C-CH}_{4,\text{cal1}}) / (\delta^{13}\text{C-CH}_{4,\text{obs,cal2}} - \delta^{13}\text{C-CH}_{4,\text{obs,cal1}}) \quad (7)$$

δ^{13}C-$CH_{4,cali}$ and σ^2 (δ^{13}C-$CH_{4,cali}$) for commercial reference materials have to be provided by the gas supplier and provide traceability to primary reference materials. Note the need to develop an equivalent data calibration framework for measurements of CH_4 mole fractions.

Depending on the analyser, the analytical task and uncertainty requirements, the reading of the analyser (δ^{13}C-$CH_{4,obs}$) has to be corrected for differences in CH_4 amount fractions, gas matrix composition and the abundance of spectral interferants, between sample and reference gases, as discussed in detail in Sections 4.4 and 4.5. Relevant corrections will be part of the mathematical model and subsequently need to be included in the uncertainty evaluation [90]. Eq. 8 extends Eq. 5 to provide an exemplary formalism to correct δ^{13}C-CH_4 observations of the analyser for CH_4 amount dependence (a_{AD}: linear amount fraction dependence in ‰ (ppm CH_4)$^{-1}$, if the dependence is inverse the formalism has to be adapted [35], spectral interference (a_{SI}: correction factor in ‰ (ppm SI)$^{-1}$), gas matrix effect (a_{GM}: correction factor in ‰ (% GM)$^{-1}$). More details on the variables are provided in the table below.

$$\delta^{13}\text{C-CH}_{4,\ \text{VPDB}} = y_2 \times (\delta^{13}\text{C-CH}_{4,\text{obs}} - a_{AD} \times \Delta CH_4 - a_{SI} \times \Delta SI / \Delta CH_4 - a_{GM} \times \Delta GM) + y_1 \quad (8)$$

Wherever possible, the Principle of Identical Treatment needs to be followed, i.e. reference gas composition needs to mimic the sample as closely as possible, to minimize or better waive the need for corrections and reduce the overall uncertainty. Furthermore, the presented uncertainty evaluation might be too optimistic as corrections might be more complex or not temporarily stable and not independent from each other.

TABLE 5: EXEMPLARY LIST OF SOURCES OF UNCERTAINTY FOR δ^{13}C-CH$_4$ OBSERVATIONS WITH OPTICAL INSTRUMENTS.

Variable	**Data Source**	**Standard Uncertainty**	**Type A/B**
δ^{13}C-CH$_{4,obs}$	analyser observation	σ^2 (δ ^{13}C-CH$_{4,obs}$ (t))	A
$CH_{4,\,obs}$	analyser observation	σ^2 (CH$_{4,obs}$ (t))	A
δ ^{13}C-CH$_{4,cali}$	certificate reference material i (1, 2)	σ^2 (δ ^{13}C-CH$_{4,cali}$)	B
a_{AD}	amount fraction correction factor	σ^2 (a_{AD})	B
a_{SI}	spectral interference correction factor	σ^2 (a_{SI})	B
a_{GM}	gas matrix correction factor	σ^2 (a_{GM})	B
ΔCH_4	Difference in CH$_4$ amount fractions between sample and reference gases	σ^2 (CH$_{4,sa}$); σ^2 (CH$_{4,cal}$)	B
ΔSI	Difference in spectral interferant (SI) amount fractions between sample and reference gases	σ^2 (SI$_{sa}$); σ^2 (SI$_{cal}$)	B
ΔGM	Difference in gas matrix (GM) amount fractions between sample and reference gases	σ^2 (GM$_{sa}$); σ^2 (GM$_{cal}$)	B

The use of standard deviations or standard errors needs to be clearly stated and always be reported with associated degrees of freedom (n-1), where n is the number of data.

7. SAMPLING AND MEASUREMENT SYSTEMS

7.1. GENERAL INSTRUCTIONS

Researchers need to clearly define their goals before the sampling/measurement campaign so that the most suitable observation method and sampling materials can be selected to enable data of high quality. The research goals determine where, when and how to make the most suitable observations. Table 6 may help with that decision making. In order to determine δ^{13}C-CH_4 from specific point sources using flask/bag samples, analysts need to sample downwind of the CH_4 source and across the emission plume, as well as upwind from the observed CH_4 source to define background air values for CH_4 and δ^{13}C-CH_4. The sampling frequency needs to be sufficient to resolve the expected variability in the air. Filling flasks or bags need to be informed by a field deployed analyser for CH_4 mole fractions, to ensure that the samples cover a sufficient range in CH_4 for Keeling Plot Analysis (Section 10.1). In case, the CH_4 mole fraction in a sample exceed the operation range of the optical analyser, dilution with zero air (T-5, Table 3) can be applied (Section 4.4). To study urban or local CH_4 emissions with high temporal resolution, researchers may deploy an in situ analyser into the field. For studies on regional / larger scales analytics with high sensitivity is required and in situ monitoring of δ^{13}C-CH_4 is strongly preferred. Data interpretation might be supported by atmospheric modelling and comparison to emission inventories (e.g., Ref. [11]).

It is critical that in situ measurements or samples taken back to the laboratory for analysis are not affected by sampling artefacts. Materials used for air inlet systems and sampling vessels have not to alter the composition of the sample. Details of the equipment design depend on the instrumentation used, the anticipated signal, the field site (ease of transporting samples, etc), the DQOs, and ultimately the goals of the measurement campaign.

TABLE 6. OVERVIEW ON POSSIBLE RESEARCH GOALS AND SUITABLE OBSERVATION AND SAMPLING TECHNIQUES. BACKGROUND MEASUREMENTS ARE GENERALLY CONDUCTED BY DISCRETE SAMPLING AND SUBSEQUENT IRMS LABORATORY ANALYSES AND ARE NOT DISCUSSED HERE.

Research Goal	**Sampling Location**	**Expected Signal Strength**	**Sampling Strategy / Frequency**	**Examples**
Characterizing isotopic value of specific sources	Close proximity to CH_4 sources, e.g., feed lot, farm, wetland, natural gas source	Large signals expected (possibly dilution), potential for high interferant mole fractions.	Discrete samples in flasks or bags, or mobile sampling platform with air core type play back system, sampling over a range of CH_4 mole fractions	[37, 39, 40, 43, 45, 61, 91, 92]
Identifying and monitoring of urban / local sources;	At central location with sensitivity to local sources	Medium-sized signals expected	In situ continuous or discrete sampling	[39, 42, 46]
Identifying and monitoring of regional / larger scale sources	Distant from local point sources	Small signals expected, high sensitivity required	In situ continuous preferred, or discrete automated sampling (event-driven)	[10, 38, 93]

7.1.1. Materials, components and general instructions to build equipment for air sampling and measurements

Components applied for air sampling need to be approved by monitoring networks (e.g., WMO-GAW, [31] ; ICOS IR, [77]) or tested to demonstrate they do not induce artefacts on the measurement (requirement).
All fittings and components with wetted parts need to be specified for use in ultra-high purity applications (Section 5.2). If components include polymers, such as gaskets, valve seats etc, ensure these are made from PEEK, PTFE, PCTFE or Viton. All other polymers need to be avoided or tested, as they may cause contamination (requirement).

7.1.1.1.Tubing:

- Tubing need to be Dekabon, Synflex or cleaned stainless steel, without residues from manufacturing (Section 5.2.2). All lines and connections need to be made of a minimum number of parts to minimize leaks.
- Lines and connections need to be tested to be leak tight, either with a helium leak detector, or by testing to see if components can hold pressure or hold vacuum (requirement).
- Tubing diameter and flow rate define the residence time in the inlet. It is generally advised to minimize the residence time of the sample in the tubing to prevent artefacts. Air inlet lines at towers have been made from 1/4" OD, while the flow rate is increased by an additional flushing pump (Miles et al., 2018). Tubing to connect the analyser to the air inlet line, calibration gas cylinders and flask/bag samples need to have smaller diameters, ideally 1/16", only use 1/8" if needed (Section 6.7). Minimizing the internal volume also minimizes system memory and therefore time after changing between sample gases (e.g., t_{90} in Section 4.3). Re-check timings, gas flow rates and pressures after replacement of tubing and other components.

7.1.1.2.Inlet and filter

- The air inlet of the sampling line needs to be protected from rainwater, snow, ice and fog. Water condensation inside the air intake needs to be avoided, which can form when the dew point in air samples is above air-conditioned laboratory temperature. The analyser will be severely damaged if liquid water enters the cell. A downwards-opening funnel-shaped or cup-shaped air inlet allows water droplets to drop off and reduces the velocity of the air stream at the cross section of the funnel/cup. This eliminates the risk of water ingress due to wind turbulence or pumped air flow (requirement).
- Ensure the sample inlet won't get clogged with dirt or biogenic material from plants, insects, rodents, etc. Consider potential impacts specific to the sampling site. For instance, filters may need to be incorporated to remove water droplets, dust or sulphur components. Emissions from landfills, wastewater treatment plants and geological CH_4 sources may also include corrosive or otherwise damaging substances. Cascade systems holding a series of PTFE filters with decreasing mesh size (in flow direction) could be applied. Mesh size examples are >10 µm on the first filter, <10 µm and > 2.5 µm on the second filter and <2.5 µm and >0.3 µm on the third filter (requirement).
- In addition to the filter at the ambient air inlet specified above, a second filter is required upstream of the analyser to prevent damage of the equipment or reduced data quality. Inline filter units with sintered stainless-steel filter insert and a mesh size between 0.5 and 7 µm are advisable (requirement).

- For all applied filter systems, it needs to be verified that they do not alter the composition of the air, and that the filter diameters are large enough to enable sufficient air flow rate. Used filter inserts have to be changed in appropriate frequency to prevent build-up of filtrates, which can alter the composition of the air (requirement).
- Automated inlet systems need to be used to make measurements most efficient and reproducible. This applies to both, continuous observations and the analysis of flask/bag samples.

7.1.1.3.Introduction of standard or sample gas

- The sample gas needs to be dried to < 0.1 % H_2O (dew point < -20°C) with an appropriate technique (e.g., counter-flow membrane dryer, desiccant) as the instrument's water correction might not be sufficient for accurate $\delta^{13}C\text{-}CH_4$ measurements [38, 45]. Note that counter-flow membrane dryers require constant flow and pressure regimes (requirement).
- Standard or sample gases need to be introduced to the sample inlet system via multi-position rotary valves (Section 7.2). The design of the multiport rotary valves ensures that the entire section of the selected line is continuously flushed. In comparison, some commercial sample inlet units were made from an array of solenoid valves that included “dead ends” in the plumbing scheme. These are small sections that are not flushed but contain remnant air from previous samples and therefore create the risk to system memory (Section 4.3).
- Adjust the supply-pressure on working standards and quality control gases to be ≤ 0.5 bar above ambient air pressure. Considering flow resistance within the inlet system, ensure that the pressure at the analyser inlet is always slightly above ambient air pressure during measurements of working standards and quality control tanks to minimize the risk of contamination with laboratory air in case of a small leak. Observe and try to match instrument pressure and sample flow rate changes during measurements of cylinder and sample air. Adjust the supply pressure on the cylinders so that changes in instrument pressure and sample flow rate are minimized (requirement).
- If instrument pressures and sample flow rates do not stabilize, use a mass flow controller for working standards and quality control gases. Control the gas flow from each cylinder using normally closed solenoid valves as shown in Figure 11. Plumb all cylinders into one line feeding a mass flow controller. Use a t-fitting downstream of the mass flow controller, where one line feeds into the multi-position valve, and the other line is used as vent line (open split). Set the flow rate on the mass flow controller to exceed the flow rate of the analyser by ~10 mL/min, where the excess flow is vented through a vent line of 1/16” or 1/8” outer diameter and 0.5 m length. This open split configuration decouples the flow control of the mass flow controller and the pressure control of the analyser.
- The operating software of the analyser needs to be used to programme measurement sequences, i.e., the timing of calibration gas and samples measurements (Section 8.2). The software will then store valve positions and sample identifiers in the resulting data file.

7.1.1.4.Meteorological data

- Basic meteorological data are essential for interpreting results, e.g., for relating CH_4 plume observations to specific CH_4 sources, for the potential assessment of emission strength and for the understanding of parameters controlling emissions. Researchers need to consider collecting wind speed and direction, temperature, and pressure data. Meteorological instruments need to be selected with small uncertainty, for example, ICOS approves sensors with uncertainty of ≤0.2 K for temperature, ≤3 % for relative humidity, ≤0.3 hPa for barometric pressure, ≤0.5 m/s for wind speeds below 5 m/s and ≤10 % for wind speeds above 5 m/s, as well as 1° for wind direction [77].

