21GRD06 MetCCUS

D5: Paper on new Primary Reference Materials for gas composition for carbon capture, utilisation and storage and how they support industry and meet the technical specifications of European manufacturers, including a summary of the validation and stability data of the mixtures produced submitted to an open access peer-reviewed journal

Authors: Noor Abdulhussain[1], Manohara Gudiyor Veerabhadrappa[2], Ludek Kral[3], Florbela Dias[4], Richard Högström[5], Jacob Stang[6], Iris de Krom[1]

Organisation name of the lead participant for the deliverable:
VSL B.V.[1]
Other participants: NPL[2], CMI[3], IPQ[4], VTT[5], SINTEF[6]

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TABLE OF CONTENTS

Summary

This report presents the development and validation of new Primary Reference Materials (PRMs) for impurities in carbon dioxide (CO_2), addressing a critical gap in the metrological support required for carbon capture, utilisation, and storage (CCUS). As CO_2 streams captured from industrial processes inevitably contain impurities such as water, sulfur oxides, nitrogen oxides, hydrogen, and hydrocarbons, their accurate quantification is essential for safeguarding transport infrastructure, ensuring compliance with project specifications, and enabling safe long-term storage. International and project-specific guidelines, including those from ISO TR 27921, Porthos, and Northern Lights, define strict thresholds for impurities, highlighting the need for traceable gas standards that can be used to calibrate analytical instruments with high accuracy and comparability.

Within this framework, binary and multi-component PRMs were prepared by VSL, NPL, CMI, IPQ, and SINTEF ER, following ISO 6142-1 gravimetric methods. The selected impurities covered sulfur dioxide, hydrogen sulfide, nitrogen dioxide, nitrous oxide, water, dimethyl sulfide, ethanol and non-condensable gases (N_2, Ar, H_2, O_2, CH_4 and CO) at amount fractions relevant to CCUS specifications. To address possible adsorption and degradation effects, mixtures were prepared in different cylinder materials and surface treatments, such as Aculife IV and polished aluminium. In parallel, dynamic preparation systems and a portable trace gas generator were validated to provide flexible alternatives for generating low-level mixtures of reactive species like ammonia.

The stability of the PRMs was systematically studied over two years. Results demonstrated that several impurities, including sulfur dioxide, hydrogen sulfide, dimethyl sulfide, ethanol, and nitrous oxide, remained stable within their expanded uncertainties. For multi-component mixtures, major components such as methane, hydrogen, and nitrogen proved stable, while sulfur dioxide, nitrogen dioxide, and nitric oxide displayed significant degradation, indicating strong reactivity and wall effects in both treated and untreated cylinders. Dynamic dilution systems developed by VSL and NPL provided mixtures that agreed with static PRMs within one to five percent, confirming the robustness of these approaches, while the portable trace gas generator further demonstrated accurate production of ammonia in CO_2 within a relative uncertainty of about two percent.

In conclusion, this work has established a solid metrological foundation for impurity analysis in CO_2 by delivering new PRMs with proven stability for several key species. The PRMs developed in MetCCUS directly support industry by providing traceable calibration capabilities aligned with CO_2 quality specifications from ISO/TR 27913, Porthos, Northern Lights and other European initiatives. These materials enable operators to verify analytical performance, monitor impurity thresholds and ensure safe and reliable CO_2 transport and storage across Europe.

1 Introduction

Carbon capture, utilization, and storage (CCUS) includes technologies that support global energy and climate objectives. Both carbon capture with permanent storage (CCS) and carbon utilization (CCU) are effective strategies for reducing carbon dioxide (CO_2) emissions, thereby contributing to the climate targets set by the European Commission (1; 2). According to European green deal the production of CO_2 should be reduce of 55 % by 2030 and eliminated by 2055. To achieve these targets, large-scale deployment of CCUS is necessary. CO_2 can be captured from various industrial sources, including cement and steel production, biogas upgrading, fossil fuel combustion, and even directly from the air through direct air capture. Once captured, CO_2 is transported, typically via pipelines or ships, to designated storage sites, where it is injected into geological formations for long-term storage, or delivered to facilities for industrial utilization. The required quality of CO_2 depends on its source and the capture technology used, as this ensures proper process performance, protects system components, and safeguards health and safety. ISO/TR 27291:2020 (3) outlines how impurities in the CO_2 stream can impact storage, with effects categorized as physical, chemical, microbiological, or toxicological. These impurities may alter the thermodynamic and transport properties of CO_2, influencing factors such as operating pressure, temperature, fluid density and safety risks.