- For the purpose of forecasting wind direction and strength, freely available online tools may be useful when planning field campaigns.

7.2. SYSTEM FOR CONTINUOUS AMBIENT AIR MONITORING

Optical analysers of methane are ideal for generating long time series of methane isotope measurements with high temporal resolution. Continuous CH_4 and δ^{13}C-CH_4 observations were used to partition the relative contributions of agricultural and industrial CH_4 emissions. In situ sampling has also been used to detect emissions from fossil fuel extraction on land [38, 94] and on oil and gas platforms at sea [95].

A measurement system for continuous δ^{13}C-CH_4 analysis with an optical analyser typically consists of an analyser, an automated multi-position valve with calibration gases, a sample drying system, and a computer and communication device to download and transfer the data. An example of a schematic laboratory set-up is shown in Fig. 11. It is best practice to create measurement routines that automatically alternate between calibration gases, quality control gas, and sample at well-defined intervals (Section 4.1) and that record information to identify sample and reference gas measurements in the data output file.

7.2.1. Considerations:

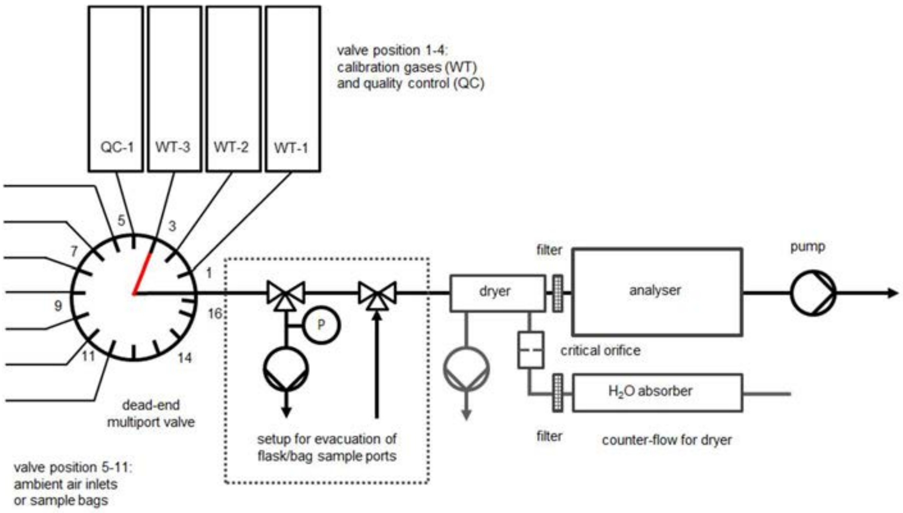
- Location of station and inlet height (e.g., rooftop or tower) need to reflect the research question (requirement),
- If possible, perform footprint, wind rose or back trajectory analysis of the designated site before instrument deployment to support the research plan,
- The impact of prevailing wind direction, topography, and potential obstructions on the advection of the measured air need to be taken into account when selecting the site. I.e., does the prevailing wind direction allow for the observation of CH_4 emissions from target regions, or is the measured air advected from targeted regions or is the air flow altered by local features, such as buildings, vegetation, topography? (requirement),
- Consider potential sources of CH_4, interferences in the vicinity of the site and atmospheric effects when selecting the sampling location, i.e., industry, traffic, combustion sources, animals, effect of night-time boundary layer, etc. (requirement),
- The calibration gases and the quality control gas are provided in high-pressure cylinders and are equipped with pressure regulators that are adjusted to a small overpressure. Check whether the analyser cell pressure remains stable with enhanced inlet pressure and stabilizes quickly after gas changes. Once stable, the variability of the cell pressure when measuring gases from cylinders needs to be similar to the noise in cell pressure when the system operates without any load. If this criterion is not met, implement a mass flow controller to restrict flow for each calibration gas and the quality control gas and an open split to maintain ambient pressure at the analyser input. Alternatively, one mass flow controller can be applied for all WT / QC gases and the gas to be measured selected with individual on – off valves (Section 7.1.1and Figure 11) (requirement),
- The sample flow rate through the instrument needs to be monitored with a mass flow meter continuously or in regular intervals, in scenarios that are representative for

measurement applications (measurements of gases from cylinders, sample flasks/bags and an outside air line). Measurements might be applied downstream of the analyser to avoid contamination effects or leaks but pressure fluctuations by the pump have not to affect the measurement (requirement).

- Develop a safety plan for the event of power failures. Ideally, the analyser operates on a UPS (uninterrupted power supply). A UPS unit bridges the power supply during power cuts and thereby protects the analyser and measurements. Furthermore, a protocol needs to be implemented that switches the sample inlet valve into idling mode. It needs to be prevented that the valve stays in an "open" position and vents valuable calibration gases during or after the power cut (i.e., valves automatically close without power) (requirement),
- Consider potential for automated data transfer, e.g., network accessibility.

Figure 11 shows a schematic of an example set-up applied for δ^{13}C-CH$_4$ analysis in ambient air or bag samples with a CRDS analyser. Sample gas from ambient air inlets or sample bags are supplied at ambient pressure. To minimize sample contamination in sample ports, a 3-port valve with membrane pump is installed downstream of the multiport valve. Different configurations can be applied for supplying WT and QC gases as well as purge air to the sample gas dryer. The counter-flow drying air can be fed from i) the vent of the analyser pump (modified from Ref. [38, 84]) routed through a desiccant trap (i.e., molecular sieve), or ii) ambient laboratory air, which requires a pump at the counter-flow drying air outlet (modified from Ref.[96]).

a)



b)

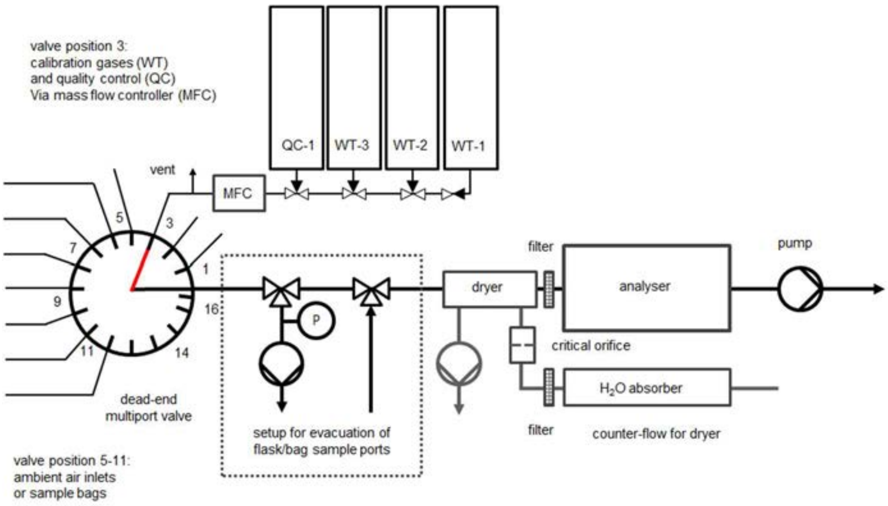


FIG. 11. Schematic of an example set-up applied for $\delta^{13}C\text{-}CH_4$ *analysis in ambient air or bag samples with a CRDS analyser. a): system configuration where calibration gases are fed into the multiport valve individually, without mass flow controller (MFC). b): system configuration using a mass flow controller (MFC) to adjust the flow rate of calibration gases. The vent line releases excess gas and counteracting effects from MFC and analyser by pressure decoupling. Two- and three-way valves are configured to prevent unflushed, dead volumes and thereby memory effects when switching between cylinders. Black triangles show normally closed paths of two- and three-way valves to prevent loss of calibration gases.*

7.3. SYSTEM TO MEASURE AIR FROM FLASK AND BAG

Flask and bag samples can be measured with a setup shown in Fig. 11. Use a 16-port multi-position sample valve for efficient sample throughput. A diaphragm pump with 3-port valve needs to be installed downstream of the flask/bag sample valve to evacuate the sample ports and thereby minimize sample contamination with laboratory air. A pressure gauge in this section will be used to leak check the pressure in the sample ports after evacuation. Use 3-way valves with small internal volume (e.g., for gas chromatographic applications) to connect the pump and the alternative air inlet. These need to have a small internal volume and also avoid "dead ends" that are not flushed with sample air during measurement. Similar to ambient air measurements described in the paragraph above, flask or bag samples need to be dried to H_2O < 0.1 %. Each measurement sequence needs to start and end with calibration gas blocks; samples need to be measured in between (Section 8.1). Quality control standards need also to be measured in the run for use in the performance chart (Section 9.2). For gas samples collected offline and subsequently analysed in the laboratory, a number of considerations need to be taken into account:

- Gas samples taken directly from CH_4 emitters or close by (e.g., natural gas pipelines, biogas plants, gas collecting systems of landfills and wastewater treatment plants), may result in CH_4 mole fractions that exceed the calibrated range of the analyser. Direct analysis may therefore not be possible or compromise data quality. In these cases, samples need to be diluted to match the operation range of the analyser. Static or dynamic dilution might be applied depending on the application / lab infrastructure. Hoheisel et al. (2019) described a dilution method, transferring 30-100 µL of the sample with a gas-tight syringe into a 3 L sample bag, filled with synthetic air, while others dilute samples dynamically using mass flow controllers (Miles et al., 2018; Harris et al., 2020) (requirement),
- Gas samples collected close to sources might contain high mole fractions of other trace gases, which interfere with target analyses. These substances need to either be removed prior to analysis, their effects corrected for or considered in the uncertainty budget (Section 8.5) (requirement),
- Gas samples with high H_2O vapour pressure need to be dehumidified during sampling to avoid condensation in the flask/bag. Similar to ambient air measurements described in the paragraph above, flask or bag gas samples need to be dried to H_2O < 0.1 % prior to analysis (requirement),
- Gas samples with a CH_4 mole fraction below ambient (e.g., soil-air samples, diluted samples) will result in very low data quality. Such samples might not be suitable for optical instruments and require specialized laboratories with GC-IRMS systems or sample preconcentration laser spectroscopy (i.e., Eyer et al., (2016)), however, this is out of scope for this document.

7.4. SYSTEM FOR MOBILE MEASUREMENTS

Optical analysers have also been used in mobile campaigns to identify plumes of methane and then measure them isotopically. This method was pioneered by Phillips et al. [91] and further developed by Rella et al. [45] , whose setup is shown in Fig. 12. The system uses the "playback" idea of an AirCore, developed by Tans [97] and described in Karion et al. [98] . An inlet tube mounted above a vehicle draws in air at high flow (~1900 mL/min) while driving. This type of system has been used by several research groups to measure methane emissions in urban areas [37, 43] and by other groups to measure emissions from fossil fuel extraction in more rural areas [45, 99].

The analyser draws a fraction of this high-flow air stream, while the rest is pulled into the long coil of tubing (for example, 15 m, 8.0 mm ID aluminium) to temporarily store the air. If the analyser detects methane mole fraction above a certain criterion, this stored air can be redirected to the analyser for measurement at a lower flow rate with longer integration time and thus higher precision. Note that the volume of the plumbing needs to be adjusted to meet analyser performance criteria, i.e., the size of the playback volume, analyser flow rate, measurement frequency and required integration time to reach DQOs.

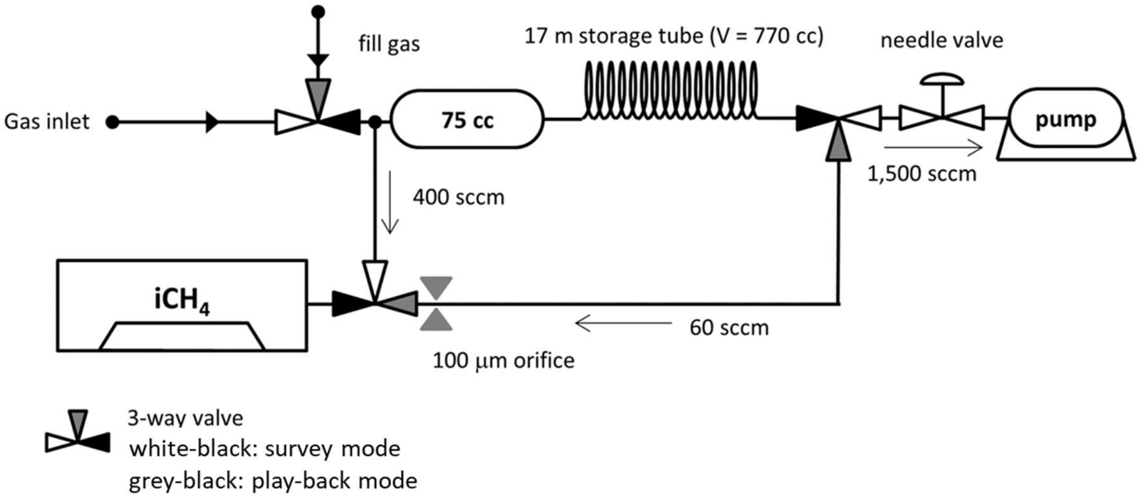


FIG. 12. Setup for measuring CH_4 mole fractions, $\delta^{13}C$-CH_4 and C_2H_6 / CH_4 ratio with a CRDS analyser in a mobile laboratory. For survey mode, all three-way valves are in "open" position (white-black), and the instrument measures the real-time signal. At the same time, sample gas is stored in the 17 m tube, with the flow through the tube being set by the pump and needle valve. When a plume is detected at the instrument, the three-way valves are switched to "play-back" position (grey-black) and the instrument slowly re-analyses the gas stored in the long tube. For simplicity, the counter-flow membrane drying unit and filters are omitted in the drawing (reproduced from Ref. [45] with permission).

7.4.1. Considerations

- A counter-flow membrane drying system needs to be employed to keep the water vapour mole fraction below 0.1% [37] (requirement),
- Though sample inlets have had different placements, it is suggested to place the inlet above roof. It is important to equip the observation platform with equipment for meteorology and GPS observations of highest possible quality and resolution, as these are the most significant factors in the uncertainty of estimated CH_4 fluxes [100],
- Care needs to be taken to avoid damage of the optical analysers during driving, i.e., vibrations on uneven roads (requirement).

7.5. VESSELS FOR DISCRETE AIR SAMPLING

Methane is generally inert and does not react with surfaces; as a result, researchers have had success collecting samples in containers made of various materials.

The chosen sample vessel size will depend on practical considerations (shipping, transporting, etc); the desire for duplicate measurements; and the amount of air required per analysis to achieve the targeted DQOs, such as measurement precision (Section 3.3). Miles et al. [38] use a measurement time of 64 minutes to achieve the target DQO. At a given analyser flow rate of 35 mL/min and assuming a stabilization time of 10 minutes, the required sample volume is > 2.5 L.

7.5.1. Stainless steel or aluminium flask

Clean stainless steel or aluminium flasks are suitable sample vessels for CH_4 and its stable isotope analysis and are capable to preserve the integrity of the sample for a long time. These vessels have the advantage of being very robust and tolerating overpressures, as well as enabling reliable, stainless steel valves for high purity applications with ultra-low leak rates. Ensure to not exceed the maximum tolerable sample inlet pressure of the analyser. Some flask models have pressure gauges, which allows to detect leakages after sampling. However, these are expensive, and their higher weight may complicate logistics and increase costs further.

7.5.2. Glass flasks

Glass flasks are less heavy, but fragile, and therefore require a well thought out system for handling and transport. PTFE o-rings are a simple, effective solution for maintaining tight seals without influencing measurement. Some manufacturers provide PCTFE seats, which outperform PTFE in stability for some gas species [101, 102]. CH_4 measurements have proven to be stable in glass flasks using greased valves, though the effect of vacuum grease on isotopic measurements has not been rigorously tested. Due to its effect on other species, and operational inconveniences, grease is still best avoided [103]. Note, however, glass valves with Viton o-rings need to be greased with a special vacuum grease of ultra-low vapour pressure, suitable for high-vacuum applications. Glass flasks can be filled to 2.5 bar absolute. At a volume of 2 L, each filling would provide 3 L of air, before the pressure in the flask drops below ambient. However, the flask filling pressure needs to be compatible with the inlet pressure of the analyser to prevent instrument failure. Avoid using flasks as below ambient pressures to prevent sample contamination with ambient air.

For practical logistical reasons, it is advised to not exceed the dangerous goods pressure limit (2.8 bar), even if the sample vessel was certified for higher pressures.

7.5.3. Multi-layer foil gas sampling bags

Multi-layer foil gas sampling bags have been used for sampling on many occasions because they are very lightweight and easy to transport [104]. Sample bags are susceptible to damage; but with careful handling they can be an economical and efficient way to fill and transport samples over long distances. However, the trade-off is that repeated use of sample bags is not advised by the manufacturer. Multi-layer foil bags are more vulnerable to storage effects than metal or glass flasks. (Note that the transparent, single-layer foil bags are highly unstable for the analysis of most gases and that artefacts are expected shortly after sampling.)

7.5.4. Considerations

- All sample containers need to be thoroughly tested for leaks, as any small leaks can be a source of isotopic fractionation (requirement),
- Sample vessels have to be able to withstand the pressure at which it will be filled, plus the potential pressure increase due to altitude difference between sampling, shipping and measurement sites. Sample bags are not tolerant to overpressure, they require additional volume capacity for air freighting (requirement),

- It is of critical importance to test all vessel types to confirm the materials, the manufacturing, and the utilization does not affect CH_4 mole fractions and δ^{13}C-CH_4. This can be accomplished by filling vessels with air from a cylinder with known CH_4 and δ^{13}C-CH_4 values. Next, allow filled vessels to sit for a length of time that is typical for the observations. Measure air from the sample vessels in direct comparison to the parent cylinder to assess the storage effect. Agreement between the sample and cylinder will reflect both the analytical uncertainty as well as any effect of leaks or wall effects of the sampling vessel. This could identify "bad" sample containers (i.e., contamination), or it could indicate a problem with the method overall (requirement),
- Robust flushing and filling protocols need to be followed. A standard rule of thumb is to flush a given volume (here the sample flask) with at least 10 volumes of sample air to replace residual air inside the volume (requirement). (For instance, a 1 L flask requires 10 L of air for flushing.),
- A fill gas of known and distinct mole fractions can be useful during flask preparation for air sampling campaigns, to identify poorly flushed/filled samples. For instance, the NOAA cooperative sampling network sends flasks to stations with very low CO_2 mole fraction so that improperly filled flasks are promptly identified by sub-ambient CO_2 levels when they return to the lab. Note, this is not applicable for sampling bags. Sampling air in paired vessels is also helpful to ensure good sampling while also providing a metric of repeatability of the analyser [105].

7.6. SYSTEM TO TAKE FLASK OR BAG SAMPLES

A simple system is required to take air samples at sites of interest for CH_4 and δ^{13}C-CH_4 analysis at a central laboratory (Fig. 13). The most basic function this unit needs to provide is i) to enable taking an air sample from a target location, ii) to remove water vapor from the air sample, iii) to direct the air sample into the target vessel, and iv) to enable thorough flushing of the target vessel with sample air. A simple sampler as the unit shown in Fig. 13 will enable air sampling without creating measurement artefacts, as long as key aspects are considered.

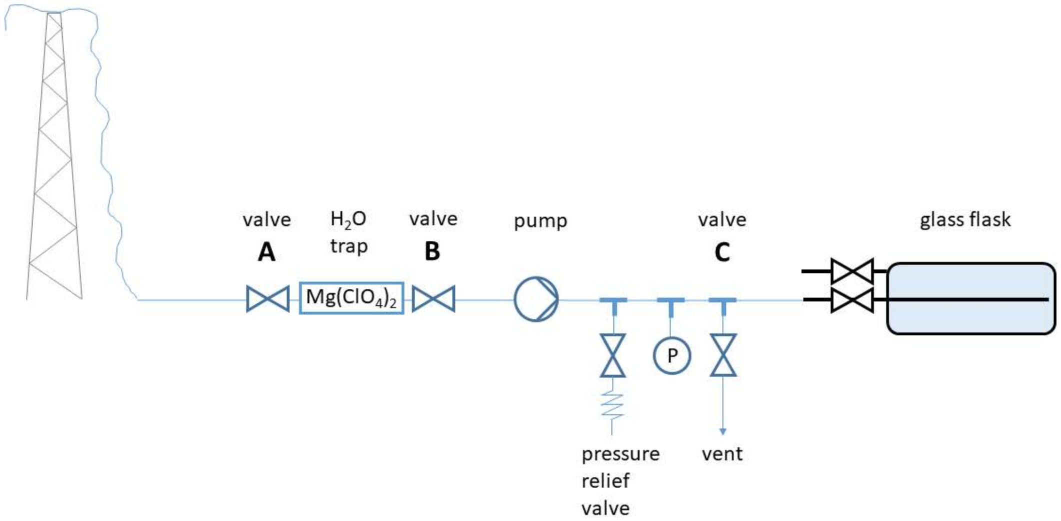


FIG. 13. Air flow is from left to right. In flow direction, sampled air is first routed through a magnesium perchlorate ($Mg(ClO_4)_2$) trap or an alternative dryer to remove water vapour and a particle filter, before the pump pushes the air towards the sample vessel. Metal components are indicated in blue, the glass flask is indicated in black. An air sampling bag or metal flask can be mounted instead of the glass flask.

7.6.1. Pump

- The sampling pump needs to be leak tight and preserve the integrity of the sample gas, reproducible results have been observed with diaphragm pumps with PTFE lined diaphragm for high-purity applications. It needs to be tested that the pump does not contaminate the sample (requirement),
- To enable field deployment in remote locations, it needs to operate on batteries, e.g., 12 V. A suitable charger (AC-DC converter) enables operation of the sampler in the laboratory,
- The pump needs to be strong enough to pull air through the $Mg(ClO_4)_2$ trap and to fill the flasks to target pressure levels (requirement),
- A maximum pressure of 2.5 bar absolute is typical for glass flasks. The pressure gauge and pressure relief valve are critical to control the target pressure and avoid damage when using glass or metal flasks. Sample bags can not be pressurized (requirement).

7.6.2. Tubing

- Materials listed in Section 6.1 are suitable for tubing.
- All tubing on the vacuum side of the pump is typically made from 1/4" tubing to balance flow resistance and internal volume to be flushed.
- Tubing on the pressure side of the pump should be of 1/8” in outer diameter.
- Valves, pressure gauge and pressure relief valve should be certified for high purity application. Valves should also be certified for very low leak rate, such as welded bellow-sealed valves (requirement).

7.6.3. Intake

- The length of the air intake needs to enable air sampling without risking sample contamination from the operator (requirement).
- It is good practice to cap the air inlet to prevent accumulation of dirt or contaminating objects. Note that the system shown in Fig. 13 does not include any protection of the air inlet or filters to prevent uptake of liquid water or contaminants into the sampling system, but that these may be urgently required, depending on the sampling plan (consideration is requirement).

7.6.4. Water trap

- An example for a water trap using $Mg(ClO_4)_2$ as desiccant is shown in (Fig. 14). Traps need to be designed so that they can be sealed without air leakage to prevent desiccant degradation from ambient air moisture during storage, e.g., with quick connector plugs. Furthermore, it is important to prevent absorption of moisture from ambient air when the traps are mounted to the sampling equipment but the sampler itself is not in use. Valves (A) and (B) in the sampler are required to isolate the $Mg(ClO_4)_2$ trap once it is mounted (Fig. 13).
- $Mg(ClO_4)_2$ traps can be made from stainless-steel or glass at different dimensions, depending on sampling requirements (Fig. 14). Manufacturers of $Mg(ClO_4)_2$ specify the drying capacity of their product. Use the drying capacity to calculate the sample volume under expected conditions that can be dehumidified per g of $Mg(ClO_4)_2$. Plan the trap design accordingly. Researchers are advised to thoroughly test the drying capacity of their traps. Utmost care has to be taken to prevent overloading $Mg(ClO_4)_2$ traps with

water, as $Mg(ClO_4)_2$ forms a corrosive sludge that will contaminate the entire sampling system and represents a health and safety hazard (requirement).