A critical aspect of a safe and efficient CCUS chain is the accurate measurement of impurities in the captured CO_2 stream. These impurities such as CH_4, O_2, H_2, CO, H_2S, N_2, Ar, and SO_2 can significantly affect the physical and chemical properties of the gas (4) (5) They influence parameters such as the bubble point and energy required for liquefaction or compression. Moreover, reactive species like H_2O, H_2S, NO_x, and SO_x may form separate acidic phases, posing serious corrosion risks to transport infrastructure (5). Reliable impurity quantification is therefore essential. It ensures compliance with specifications set by large-scale CCUS initiatives such as Porthos (6) and Northern Lights (7), protects the integrity of transport systems, and supports regulatory frameworks. Monitoring impurity levels at various stages, post-capture, during transport, and at the point of storage or utilization, can also inform operational decisions, such as whether further purification is required. To support this, robust analytical methods are essential for defining operational conditions and carrying out both online and offline measurements throughout the CO_2 capture, transport, and storage chain.

In order for these measurements to be accurate and comparable, reliable gas mixtures are needed to calibrate instruments used in monitoring impurity levels. These gas standards form the foundation of traceable measurements, enabling consistent and comparable data between monitoring systems and laboratories. However, a critical gap remains in the availability of primary reference standards (PRMs) for impurities in CO_2. Addressing this shortfall is essential to enable accurate impurity quantification and to ensure the long-term integrity and safety of transport and storage infrastructure. PRMs enable precise measurement of impurities with full metrological traceability. These materials are vital for validating analytical methods and calibrating the instruments used throughout the carbon capture and storage process.

This report paper covers the development of new PRMs for impurities in CO_2 and the systematic two-year stability study of these materials. The work includes the preparation of binary and multicomponent mixtures, validation of dynamic generation methods, and an assessment of suitable cylinder materials for long-term stability. In addition, the report outlines how the developed PRMs support industry by enabling traceable calibration of CO_2 impurity measurements and by meeting the technical requirements set by European manufacturers and CCUS projects. These materials allow operators to verify compliance with impurity thresholds and ensure safe and reliable CO_2 transport and storage.

1.1 CO_2 impurities specifications

Across the CCUS chain, from capture to transport and storage, different impurities may be present.
The Table A.1 (Annex A) brings together impurity limits from a wide range of industrial, regulatory, and research sources. Some of these specifications are project-specific, while others are the result of international standardisation efforts or technical studies. For example, the Porthos and TAQA values represent cluster-specific requirements for CO_2 transport and storage projects in the Netherlands, developed in close collaboration with industrial stakeholders. The Zero Emissions Platform (ZEP) specifications stem from a European technology platform that advises the European Commission on CCS deployment and provides guidance on common quality thresholds. Similarly, the DECARB project (Decarb WP 2.1.1) and other contributions come from the UK's National Physical Laboratory (NPL), whose ENV23 reports provide recommended impurity thresholds. In contrast, ISO/TR 27913 represents the international standard for pipeline transportation of CO_2, offering harmonised requirements that can be applied globally.

Key regulated impurities for pipeline CO_2 (as reflected in ISO/TR 27913 and industry guidelines) include water, H_2S/total sulfur, NO_x, SO_x, O_2, CO, hydrocarbons, non-condensable gases and particulates. Water (H_2O) is a dominant impurity of concern, with thresholds set between 20 and 50 ppm in most project specifications (ISO 27913, ECC, LBA), while some reservoir-based studies allow up to 300 ppm. Water is critical because even small amounts can combine with acid-forming species (SO_2, NO_x) to generate highly corrosive aqueous phases, and at higher levels can lead to hydrate formation in pipelines. Pipeline specs typically require ≤ 50 ppm (v/v) H_2O.

Hydrogen sulfide (H_2S) is one of the most toxic and corrosive impurities in CO_2 streams. Its presence can lead to accelerated metal corrosion. Across the specifications, limits are consistently set around ≤5 ppm, with slightly higher allowances (≤20 ppm). Sulfur oxides (SO_2, SO_x) and other sulfur compounds such as COS and mercaptans are also tightly controlled because of their capacity to form strong acids in the presence of water. Typical limits for SO_2 and total SO_x are ≤10 ppm, though transport-focused specifications sometimes allow up to 50 ppm. For other sulfur species, thresholds are often below 1 ppm, underlining the recognition that even traces are aggressive to materials.