- For the trap manufacturing, a piece of threaded pipe with larger outer diameter is pushed over and welded onto the ends, creating an air-tight connection. This represents the main body of the water trap. A groove at each end of the trap body holds a 1.5 x 25 mm (thickness x diameter) Viton o-ring. The knurled end caps seal against the o-ring when finger-tightened, no tools required (Figure 2). Traps with this design, a diameter of 25 mm and a length of 250 mm may hold 25-50 g $Mg(ClO_4)_2$.
- Molecular Sieve materials may potentially be applied as alternative desiccants. However, both drying performance and sample integrity need to be verified. For example, as it is known that some molecular sieve materials change the gas composition of the sample significantly, especially for CO_2. A counter-flow membrane dryer or cryogenic trap might be applied to dehumidify sample air before storage.

7.6.5. Sampler operation

- Once the system is deployed at the sample site and the sample vessel mounted, valves (A, B, C) are opened, and the pump started (Figure 13). This will flush residual air and moisture out of the sampler through the vent valve. Note that the “dead ends” within the sampler including the flask ports will not get flushed with the continuous air stream, which is critical in particular for bag sampling. Closing the vent valve fills the pressure side of the system against the closed sample vessel and will mix dried sample air with residual air inside the “dead ends”. Opening the vent valve will release the air from the “dead ends”. The goal is to create pressure-cycles within this part of the sampler to incrementally dilute and therefore remove residual, moist air. Ten repeats may be sufficient.
- Next, the vent valve is closed, causing immediate pressure increase. The inlet valves of the sample vessel can now be opened. When using air sampling bags, simply fill the bags and closely watch the bag expand. Fill sample bags to a point where the maximum filling level will not result in a pressure increase with the expected altitude changes. For sampling of flasks, fill the flasks until the gauge indicates overpressure. Then, open the outlet valve and flush the residual air. At least 10 air volume replacement with fresh sample air are needed. Close the outlet valve and fill the flask until the target pressure is reached. Close the inlet valve of the flask.
- Finally, switch the pump off and close the valves at the $Mg(ClO_4)_2$ trap.

7.6.6. Further considerations

- Some research groups or networks [77] have used sampling packages where the flushing and filling of sample container is automated and hence removes potential for operator errors. This is also advantageous for remote locations, or for filling from aircraft [106]. Unmanned aerial vehicles have also been used to collect samples as reviewed in [107].
- Chambers have been used to sample methane emitted from wetlands: samples are pulled either with syringes into glass vials [108] or diaphragm pumps into sample bags [104]. Chambers have also been used to collect samples for analysis of emissions from abandoned gas wells. These can then be transferred into bags or flasks by pump or syringe [109]. Bubble traps can also be used to trap methane from lakes [110]. A handheld aspirator can also help flush samples if battery pumps are not available [105].

FIG. 14. Water trap design used at NIWA. Top: Schematic of the water trap, showing the position of the Viton o-ring and the extent of the glass wool. Bottom: Photo of filled water trap with quick connectors and brass caps on both ends to prevent moisture absorption while trap is not used.

8. MEASUREMENT AND DATA PROCESSING PROTOCOLS

8.1. DEVELOP MEASUREMENT PROTOCOL

As described previously, in the planning of a measurement task, e.g., continuous monitoring or flask/bag sample analyses, researchers need to be fully aware of their analyser's performance, i.e., Allan precision, averaging time, long-term drift effects, stabilization time, amount dependence, gas matrix effects and spectral interferences, as these are key factors to consider in the measurement protocol. Another important parameter is the expected sample gas composition. If the sample gas composition falls outside the range considered during instrument testing, the researcher needs to evaluate whether additional performance tests are required. Measurement protocols are developed and refined to account for analytical biases and to achieve optimal analytical performance. Optimized measurement protocols are therefore specific to the analyser type (e.g., CRDS) and even instrument model (wavelength region etc.), the analyser performance, DQOs, as well as the predominant sample and calibration gas composition. Consequently, established measurement protocols might need to be adapted for specific sample compositions, instrumentation, and research goals.

For simplicity, terms of “LO”, “MID” and “HI” are used to discuss calibration gases with “low”, “mid-range” and “high” mole fraction levels of the target gas (e.g., CH4), respectively. Examples for “LO” are the gases with ambient mole fractions, e.g., WT-1 and WT-2, WT-5 and WT-6 for “MID”, while WT-3 and WT-4 are examples for “HI” in Table 3.

8.1.1. Selection of calibration gases for measurement sequence:

- Calibration gases need to match the sample gas composition in aspects relevant for the analyser performance, e.g., they need to cover the range in CH_4 mole fractions, δ values, gas matrix and interfering trace gases expected in the samples (Section 4 and 6.4) (requirement). Table 3 lists examples for calibration gases following Miles et al. [38] and Hoheisel et al. [37] . For other applications or other analysers, the specifications of scale transfer gases and working standards might have to be adapted.
- The calibration approach and quantifying the CH_4 amount effects can be implemented using two “LO” tanks (WT-1, WT-2) and two “HI” tanks (WT-3, WT-4) (Table 3). Up to two gases in the “MID” range (WT-5, WT-6) might be included if a significant portion of the sampled air is of this mole fraction range, or to replace the "HI" or "LO" tanks if the full mole fraction range (“LO” – “HI”) is not needed.
- For the establishment of a newly implemented analytical system, measurements of test gases are critical to identify Allan deviation, long-term drift effects and memory effects. This will determine the measurement periods for further testing/calibration (requirement).
- A larger number of working standards (WT) is suggested for an initial period, i) to assess systematic characteristics of the instrument response to different gases, e.g., test linearity within the calibrated range, and ii) to thoroughly understand calibration requirements of the new instrument. Researchers need to be able to demonstrate that the system is capable to reproduce isotopic differences at “LO” and “HI” CH_4 mole fraction levels, e.g., differences between WT-1 and WT-2 as well as WT-3 and WT-4. Once the system is established, researchers are advised to assess opportunities to reduce working standard measurements without compromising DQOs in order to minimize working standard gas consumption and to maximize sample throughput. For example, researchers may decide to continue measuring WT-1 to WT-4 but not use all tanks to calculate calibration factors. This would allow the treatment of the “unused” tanks as an

additional quality control standard, which may provide useful insights into the robustness of the calibration approach at the respective CH_4 mole fraction level. Once the robustness is verified, the number of measured tanks may be further reduced. This can go as far as implementing an alternative, instrument specific calibration approach as published by Miles et al. [38] , who ended up using one “LO” tank, one “HI” tank and one quality control standard, only.

8.1.2. Selection of quality control gases for measurement sequence

A quality control standard needs to be included in every measurement sequence and selected to match the expected composition of measured samples (requirement). QC-1 (Table 3) is a suitable gas mixture to accompany measurements of air with small CH_4 enhancements. If most of the measured sample air shows strong CH_4, CO_2 and C_2H_6 enhancements extending into the “MID” range, WT-5 or WT-6 might be more suitable as quality control standard than QC-1, unless they are used for calibration purposes.

8.1.3. Timing of calibration gas measurements

- The timing of calibration gas measurements needs to be defined based on the experimentally verified analyser performance, in particular from the Allan plot for respective CH_4 mole fractions, long-term drift effects and formulated DQOs (requirement).
- The optimal length of calibration gas measurements can be assessed using the Allan variance technique. As the Allan standard deviation decreases with integration time, the achievable measurement precision improves (Section 4.1). Assess the length of measurement time that is required to achieve DQOs for each calibration gas (τ_{min}). Note, the achievable measurement precision for isotope ratio measurements increases notably with CH_4 mole fractions. Consequently, calibration gases with 10 ppm CH_4 might require only 4 minutes averaging time while calibration gases with 2 ppm CH_4 require 64 minutes to achieve the same DQOs (0.1 ‰) for $\delta^{13}C\text{-}CH_4$ [38].
- The calibration frequency or time between blocks of calibration gas measurements needs to also be inferred from the Allan plot (Section 4.1), as the maximum integration time, before the Allan standard deviation increase above DQOs (τ_{max}, Section 4.1) [111]. As an example, Miles et al. (2018) measured the “LO” calibration gas every 420 minutes (3.4 times per day on average) for 20 minutes each time. 20 minutes measurements of the “LO” tank resulted in lower precision (0.2 ‰) per measurement, but shorter interruptions of atmospheric measurements, which was favoured over continuous blocks of 64 minutes of measurements (at 0.1 ‰), during which no atmospheric measurements could have taken place. This approach is comparable to Hoheisel et al. (2019), who measured calibration gases in intervals of 600 minutes. It is advisable to repeat Allan variance experiments in regular intervals to assess analyser performance over time, for example prior / after important campaigns, instrumental changes or periodically (e.g., annually).
- The measurement times of every sample or calibration gas s also include the stabilization time after gas changes (t_{90}, Section 4.3). The system described by Miles et al. [38] required 8 minutes to complete the gas transition. The total measuring time for a cylinder or sample would be determined as τ_{min} plus 8 minutes. At an analyser flow rate of 35 mL/min, a sample volume of 280 mL was required for the transition before each measurement, which needs to be accounted for in the calculation of gas consumptions and flask/bag sample sizes.

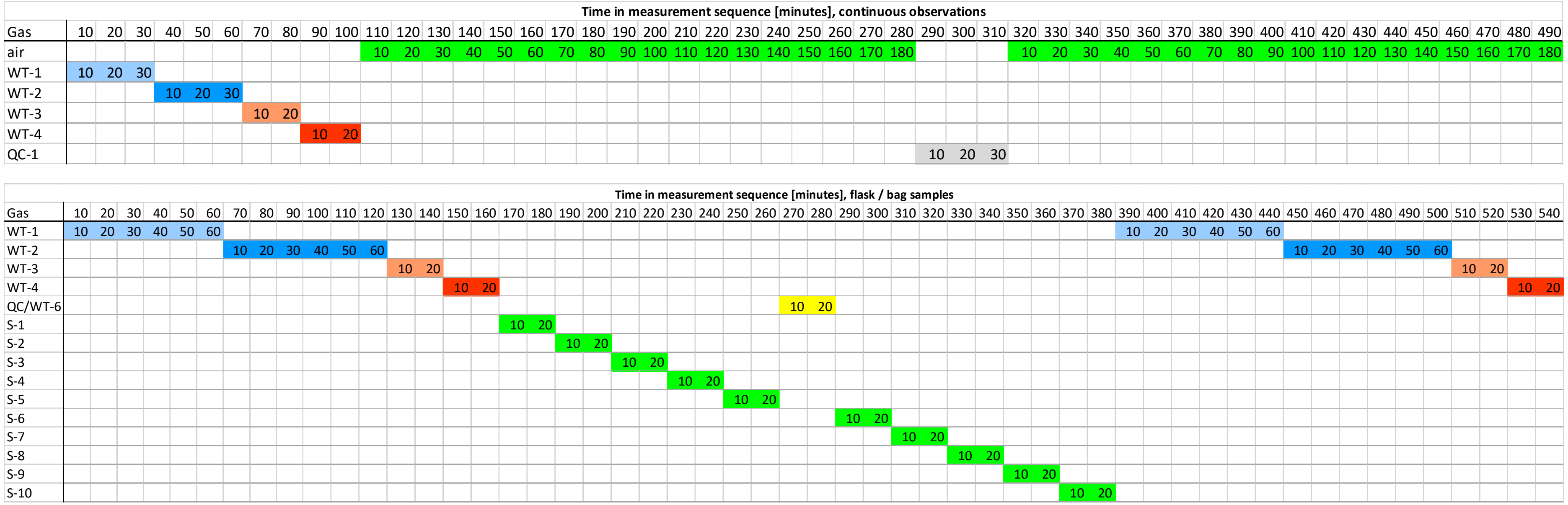
8.1.4. Optimizing the measurement sequence

The length and frequency of calibration and quality control gas measurements is a balance between optimizing the analytical performance versus the calibration / quality control gas consumption and the time available for sample or ambient air measurements. As indicated in Fig. 15 optimized measurement sequences may be different for continuous observations and for measurements of flask or bag samples, where the latter may include higher CH_4 mole fraction variations and require shorter measurement times or generally hold a higher variability in composition. If all flask or bag samples were at near-ambient CH_4 mole fractions, the measurement time for all samples to achieve DQOs may exceed T_{max} and therefore require an additional block of working standard measurements.

8.2. EXAMPLES OF MEASUREMENT SEQUENCES

Figure 15 provides two examples for measurement sequences with high control on instrument variability via working standards (WT-1, WT-2, WT-3, WT-4) and quality control gases (QC-1). The sequence for continuous measurements includes two 180-minute blocks to measure unknown air samples within a period of 490 minutes. The timing of QC-1 is selected to probe for maximum instrument drift, as its timing is furthest away from calibration gas measurements (WT-1, WT-2, WT-3, WT-4). Since continuous measurements repeat the same measurement sequence in endless loops, the sequence in the example below would be measured 2.9 times each day, thus providing 64 minutes of measurement time for the “LO” tanks WT-1 and WT-2 per day after exclusion of 8 minutes of transition time (t_{90}).

In contrast, measurement sequences for flask / bag samples will be executed as individual runs and therefore start and end with the full block of calibration gas measurements, e.g., WT-1, WT-2, WT-3 and WT-4. For illustration, this example sequence is designed for measurements of bag samples with high CH_4 enhancements of 5 to 10 ppm, where DQOs are readily achieved after short measurement intervals due to the high CH_4 mole fractions. Therefore, a large number of samples can be processed in relatively short time. Also, note the selection of WT-6 as quality control gas due to the enhanced CH_4 mole fractions in the samples; this will also require less measurement time. If the CH_4 mole fractions in the flask / bag samples were close to that of ambient air, the measurement time would need to be extended accordingly. Researchers need to ensure that the maximum length of time between the blocks of calibration gas measurements does not exceed τ_{max} (Section 4.1) for the lowest mole fraction of their calibration gases. If the combined measurement time for the samples does exceed τ_{max}, researchers need to either reduce the number of sample measurements or add additional blocks of calibration gas measurements to ensure robust drift control and to achieve DQOs (Section 4.3).



	Time in measurement sequence [minutes], continuous observations																																																
Gas	10	20	30	40	50	60	70	80	90	100	110	120	130	140	150	160	170	180	190	200	210	220	230	240	250	260	270	280	290	300	310	320	330	340	350	360	370	380	390	400	410	420	430	440	450	460	470	480	490
air											10	20	30	40	50	60	70	80	90	100	110	120	130	140	150	160	170	180				10	20	30	40	50	60	70	80	90	100	110	120	130	140	150	160	170	180
WT-1	10	20	30																																														
WT-2				10	20	30																																											
WT-3							10	20																																									
WT-4									10	20																																							
QC-1																													10	20	30																		

	Time in measurement sequence [minutes], flask / bag samples																																																				
Gas	10	20	30	40	50	60	70	80	90	100	110	120	130	140	150	160	170	180	190	200	210	220	230	240	250	260	270	280	290	300	310	320	330	340	350	360	370	380	390	400	410	420	430	440	450	460	470	480	490	500	510	520	530	540
WT-1	10	20	30	40	50	60																																	10	20	30	40	50	60										
WT-2							10	20	30	40	50	60																																	10	20	30	40	50	60				
WT-3													10	20																																					10	20		
WT-4															10	20																																					10	20
QC/WT-6																											10	20																										
S-1																	10	20																																				
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S-10																																					10	20																

FIG. 15. Example measurement sequence for continuous monitoring with long (3 hour) time intervals for sample measurements (top) and for flask / bag sample analyses with high CH4 enhancement and short (20 minute) time intervals for sample measurements (bottom).

8.3. RAW DATA HANDLING

It is essential to have an automated data backup system in place so that no data are lost due to local hard drive failure. Redundant data files can be saved either to an external hard drive or the cloud. The cloud, or other offsite storage, has the advantage of being safe in case of catastrophic damage to the lab, however, the type of system that is most appropriate may depend on the situation, local internet accessibility, etc. There are free software platforms that manage data-saving tasks; either a full system back up, which takes time, or a differential backup, which saves the data that have been changed or added since the last backup. A research group's local information technology office may have guidance on which of these or other free services are most appropriate and comply with their data security policy, or they may have purchased accounts with services, so consulting with the local experts is advised.

In situ analyser generate large data volumes, including during idling time. It is important to ensure the disk of the analyser is not running out of memory capacity, as this for example, could slow down the analyser and eventually leads to degrading performance and data loss.

8.4. AUTOMATED DATA PROCESSING

Optical analysers produce large data volumes which need to be handled efficiently. The analyser software typically generates one data file every 24 hours, data collection is manually restarted / interrupted. With data coming in at approximately 1 Hz, simple spreadsheets will not be able to handle data files from a day of mobile sampling or in situ measurements. Using specifically written data processing code is advisable to ingest these large files and to reduce the data to more manageable sizes. Researchers may want to use the code to calculate average measurement values for calibration gases and discrete samples, e.g., reduce atmospheric data from continuously deployed analysers to 5-minute averages. Following the data reduction, the code needs to also be developed to perform the measurement correction (Section 8.5) and measurement calibrations (Section 8.6). Uncertainties of all measurements need to be propagated following accepted protocol (Eq. 4, Section 6.8). The code needs to also enable an easy way to reprocess the data to account for future revisions of mole fraction or isotope scales (Sections 6.2, 6.3). Processed data can be printed to files, or better yet, to a relational database that can then be queried.

The instrumentation may come with data handling techniques, for instance to distil a period of measurement of a discrete sample to an average and standard deviation and Allan variance. Otherwise, researchers may want to add "triggering" so that the data streams can be notated to indicate different valve positions, etc (e.g., Ref. [112]). Processing code can look for these indicators to recognize when standards, surveillance cylinders, or samples are being measured.

For playback systems, e.g., mobile samplers, there might be the need for customized "triggering" to note in the data streams which air is being measured, etc. Furthermore, the researcher needs to consider timing factors specific to their playback system following Rella et al. [45] , which include a time delay (storage time), the reversal of the signal in the tube, and the compression of the time axis, as the instrument flow during reanalysis might be different from the gas flow during storage. Likewise, for in situ data, the researcher needs to account for differences between the measurement time and the sample time (lag time); which is the travel time of the sample from the inlet to the analyser [38].

8.5. EXAMPLE FOR MEASUREMENT CORRECTION PROTOCOL

The following Section describes examples of measurement corrections.

8.5.1. Accounting for the CH_4 amount effect

It is very likely that optical isotope analysers return non-linear responses in reported $\delta^{13}C\text{-}CH_4$ values with changes in CH_4 mole fractions [35, 38, 45, 74]. Researchers need to assess this effect for their specific instrument and adopt a suitable method to account for the CH_4 amount effect on the measured isotope delta value.

Harris et al. [74] linearized the amount effect for different CRDS, OA-ICOS and QCLAS analysers by regressing the reported delta values over the inverse mole fractions to derive a correction functions. Miles et al. [38] applied the CH_4 amount correction technique from Rella et al. [45] to four identical CRDS instruments but found that the CH_4 amount effect and therefore the correction parameters vary for each instrument. Griffith [35] suggested an alternative approach that calibrates the mole fractions of the measured isotopologues, before these are calculated into delta values, however, this technique has not been applied to commercial CRDS analysers so far. In contrast to all of the aforementioned techniques, Hoheisel et al. [37] carefully designed their observations for low variability in CH_4 mole fractions and carefully matched CH_4 mole fractions in working standards to air samples and therefore avoided the need for this correction. Because the significance of these effects varies with analyser type, research application, and DQOs, this document refrains from suggesting either of these specialized approaches but seeks to guide the reader to these directions. This document provides a correction scheme example following Hoheisel et al. [37] .

8.5.2. Correcting for interferences

The baseline with respect to corrections is set by working standards (e.g., WT-1 and WT-2, or WT-3 and WT-4). Correction functions are to be developed in the initial analyser testing phase (see Section 4), but need to be revisited regularly, in particular after instrument service. The tests need to also establish a threshold value for the difference in the mole fraction of an interfering gas species between the sample gas and a working standard, above which a correction needs to be applied. The decision tree shown in Fig. 16, was developed for a CRDS analyser and helps to identify the required correction protocol.

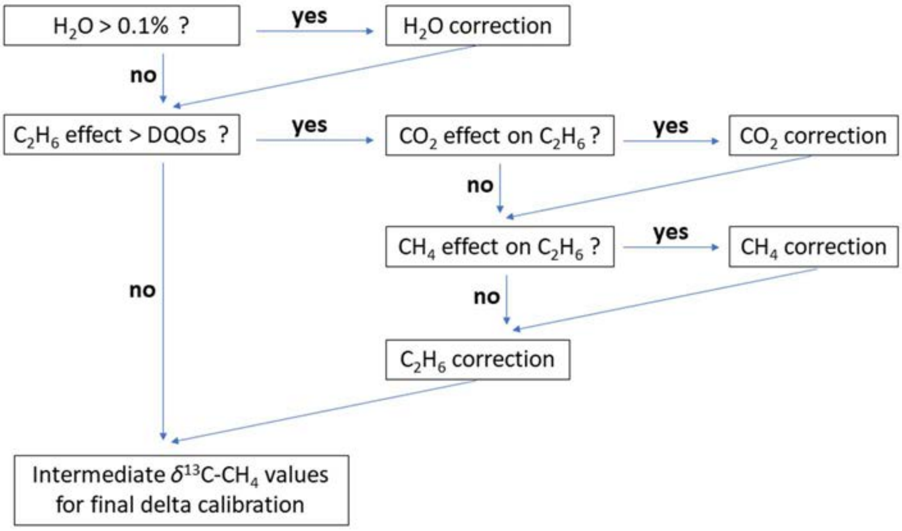

FIG. 16. Decision tree for an example CRDS analyser (G2201-i) to design a correction scheme. Use DQOs as decision criteria to gauge acceptable levels of interferences on δ^{13}*C-*CH_4 *and* C_2H_6*, e.g.,* ≤ *0.1 ‰ for* δ^{13}*C-*CH_4*. Calculate a threshold value for the interferant mole fraction above which a correction is required. If a correction was required, apply the correction functions derived in the initial analyser testing.*

For example, with a spectral interference of C_2H_6 on δ^{13}C-CH_4 analyses of +40.87 ± 0.49 ‰ ppm CH_4 (ppm C_2H_6)$^{-1}$ (Table 2), a 5 ppb difference in C_2H_6 between sample and working standards at 2 ppm CH_4 might be defined as a threshold value, as it corresponds to a change in apparent δ^{13}C-CH_4 values of 0.1 ‰. Any sample (especially thermogenic methane sources) with C_2H_6 more than 5 ppb different than the WT would require a suitable C_2H_6 correction scheme. For such analyses C_2H_6 would be regarded as a target measurand, and researchers may choose to select working standards covering the expected C_2H_6 range to derive calibration functions on a daily basis, e.g., by including a working tank with enhanced C_2H_6 (WT-5 or WT-6). However, when measuring samples with CH_4 enhancements from biogenic sources, the C_2H_6 of these samples might be low and match the C_2H_6 in working standards WT-1 to WT-4 and thus, a C_2H_6 correction would not be required [37]. The same principle applies to other interferences, such as H_2O on δ^{13}C-CH_4 or CO_2 and CH_4 on C_2H_6, for which an effect has been identified in the analyser testing phase. The DQO for C_2H_6 depends on the study focus, whether high accuracy is required, or if it is mainly used for correction of interferences on δ^{13}C-CH4.

Fig. 17 shows a schematic of the sequence and the algebra Hoheisel et al.[37] used to correct for interferences. Capital letters indicate correction factors as referred to in the caption of Figure 17, which need to be determined during the testing of the system.