Nitrogen oxides (NO_x) contribute to the formation of nitric acid when water is present, leading to rapid corrosion. Specifications vary from extremely strict (≤0.5 ppm in NPL studies) to more lenient (≤10 ppm in ISO/TR 27913). In practice, NO_x levels in captured CO_2 depend on the source (post-combustion flue gas can introduce 10–100+ ppm NO/NO_2 unless scrubbed). Because NO_2 is particularly reactive/unstable (it can dimerize to N_2O_4 and adsorb or form HNO_3 in moist conditions). Ammonia (NH_3) is often restricted to ≤3–10 ppm (Porthos, ISO 27913), though up to 50 ppm is allowed in some storage specifications; amines are set at ≤1 ppm in Porthos, with other reports suggesting ≤10 ppm, glycols are restricted to trace levels (≤0.025–0.05 ppm). Hydrogen (H_2), although not corrosive by itself, poses risks for material integrity. Exposure to H_2 under high-pressure transport conditions can lead to hydrogen embrittlement in steels, weakening the pipeline structure. For this reason, specifications generally restrict H_2 to ≤0.75% (Porthos, TAQA, ISO 27913), with some studies suggesting even stricter values (≤0.3%). Oxygen (O_2) is often limited to low levels (as O_2 can induce oxidative corrosion and fuels side-reactions). For example, one CO_2 network set O_2 < 10 ppmv, whereas some specs allow O_2 in the order of 100 ppm.

An important objective is to map Primary Reference Materials (PRMs) against industrial specifications for CO_2 quality in transport and storage. Pipeline and storage operators define allowable impurity limits to ensure safe, non-corrosive operation and compliance with environmental rules. Notably, ISO 27913:2024 (for CO_2 pipeline transport) now stipulates that total impurities in the CO_2 stream should not exceed 5% (molar), with multiple requirements to safeguard pipeline integrity. This effectively requires ≥95% CO_2 purity, consistent with typical project specs ranging 93–98% CO_2 minimum. The balance (≤5%) can include N_2, O_2, Ar, H_2, CH_4 and other gases, but individual reactive impurities are constrained by stricter sub-limits. Therefore strict traceable gas composition measurements are required.

In the MetCCUS project, European National Metrology Institutes (NMIs) have prepared a suite of PRMs, i.e. high-accuracy calibration gas mixtures, to support traceable measurement of key impurities in high-purity CO_2 streams. These PRMs target the low-level contaminants expected in captured CO_2 prior to transport and storage. Table 1 summarizes the PRMs developed by various NMIs, including the impurity species and amount-of-substance fractions (concentrations) achieved.

Table 1 Overview of selected impurities, amount fractions, and cylinder types for mixtures prepared by participants

	Mixture 1			**Mixture 2**			**Mixture 3**
Participants	Impurity	Amount fraction	Cylinder type	Impurity	Amount fraction	Cylinder type	Impurity
VSL	H_2O	10 ppm	Aculife IV	NO_2	10 & 1 ppm	Alphatech	SO_2, ≤20 ppm
NPL	C_2H_5OH	≤20 ppm	-	DMS	≤1 ppm	-	-
CMI	NO_2	≤ 100 ppm	AL/ Aculife	N_2O	≤ 10 ppm	AL/ Aculife	-
IPQ	H_2S	10 ppm	Aculife III/ IV	SO_2	≤20 ppm	Aculife III/ IV	-
SINTEF ER	SO_2	≤40 ppm	Aculife III/ IV	-	-	-	-

Table 1 summarises the impurities and mixtures prepared the participants. VSL prepared mixtures of H_2O (10 ppm), NO_2 (10 ppm and 1 ppm) and SO2 (20 ppm), while IPQ focused on H_2S (10 ppm) and SO_2 (20 ppm). CMI selected NO_2 (100 ppm) and N_2O (10 ppm) at higher concentration levels, and SINTEF ER prepared SO_2 (20 ppm) and H_2O mixtures (50 ppm). NPL contributed ethanol (≤20 ppm) and dimethyl sulfide (≤1 ppm). MetCCUS included O_2 in multi-component reference mixtures, see Table 2 (e.g. NPL and IPQ prepared mixtures of CO_2 containing O_2 along with CO, SO_2 or H_2S). Methane (CH_4) was included in certain multi-component mixtures (IPQ prepared an $H_2S+CO+CH_4+O_2$ in CO_2 mixture).

Table 2 Overview of selected impurities, for multi-component mixtures prepared by participants

Participant	**Multicomponent mixture**	**Amount of fraction (µmol/mol)**	
		Mixture 1	**Mixture 2**
NPL	H_2	2500	2500
	O_2	50	95
	CO	50	100
	CH_4	15000	10000
	N_2	10000	20000
	Ar	10000	7500
	NO	10	5

	SO_2	5	10
CMI		**Mixture 1 (Aluminium)**	**Mixture 2 (Aculife IV)**
	N_2O	9.5	9.4
	SO_2	9.00	8.7
	NO_2	23	27.2
	H_2	6986.4	7070.2
	CH_4	35140.9	22552.8
	N_2	20611.9	19618.4
IPQ		**Mixture 1**	**Mixture 2**
	CO	666.1	669.5
	O_2	0.594	0.586
	CH_4	-	1.9685
	SO_2	14.26	-
	H_2S	-	9.83

2 Stability data

The binary PRMs developed in this project were evaluated over periods of up to two years to assess their long-term stability and suitability as traceable calibration materials for impurity analysis in CO_2. The stability study applied repeated verification measurements following ISO 6143 procedures, with the detailed measurement results, analytical datasets, and uncertainty evaluations provided in Annex B. Overall, the stability behaviour of the binary mixtures was strongly impurity-dependent, with several species demonstrating excellent long-term stability while others exhibited clear compositional degradation driven by adsorption, chemical transformation, or interactions with cylinder surfaces.

Among the stable species, sulfur dioxide (SO_2) mixtures prepared by both VSL, IPQ and SINTEF showed highly consistent performance. The VSL mixtures displayed a small decrease of approximately one percent within the first six months after preparation, followed by stable behaviour for the remainder of the 600–750 day monitoring period. IPQ mixtures similarly showed no statistically significant deviation from the gravimetric values, as indicated by normalized error values consistently within |En| ≤ 1. The expanded uncertainties associated with these verifications, typically between one and one-and-a-half percent (k = 2), fully encompassed the observed variations. The stability evaluation of the SO_2 cylinder of SINTEF shows that both mixtures remain stable more than one year after preparation. Across three verification measurements performed in 2025, the observed amount fractions for both cylinders remained constant within their expanded uncertainties (*k=2*). Hydrogen sulfide (H_2S) exhibited comparable stability characteristics: across all IPQ measurements over 12–18 months, the observed differences between verification points remained within the combined uncertainty, confirming that H_2S can be maintained as a static PRM in CO_2 when stored in appropriately treated cylinders.

Nitrous oxide (N_2O) was found to be one of the most stable impurity species in this study. Mixtures prepared at CMI in both Aculife-treated and polished aluminium cylinders showed negligible drift over 24 months, with all measurement points remaining within approximately 0.4 $\mu mol\ mol^{-1}$ of the gravimetric value. The expanded uncertainties associated with N_2O measurements, typically around one to one-and-a-half percent, were sufficient to account for all observed variability. Volatile organic impurities such as dimethyl sulfide (DMS) and ethanol (EtOH) produced by NPL also demonstrated very good stability. DMS mixtures showed no measurable degradation over 25 months, with analytical values consistent with gravimetric preparation within the four-

percent uncertainty envelope. Ethanol behaved similarly, with verification results over a 23-month period revealing no systematic drift and combined relative uncertainties consistently below three percent.
In contrast, the stability of water (H_2O) in CO_2 proved more challenging. VSL's binary water PRMs showed an initial loss of approximately five to ten percent shortly after preparation, attributable to adsorption processes on cylinder walls or internal treatments. After this initial decline, the mixtures stabilised and subsequent verification results remained consistent within the four-percent measurement uncertainty. Nevertheless, the variability observed between different cylinders suggests that surface interactions and storage conditions have a significant influence on water stability, and regular re-verification is recommended to ensure continued traceability.