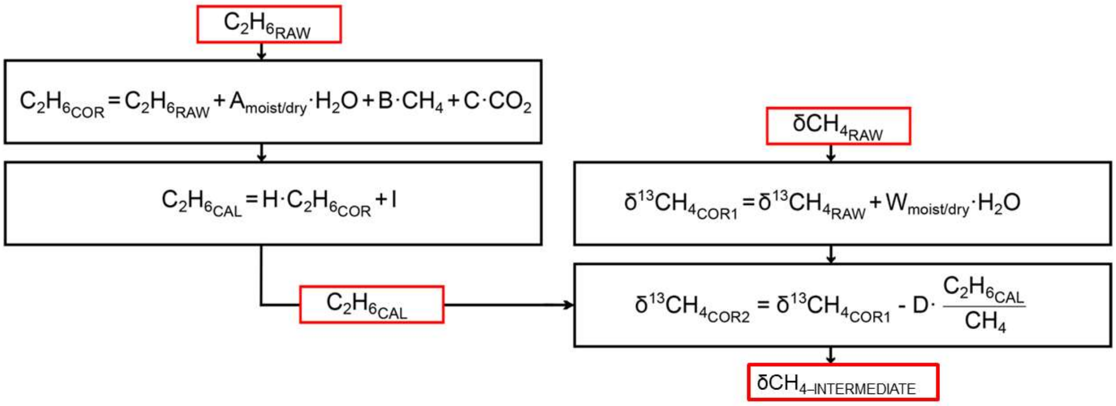

FIG. 17. Scheme to correct interferences on C_2H_6 and $\delta^{13}C$-CH_4 before the calibration of $\delta^{13}C$-CH_4 values to the $\delta^{13}C_{VPDB}$ scale in the final step. The scheme suggests correction factors for the effect of i) CH_4 on C_2H_6 (B), ii) CO_2 on C_2H_6 (C), iii) C_2H_6 on $\delta^{13}C$-CH_4 (D), iv) a linear C_2H_6 calibration function (slope = H, intercept = I), as well as v) water vapour on $\delta^{13}C$-CH_4 (W) and vi) water vapour on C_2H_6 (A), iii), where the latter two are generally considered to be negligible due to dehumidification to < 0.1% H_2O. Correction factors determined in Hoheisel et al. (2019) are analyser specific and shown in Table 2 as indication. (Modified from Ref [37] with permission).

8.6. EXAMPLE FOR MEASUREMENT CALIBRATION PROTOCOL

The following Section describes examples of measurement calibration.

8.6.1. Calibrating $\delta^{13}C$-CH_4 to $\delta^{13}C_{VPDB}$

Two fundamentally different calibration approaches have been implemented for isotope analyses by optical analysers, each of which requires a different measurement protocol and different calibration gases.

This document adopts the “delta calibration approach”, in which delta values (e.g., $\delta^{13}C$-CH_4) of samples are calibrated by accounting for the differences between measured and target delta values of calibration gases (e.g., Ref. [37, 38, 45, 74]). In the delta calibration approach, $\delta^{13}C$-CH_4 values from two or more working standards are used to formulate a calibration function to anchor the $\delta^{13}C$-CH_4 values of the unknown samples on the $\delta^{13}C_{VPDB}$ scale. Graphically, this is done by plotting the $\delta^{13}C$-CH_4 target values of the working standards on the y-axis over their measured $\delta^{13}C$-CH_4 values on the x-axis (Fig. 18). The linear regression function can then be applied to the intermediate $\delta^{13}C$-CH_4 values (after interference corrections, Section 8.5) of the sample gases, to calibrate the samples to $\delta^{13}C_{VPDB}$. In practice, the parameters of the calibration function may change with time, i.e., due to analyser drift. This can be accounted for by averaging two blocks of calibration measurements and applying the resultant function on sample gases analysed in-between. For continuous monitoring, more sophisticated data analysis algorithms can be applied to interpolate calibration measurements.

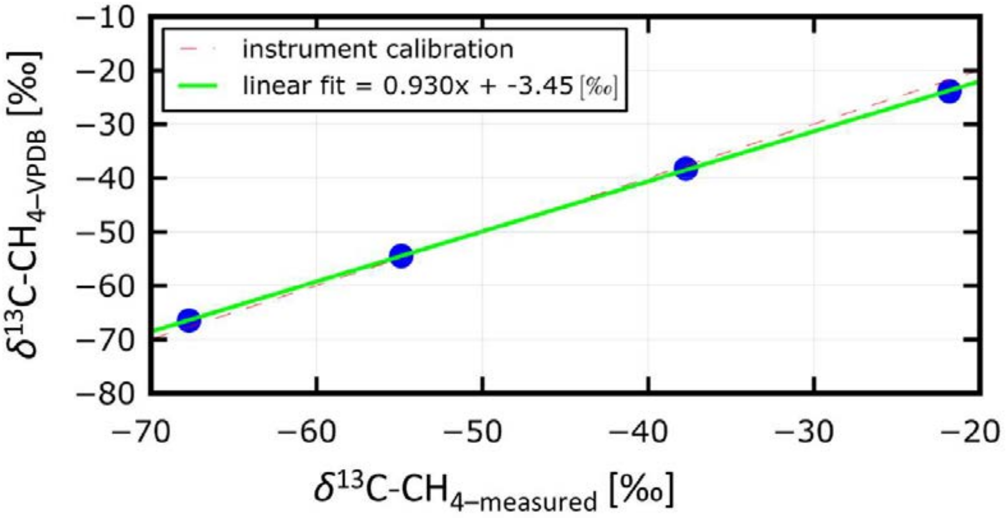

FIG. 18. Defining isotope calibration function for $\delta^{13}C\text{-}CH_4$. Measured $\delta^{13}C\text{-}CH_4$ values of calibration gases are plotted on the x-axis, their target values on the y-axis. Applying the linear regression calibrates intermediate $\delta^{13}C\text{-}CH_4$ values of unknown samples to the $\delta^{13}C_{VPDB}$ scale (green line). The red dashed line shows the manufacturers' instrument calibration line (Reproduced from Ref. (Modified from Rella et al. (2015), with permission).

A promising alternative is the calibration of isotopologue mole fractions and consecutive conversion to delta values as proposed by Griffith [35] , referred to as the "isotopologue mole fraction calibration approach". The mole fraction approach may waive the need to account for the CH_4 amount effect and needs to be regarded as an option for potential adoption in future. Rennick et al.[33] specifically applied this approach for $\delta^{13}C\text{-}CH_4$ and $\delta^{2}H\text{-}CH_4$. The implementation of the mole fraction calibration approach requires isotopologue mole fraction data that some $\delta^{13}C\text{-}CH_4$ analyser do not report as an output. Furthermore, this technique requires reference gases comprising CH_4 with precisely calibrated $\delta^{13}C\text{-}CH_4$ and amount fraction values, which can be difficult to obtain at the required accuracy.

8.6.2. Calibrating mole fractions to the respective scales

Mole fraction measurements for CH_4 and CO_2 need to be calibrated to the WMO X2004 and WMO X2019 scales, respectively [59, 113]. Mole fractions of C_2H_6 need to be calibrated using NPL primary reference materials [78]. The calibration gases shown in Table 3 provide access to these scales. In practice, calibration functions for these three measurands need to be defined and applied, using the method shown in Fig. 18 for isotope ratios. Uncertainties need to be propagated accordingly (Eq. 4).

9. TOOLS TO ASSESS DATA QUALITY

9.1. ASSESS INSTRUMENT VARIABLES, RAW DATA, AND DATA PROCESSING

Researchers need to create an automated system to plot system variables that can be indicative of the analyser performance and any other parameters that may affect instrument conditions. Data can be plotted automatically so that the researcher can quickly assess data quality. These can be simple (data entered automatically into excel) or complex (custom code that retrieves data and automatically produces charts); but the data need to be be assessed daily for continuous observations, or for every measurement sequence when measuring discrete samples, to ensure that data are meeting DQOs. The following examples show how this can be achieved.

- Plot available instrument variables, e.g., cell pressure, cell temperature, sample pressure, analyser flow rate, laboratory temperature, and other available variables. Plot both, over time and for measurements of samples and calibration gases.
- Plot raw data of all measurements in calibration and sample gases (e.g., CH_4, $\delta^{13}C$-CH_4, CO_2, C_2H_6, H_2O), including meaningful averages and standard deviations.
- Plot data correction functions and intermediate data, i.e., after each data correction step. These may include amount effect corrections and interference corrections.
- Plot data calibration functions and the calibrated data including residuals, including propagated uncertainties (Eq. 4).
- Plot meteorological data at the time of measurement, i.e., ambient pressure, ambient temperature, ambient humidity.

9.2. LABORATORY REPRODUCIBILITY WITH PERFORMANCE CHART

Performance charts have been proposed as a tool to record and demonstrate measurement reproducibility [80]. An example of a performance chart figure is given in Fig. 19, which was prepared for an analyser measuring CO_2 and its stable isotope ratios [84]. Fully processed data from daily measurements of the quality control standard are plotted over the measurement date. The standard deviation of all quality control standard results is indicative of the measurement reproducibility. Performance charts can alert a researcher to any changes in performance or reassure the researcher that the data coming in are reproducible.

- Create performance chart by plotting results from quality control standard measurements (QC-n) over time. Use of one measurement per sequence for the analysis of flasks or bag samples, or of one measurement per day for field deployed analysers is sufficient.
- For every measurement day or measurement routine, add one quality control standard measurement to the performance chart.
- Calculate the standard deviation of all quality control standard measurements.
- Assess reproducibility with performance chart in daily quality assurance protocol. The standard deviation of the quality control standard measurements needs to reflect defined DQOs. It needs to also be close to the Allan Precision value, considering the mole fraction range of the quality control standard and the applied integration time.
- Test for trend in quality control standard measurements over time. Trending quality control standard measurements likely suggests a drifting cylinder, which could be the quality control standard itself or a working standard used for correction and calibration.

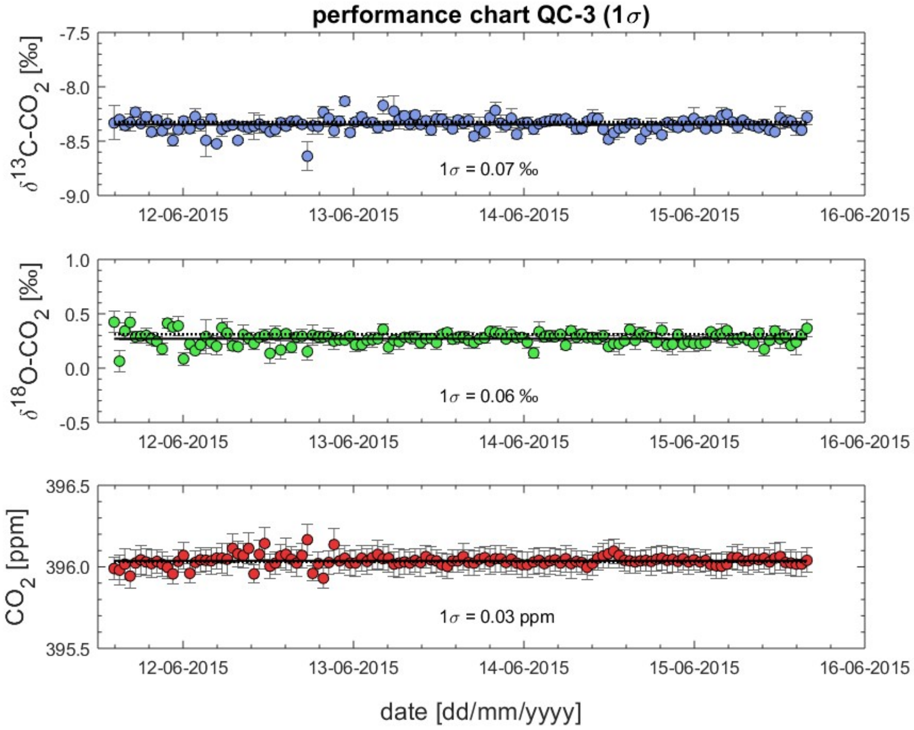

FIG. 19. Performance chart prepared for fully processed measurements of $\delta^{13}C$-CO_2, $\delta^{18}O$-CO_2 and CO_2 in the quality control standard QC-3 (Reproduced from Ref.[84]),with permission).

9.3. LABORATORY INTERCOMPARISONS: ROUND ROBINS AND CO-LOCATED SAMPLES

Intercomparison measurements are a helpful gauge of compatibility – whether measurements between laboratories agree within DQOs. Same-air comparisons are useful because they minimize any sampling error and allow labs to compare the same air mass from a cylinder or flask. High pressure cylinders are especially useful because they can be measured by many laboratories over an extended time frame.

Round robins for CO_2, CH_4 and other GHGs are organized by NOAA-GML. A 4-cylinder round robins for methane isotopes was initiated in 2019 by INSTAAR and NIWA (with support from NOAA-GML). These cylinders have been circulating the globe and may be available to up-and-coming labs that maintain global, regional or national fixed site monitoring networks for future comparisons.

However, round robins only capture measurement from each lab at discrete points in time. Furthermore, cylinders are expensive to transport. Exchanging co-located samples with other laboratories to compare measurement performances are also helpful as they validate whether an isotopic signal seen by one research group is also detected by another. If not, it could be an artefact of measurement or calibration. Free sharing of data in a timely manner is very helpful means to investigate these signals or to identify potential problems with the data.