Nitrogen dioxide (NO_2) exhibited the most pronounced instability among all binary mixtures. For 10 $\mu mol\ mol^{-1}$ mixtures, a modest decline of around two percent was observed over 600 days; however, the behaviour at lower levels was more severe, with decreases of up to ten percent for 1 $\mu mol\ mol^{-1}$ mixtures. The studies conducted by CMI highlighted an even more dramatic dependence on cylinder material. In Aculife IV-treated aluminium cylinders, NO_2 showed ongoing degradation but remained detectable over the 24-month period. In polished aluminium cylinders, however, NO_2 concentrations dropped to near-zero within 12 months, followed by partial re-desorption at the 24-month point. Additional analysis confirmed the formation of secondary species including N_2O_4 and HNO_3, indicating that NO_2 undergoes chemical transformation rather than simple physical adsorption.

The uncertainty evaluation across all binary mixtures reflects two dominant contributions. The first arises from the initial gravimetric preparation according to ISO 6142-1, which typically contributes between 0.1 and two percent to the overall uncertainty depending on impurity purity, weighing precision, and gas molar masses. The second source relates to stability, measured through repeat verifications over time. For stable species such as SO_2, H_2S, N_2O, DMS and ethanol, the stability component remains small and generally negligible compared to analytical uncertainty. For water and especially NO_2, stability contributes significantly to the expanded uncertainty and must be explicitly included to avoid underestimation of the total uncertainty when these mixtures are used as calibration materials.

In summary, the binary stability study confirms that several impurities critical for CCUS, most notably SO_2, H_2S, N_2O, DMS and ethanol, can be realised as long-term stable PRMs in CO_2, with performance fully compatible with industrial calibration needs. Conversely, H_2O and particularly NO_2 exhibit impurity-specific instabilities that require careful consideration of cylinder materials, regular re-verification, or the use of dynamic and generator-based reference methods. The complete datasets supporting these conclusions are available in Annex B.

Alongside the stability studies, dynamic methods were established to enable the generation of mixtures across a range of amount of fractions. Dynamic gas mixture preparation systems developed at VSL and NPL were validated as complementary methods for generating traceable low-level impurity mixtures in CO_2. Verification by NPL against static PRMs demonstrated that dynamically prepared mixtures agreed with gravimetric reference values typically within 1–5 %, with relative expanded uncertainties ranging from 0.04 % for major components to ~6 % for trace species. For permanent gases by VSL, such as N_2, CH_4, O_2, Ar and H_2, dilution factors were reproduced reliably, and biases remained below 4 %. The VTT trace gas generator produced NH_3 at 10–20 $\mu mol\ mol^{-1}$ with a relative expanded uncertainty of ~1.9 %. Overall, the results confirm that dynamic dilution offers a robust and traceable route for producing reference mixtures when static PRMs are impractical or when extremely low amount fractions are required. The full validation procedures and detailed results is provided in Annex B.2.

3 Use of PRMs by CCUS industry and compliance with specifications

The reference materials developed within the MetCCUS project address a critical need across the CCUS value chain, where accurate quantification of impurities in captured, transported and injected CO_2 is essential for process control, safety, and regulatory compliance. Industrial stakeholders, including capture plant operators, pipeline network owners, storage site operators and suppliers of online gas analyzers, rely on traceable calibration materials to verify the performance of sensors and analytical systems that monitor impurities such as SO_2, H_2S, H_2O, NO_x, VOCs and oxygen. These impurities influence corrosion behaviour, compressor efficiency, pipeline integrity, geochemical interactions in storage reservoirs and compliance with pipeline specifications.

The binary PRMs produced in this project provide industry with high-quality calibration materials that enable traceability to the SI and support harmonised monitoring strategies across Europe. They can be used to calibrate or verify online analyzers (e.g., TDLAS, CRDS, NDIR, UV-Vis, electrochemical sensors), to perform laboratory-based validation using GC-SCD, GC-MS, FTIR or other reference techniques, and to support comparability assessments across different industrial sites or monitoring campaigns. For pipeline operators and transport network developers, PRMs directly support the qualification and acceptance testing of measurement instrumentation required to demonstrate compliance with maximum impurity thresholds. Similarly, for storage-site operators, these materials help ensure that CO_2 streams entering injection wells meet the impurity limits necessary to avoid operational problems such as scale formation or unintended reservoir reactions.