10. TOOLS FOR DATA INTERPRETATION

The following Section describes examples of tools for data interpretation.

10.1. KEELING PLOT AND MILLER-TANS PLOT ANALYSIS

Keeling Plot Analyses is a two-component mixing model. The CH_4 mole fraction of an air mass under non-background conditions can be assumed to be a combination of background CH_4 and CH_4 emissions from nearby sources. Depending on the isotopic signature and strength of the source, the isotope ratio of the air mass changes compared to the background, where the latter is assumed stable, which may require verification.

The measured mole fraction is composed of background mole fraction $CH_{4,bg}$ and the emitted $CH_{4,s}$ from a source. Thus, the measured $CH_{4,obs}$ mole fraction and isotopic signature $\delta^{13}C\text{-}CH_{4,obs}$ can be described by the following two equations.

$$CH_{4,obs} = CH_{4,bg} + CH_{4,s} \qquad (8)$$

$$\delta^{13}C\text{-}CH_{4,obs} \times CH_{4,obs} = \delta^{13}C\text{-}CH_{4,bg} \times CH_{4,bg} + \delta^{13}C\text{-}CH_{4,s} \times CH_{4,s} \qquad (9)$$

This relation between source signature $\delta^{13}C\text{-}CH_{4,s}$ and measured $CH_{4,obs}$ as well as measured $\delta^{13}C\text{-}CH_{4,obs}$ can be used to determine the former. Note that this model does not consider a sink term. Due to the atmospheric lifetime of 9.1-11.8 years [51], sink effects are assumed insignificant when measuring close to CH_4 sources.

Keeling [66] derived a linear dependence between the reciprocal value of the measured mole fraction and the isotopic composition of CO_2 in air. In this case, the measured CH_4 mole fraction and the measured isotopic composition $\delta^{13}C\text{-}CH_{4,obs}$ are used by combining the two equations above. The isotopic signature of a CH_4 source $\delta^{13}C\text{-}CH_{4,s}$ can be determined by plotting the measured isotopic composition $\delta^{13}C\text{-}CH_{4,obs}$ against the reciprocal of the measured $CH_{4,obs}$ mole fraction. The intercept of a linear regression then gives the isotopic signature of the source $\delta^{13}C\text{-}CH_{4,s}$.

$$\delta^{13}C\text{-}CH_{4,obs} = \frac{CH_{4,bg}}{\delta^{13}C\text{-}CH_{4,bg} - \delta^{13}C\text{-}CH_{4,s}} \times \frac{1}{CH_{4,obs}} + \delta^{13}C\text{-}CH_{4,s} \qquad (10)$$

Instead of the Keeling plot approach, the so-called Miller-Tans approach can be used, too. Miller and Tans [67] rearranged Eq. 10 so that a linear dependence between the measured $CH_{4,obs}$ mole fraction and the product of the measured mole fraction $CH_{4,obs}$ and measured $\delta^{13}C\text{-}CH_{4,obs}$ is given. In this case, the source signature $\delta^{13}C\text{-}CH_{4,s}$ is determined by the slope of a linear regression.

$$\delta^{13}C\text{-}CH_{4,obs} \times CH_{4,obs} = \delta^{13}C\text{-}CH_{4,s} \times CH_{4,obs} + CH_{4,bg} \times (\delta^{13}C\text{-}CH_{4,bg} - \delta^{13}C\text{-}CH_{4,s}) \qquad (11)$$

Thus, both the Keeling plot as well as the Miller-Tans approach can be used to determine the isotopic signature of a source (Fig. 20). Several studies, in particular Zobitz et al. [114] found no significant difference between the Keeling plot or Miller-Tans approach.

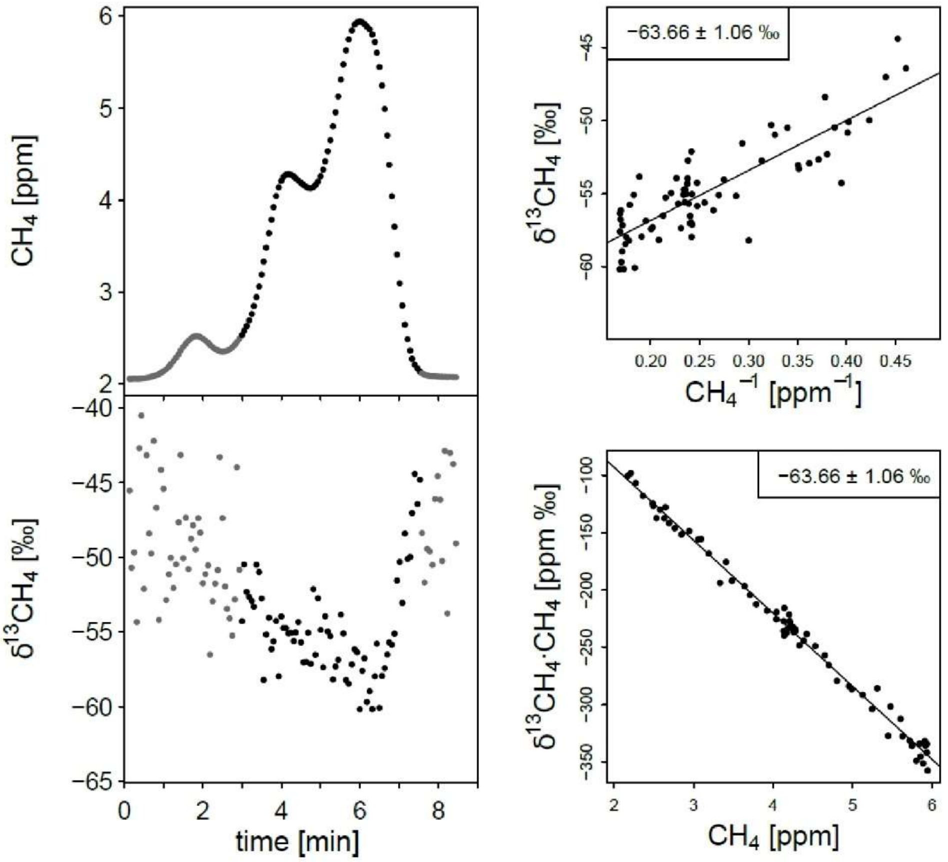

FIG. 20. Keeling plot and Miller-Tans analysis of mobile measurements near a CH_4 source (Reproduced from Ref. [37] with permission).

Both the background mole fraction $CH_{4,bg}$ and the background $\delta^{13}C\text{-}CH_{4,bg}$ need not be known in either approach (when using Eq. 10 or 11). However, Keeling Plot Analysis assumes that the background is constant for the duration of the measurement. For small time scales of a few minutes to hours, this assumption is valid, e.g., for the analysis of mobile measurements.

One specific advantage of the Miller-Tans method is that it can be used under variable background conditions, requiring sample pairs where one sample is used to define background and the other sample to characterize the air with the additional emissions [67]. If the background mole fraction $CH_{4,bg}$ and the background $\delta^{13}C\text{-}CH_{4,bg}$ are known in addition to the measured mole fraction $CH_{4,obs}$ and isotopic signature $\delta^{13}C\text{-}CH_{4,obs}$, the isotopic source signature $\delta^{13}C\text{-}CH_{4,s}$ can be determined using a rearranged form of Eq. 11 as described by Miller and Tans [67] .

$$\delta^{13}C\text{-}CH_{4,obs} \times CH_{4,obs} - \delta^{13}C\text{-}CH_{4,bg} \times CH_{4,bg} = \delta^{13}C\text{-}CH_{4,s} \times (CH_{4,obs} - CH_{4,bg}) \qquad (12)$$

Regardless of the choice of the approach (Keeling plot or Miller-Tans), there are several aspects to consider for the choice of the fitting algorithm to determining the isotopic source signature. A variety of methods are used in publications like ordinary least-squares (OLS) minimization by Fujita et al. [115] , orthogonal distance regression (ODR) by Menoud et al. [11, 46] , geometric mean regression (GMR) by Pataki et al. [116] , Bayesian regression by Lu et al. [22] or York's solution by Hoheisel et al. [37] . A distinction is usually made between Model I and Model II regression. Model I regressions like OLS minimization consider error only in y, while Model II regressions such as ODR or GMR consider error in x and y. Several studies have systematically examined different fitting algorithm for the application in the Keeling plot and

Miller-Tans approach in connection with CO_2 and $\delta^{13}C$-CO_2. While Zobitz et al. [114] , for example, recommend the use of Model I regression, Pataki et al. [116] , among others, advocate Model II regression. On the other hand, Wehr and Saleska [117] state that OLS, ODR and GMR are special cases of York's general least-squares solution. They demonstrated that York's solution is the least biased compared to OLS, ODR and GMR.

Keeling plot analysis can be applied to a wide range of observations, e.g., using a set of samples from one CH_4 source to characterize the $\delta^{13}C$-CH_4 source value (e.g. Ref. [37, 39, 40, 42]) While Sperlich et al. [84] manually selected individual events from continuous observations manually, to ensure the mole fraction enhancements of the target gas exceeded a specified threshold to meet DQOs, Röckmann et al. [10] introduced the so-called "moving Keeling plot" method that can be automatically applied to data from continuous CH_4 and $\delta^{13}C$-CH_4 observations.

10.2. OPTIMIZING AIR SAMPLING TO ACHIEVE TARGET DQOS

The uncertainty of $\delta^{13}C$-CH_4 source values needs to be minimized by implementing an optimal sampling strategy.

- Measurements covering a larger range of CH_4 mole fractions, i.e., higher CH_4 enhancements yield lower uncertainty of estimated $\delta^{13}C$-CH_4 source signatures (Fig. 21). In situ measurements of CH_4 mole fractions while taking air samples in flasks or bags need to ensure the air samples include the required CH_4 enhancements to meet DQOs.
- Increasing the number of samples will also contribute to reducing the uncertainty of determined $\delta^{13}C$-CH_4 source signatures. Researchers need to adjust the number of samples to meet DQOs.
- Researchers need to estimate the error of the $\delta^{13}C$-CH_4 source signatures as a function of CH_4 mole enhancement and sample number (see Fig. 21) when planning and conducting air sampling campaigns, to ensure samples meet CH_4 enhancement criteria and adequate numbers to achieve a target uncertainty in $\delta^{13}C$-CH_4.

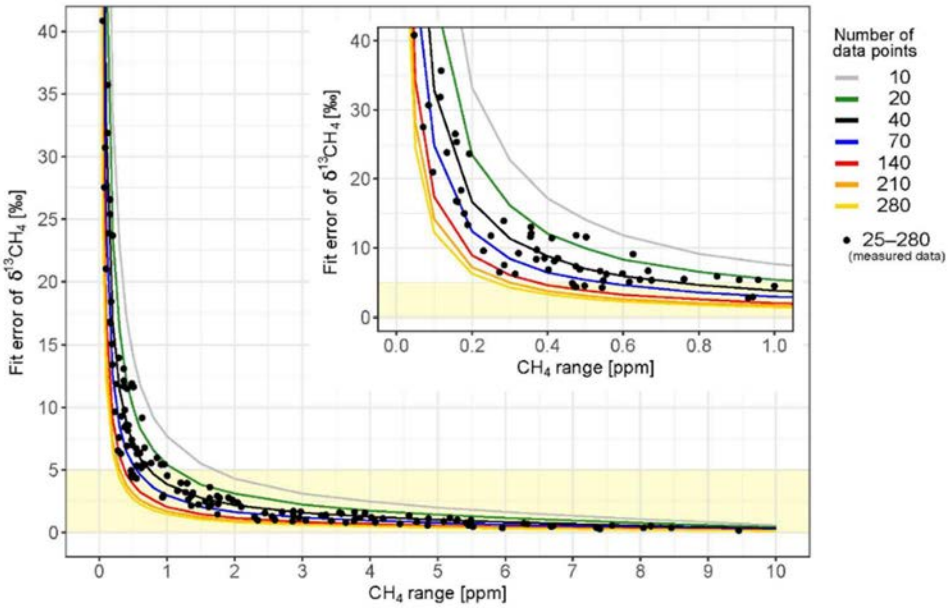

FIG. 21. Dependency of the uncertainty in $\delta^{13}C$-CH_4 source signatures on the CH_4 mole fraction range above background levels covered with the analyses. The coloured lines represent results estimated from synthetic data using the Miller-Tans technique / York's regression approach. The black dots are uncertainties for source signatures calculated from measured data with 25 to 280 data points (reproduced from Ref. [37] with permission).

APPENDIX I. δ^{13}C-CH_4 IN AIR AND VPDB SCALE

In contrast to the mole fraction scales, isotope measurements are not traceable to the SI system (Fig. 10, CIPM, March 2015). Isotope delta scales are conventions and are established by international agreements. They are defined by the isotope ratio assigned to primary reference materials, overseen by the International Atomic Energy Agency (IAEA). This approach is established due to the nature of the instruments used to measure stable isotopes; isotope ratio mass spectrometers measure relative differences in isotopes rather than absolute isotope abundances.

Stable carbon isotope ratios are referenced to the international VPDB scale ($\delta^{13}C_{VPDB}$), which was initially realised only by NBS19. In 2006, two-point realisation was introduced and LSVEC was added as the second anchor [118]. Since the discontinuation of LSVEC and depletion of NBS 19, IAEA-603 has been proposed as a replacement for NBS 19 [119] and USGS44 calcium carbonate [120] as a replacement for LSVEC allowing two-point calibration of the scale. In the meantime, IAEA prepared and released other three calcium carbonate secondary reference materials, IAEA-610, IAEA-611 and IAEA-612, for stable carbon isotope scale normalization, to utilize multipoint realisation of the δ^{13}C VPDB scale [121, 122].

According to Hélie et al., (2021) δ^{13}C values obtained using IAEA-603, IAEA-610, IAEA-611, IAEA–612 series are consistent with those of the original VPDB scale realisation based only on NBS 19 (i.e., prior to introduction of LSVEC as a scale anchor). However, values obtained with IAEA new carbonates series (VPDB scale) are consistent with those obtained using NBS 19 and LSVEC or NBS 19 and USGS 44 (VPDB-LSVEC scale) when they are close to 0 ‰, but show discrepancies of up to 0.2 ‰ for the measurement of ^{13}C-depleted samples, such as CH_4 [123].

In case of measurement of δ^{13}C-CH_4 in air, samples are gaseous materials, while available RMs are not. Therefore, analytical systems to process and measure δ^{13}C-CH_4 in air samples are fundamentally different from those systems used to process and measure δ^{13}C in calcium carbonate samples. Consequently, anchoring the measurements of δ ^{13}C-CH_4 in air on the $\delta^{13}C_{VPDB}$ scale break the Principle of Identical Treatment (PIT) [80]. Laboratories have developed different calibration approaches over time, resulting in localised $\delta^{13}C_{VPDB}$ scale realisations for δ^{13}C-CH_4 in air. It is important to appreciate that this resulted in significant laboratory-specific calibration offsets, exceeding 0.5 ‰ for δ^{13}C-CH_4 and 13 ‰ for δ^{2}H-CH_4 [69, 124]. However, specialised laboratories are capable to make highly precise and very reproducible δ ^{13}C-CH_4 and δ^{2}H-CH_4 in air measurements, generally on the order of <0.2 ‰ [10, 23–25, 32, 33, 125–127] and <5 ‰ [10, 32, 33, 125, 128], respectively.

For laboratories currently measuring δ^{13}C-CH_4, it is of utmost importance to thoroughly calibrate their measurements in a two-point [118] or three-point [129] calibration using suitable reference materials. Based on the reference materials used for calibration, two carbon isotope delta scales are in existence and in use: VPDB and VPDB-LSVEC. It is therefore imperative to thoroughly document the reference materials and isotope ratio values used at the time (see Section 6).

APPENDIX II. TECHNICAL PROBLEMS, TROUBLESHOOTING

- Leaks in analytical systems cause ambient air to mix with sample or calibration gases. This effect is likely to vary over time and is most likely impossible to be corrected for in hindsight. Thoroughly leak check all components and plumbing sections before operating the system unattended. Repeat leak check periodically.
- Air leaks in tubing may lead to sample loss, isotope fractionation or contamination with ambient/laboratory air. Develop robust protocol for leak checking of the analytical system. I.e., CO_2 leaks can be tested by blowing on the components or spraying the component with gas from a cylinder with high CO_2, i.e., T-8.
- Minimize gas matrix effects using calibration gases filled/diluted in ambient air.
- Insufficient control of mole fraction effect on reported isotope data.
- Measurement of flasks and cylinders with variable pressure at the air inlet may cause pressure variation in the analytical cell. This will result in noisy measurements and high probability to fail meeting DQOs. Design system to deliver sample and calibration gases so that analyser can maintain stable cell pressure.
- Dirt or dust may enter the analyser and degrade its performance or obstruct gas flow.
- Condensation of water inside the analyser will severely damage the instrument.
- Install filter at gas inlet and upstream of the calibration unit or analyser and ensure effectiveness for continuous observations in extreme environments, e.g., sea salt aerosol. Condensation of any impurities in highly reflective analytical cell may reduce reflectivity and therefore analyser performance. This may require very costly repairs.
- Pressure regulator contamination effects: use sufficient flushing volumes when connecting a new pressure regulator, use well-proven pressure regulator models, keep pressure regulator connected and pressurized during stand-by.
- Loss of valuable calibration gases due to undetected leak. Thoroughly leak check all plumbing and connections before using calibration gases. Close calibration gas cylinder valves when not in use for a while.
- Contamination of measurand due to use of unsuitable materials, e.g., polymers.
- Air samples in bags may become unstable due to gas loss or suffer from contaminants introduced into the bag during previous sampling.
- The counter-flow membrane dryer may become leaky or ineffective. Such membranes are sensitive to pressure changes and may fracture. Attention needs to be paid to drying capacity of desiccant to prevent unintended humidification of air samples.
- Solid magnesium perchlorate used as desiccant turns into corrosive liquid when overloaded with water and may damage the setup or the analyser.
- Avoid overheating of instrument, for example in a car. Use air conditioning, take appropriate measures, when parking the car.
- Avoid storing analyser with wet cavity, always dry cavity before shutting down, do not shut down if cavity is wet after analysis of undried sample or ambient air. Dry and then fill cavity with dry air from calibration cylinder before shutting down.
- Faulty data output may cause malfunctioning processing code, may result in wrong data used in value assignment of samples and/or reference gases.
- Inconsistencies between transition time between gas changes may affect data used for value assignment of samples and/or reference gases.
- Avoid computer hard disk reaching capacity and maintain computer operating system over time (use your local institute IT services for advice). Isolating the instrument from direct continuous internet access is advised The analyser is fed with gas from high

pressure cylinders. Ensure that the applied pressure cannot damage the analyser, verify for accidental circumstances, i.e., power cuts.

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GLOSSARY

Ambient air	Unpolluted air with natural composition, 78.08 % N_2, 20.95 % O_2 and 0.93 % Ar, e.g., currently 415 ppm CO_2, 1900 ppb CH_4, –47.5 ‰ $\delta^{13}C$-CH_4, 0.2-2 ppb C_2H_6
CH_4	Methane
CO_2	Carbon dioxide
C_2H_6	Ethane
H_2O	Water
N_2	Molecular nitrogen
O_2	Molecular oxygen
Ar	Argon
CO	Carbon Monoxide
NH_3	Ammonia
H_2S	Hydrogen Sulfide
CH_3SH	Methanethiol
C_3H_8	Propane
C_4H_{10}	Butane
C_2H_4	Ethylene
mole fraction	Scientific term for concentration of a gas
Pa	Unit for pressure in the SI system, atmospheric pressure at sea level is 101,325 Pa
bar	Metric unit for pressure, exactly equal to 100,000 Pa
δ	Delta notation for reporting stable isotope ratios
$\delta^{13}C$	Delta notation for reporting stable carbon isotope ratios
$\delta^{13}C_{VPDB}$	VPDB scale for referencing stable carbon isotope ratios, IAEA is scale custodian
$\delta^{2}H_{VSMOW\text{-}SLAP}$	VSMOW–SLAP scale for referencing stable hydrogen isotope ratios, IAEA is scale custodian
$\delta^{13}C$-CH_4	Delta notation for reporting stable carbon isotope ratios in methane

δ^2H-CH_4	Delta notation for reporting stable hydrogen isotope ratios in methane
‰	Permil, used to report the delta values
AirCore	Atmospheric sampling system, long tubing coil, samples atmosphere while preserving profile of atmospheric composition within the coil.
Scale transfer gases	Cylinders with gases used for calibration of working standard gases, measurand values are assigned from the CCL, gases of the highest hierarchy level.
Working standard gases	Cylinders with gases used for daily measurement and value assignment of unknown samples. Measurand values are assigned by calibration against scale transfer gases.
Test gases	Cylinders with gases used for instrument characterization and testing.
WMO-X2004A	CCL scale for methane mole fractions, (NOAA)
WMO X2019	CCL scale for carbon dioxide mole fractions, (NOAA)
CCL-n	Designator with enumeration, this document refers to CCL-n for scale realisation gas cylinders with the composition as specified in Table 3.
WT-n	Designator with enumeration, this document refers to WT-n for working standard tanks with the composition as specified in Table 3.
QC-n	Designator with enumeration, this document refers to QC-n for quality control standards with the composition as specified in Table 3.
T-n	Designator with enumeration, this document refers to T-n for test gas cylinders with the composition as specified in Table 3.
τ	Tau, time interval in Allan deviation
t_{90}	Time for stabilization after gas changes, where stabilization is considered when 90 % of the previous sample is replaced by the new sample.
HITRAN	High-resolution transmission molecular absorption database. HITRAN is a compilation of spectroscopic parameters that a variety of computer codes use to predict and simulate the transmission and emission of light in the atmosphere.
Synflex	Polyethylene-aluminium composite tubing, lined with high-purity polymer, light weight, mechanically stable
Dekabon	Polyethylene-aluminium composite tubing, lined with high-purity polymer, light weight, mechanically stable
Viton	Fluoroelastomers, used in o-rings and seals, high mechanic stability and heat resistance, high density.

$Mg(ClO_4)_2$	Magnesium Perchlorate, desiccant
Molecular sieve	Porous absorbent, can be used for gas drying and gas separation

LIST OF ABBREVIATIONS

GHG	Greenhouse Gas
ppm	parts per million
ppb	parts per billion
PSI	Pound per Square Inch, 1 bar ≈ 14.5 PSI
IRMS	Isotope Ratio Mass Spectrometry
CRDS	Cavity Ring Down Spectroscopy
OA-ICOS	Off-Axis Integrated Cavity Output Spectroscopy
QCLAS	Quantum Cascade Laser Absorption Spectroscopy
PIT	Principle of Identical Treatment of sample and calibration materials
UNFCCC	United Nations Framework Convention on Climate Change
IAEA	International Atomic Energy Agency
WMO	World Meteorological Organization
GAW	Global Atmosphere Watch
NIWA	National Institute of Water and Atmospheric Research, Wellington, New Zealand
EMPA	The Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Switzerland
INSTAAR	Institute of Arctic and Alpine Research, University of Colorado, Boulder, USA
NOAA	National Oceanic and Atmospheric Administration, Washington, USA
GML	Global Monitoring Laboratory (GML) of the National Oceanic and Atmospheric Administration
ICOS	Integrated Carbon Observation System
CCL	Central Calibration Laboratory, prepares, maintains and disseminates primary network standards
DQO	Data Quality Objective
UPS	Uninterrupted power supply
PEEK	Polyether Ether Ketone is chemically inert to most materials.

PTFE	Polytetrafluoroethylene, also referred to as Teflon, chemically inert to most materials.
PCTFE	Polychlorotrifluoroethylene, chemically inert, stronger and stiffer than PTFE, used for seals, lowest water vapour transmission rate
GPS	Global Positioning System, satellite based, provides geo-location with high accuracy and high spatial and temporal resolution.
OLS	Ordinary Least Squares, linear fitting method
QDR	Orthogonal Distance Regression, linear fitting method
GMR	Geometric Mean regression, linear fitting method

CONTRIBUTORS TO DRAFTING AND REVIEW

Sperlich, P.	National Institute of Water and Atmospheric Research, New Zealand
Camin, F.	International Atomic Energy Agency
Deufrains, K.	International Atomic Energy Agency
Englund Michel, S.	Institute of Arctic and Alpine Research, United States of America
Hoheisel, A.	University of Heidelberg, Germany
Mohn, J.	Swiss Federal Laboratories for Materials Science and Technology, Swiss
Schmidt, M.	University of Heidelberg, Germany
Tarasova, O.	World Meteorological Organization

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