With respect to compliance, the developed PRMs were evaluated against the typical impurity ranges defined in industrial specifications for CO_2 transport and storage. The concentration levels realised in this project generally fall within or near the ranges required for calibration of industrial instruments. For SO_2, H_2S, N_2O, ethanol and dimethyl sulfide, the prepared mixtures match the expected impurity levels found in post-combustion and industrial capture streams, and the demonstrated long-term stability ensures that these PRMs can serve as reliable reference points for industrial calibration routines.

3.1 Support for industry

The suite of PRMs developed in the MetCCUS project is designed to help industrial users meet the CO_2 purity requirements set by international standards and major CCS projects. Technical specifications such as ISO/TR 27913 and project-specific guidelines (e.g. Porthos and Northern Lights) demand that captured CO_2 be overwhelmingly pure CO_2 (typically ≥95% by volume) with tightly limited impurities to protect pipeline and storage integrity. For example, the Porthos specification requires $CO_2 \geq 95\%$ and caps critical contaminants at low levels ($H_2O \leq 70$ ppm, $O_2 \leq 40$ ppm, total NOx ≤ 5 ppm, etc.) to prevent corrosion and safety hazards. The updated Northern Lights CO_2 quality criteria likewise define strict maximum concentrations for a broad range of impurities, reflecting the latest industry insights on material compatibility and cross-reactions. By aligning with these benchmarks, the reference materials from MetCCUS directly support industry in demonstrating compliance with required CO_2 purity and impurity limits.

The PRMs cover many of the impurities that feature in CO_2 quality specifications at relevant amount fractions. In practice, this means traceable calibration gas mixtures have been prepared for key components and contaminants across the expected concentration ranges. This includes PRMs for permanent gas impurities like N_2, Ar, H_2, O_2, and CH_4 in CO_2 at percent or sub-percent levels, as allowed in transport specifications. Likewise, reactive impurities have been addressed by low-level reference mixtures: for instance, CO in CO_2 around the 1000 ppm scale, and sulfur- or nitrogen-containing species (H_2S, SO_2/SOx, NO/NOx) at ppm concentrations matching the limits in standards. These PRMs enable calibration of analyzers to detect impurities at the threshold values mandated by ISO/TR 27913 and projects like Porthos, thus ensuring that on-line monitors and laboratory analyses can reliably verify CO_2 stream quality against the specifications. In short, the available PRMs encompass most of the critical impurity types at the amount fractions relevant for carbon capture and storage operations, giving industry the necessary tools to quantify those impurities with metrological traceability.

However, the full scope of impurities listed in emerging CO_2 purity standards is broad, and not every minor compound or extreme condition is yet covered by available PRMs. Specifications such as Porthos include potential contaminants, ranging from VOCs (e.g. methanol, acetaldehyde) to amines, glycols, mercury, or particulate matter, many of which are present only in trace quantities or are challenging to stabilize in a cylinder. While the MetCCUS project's reference materials address the major categories of gaseous impurities, there remain gaps for certain species and very low concentration levels.

To help close the remaining gaps, the project has explored dynamic methods of generating reference gas mixtures on demand. The project demonstrated the use of dynamic generation systems, which offer an alternative route for achieving traceable mixtures when static PRMs are impractical. Dynamic dilution systems at VSL and NPL successfully generated low-level mixtures of permanent gases with relative expanded uncertainties ranging from approximately 0.04 % (major permanent gases at high levels) to ~6 % (trace components), with bias typically below 4 %. These results confirm that the dynamic systems are capable of producing mixtures with metrological equivalence to static PRMs for many impurity classes.
Furthermore, the portable trace gas generator evaluated within the project (VTT) demonstrated that dynamic generation can be extended to impurities that exhibit even stronger surface interactions, such as ammonia. Achieving agreement within ~3 % of the expected concentration indicates that this approach can meet industrial calibration requirements for a subset of highly reactive species. As industrial specifications continue to evolve, particularly with expected growth in amine-based capture and the associated impurities, such dynamic systems will be essential for delivering reference mixtures at $\mu mol\ mol^{-1}$ and $nmol\ mol^{-1}$ levels.

In summary, the PRMs developed in MetCCUS provide robust support for industrial compliance with CO_2 quality requirements, enabling accurate quantification of most regulated impurities through traceable, stable calibration materials. Where static mixtures are limited by chemical stability or incomplete analyte coverage, dynamic dilution and generator-based systems offer a viable and validated pathway to extend metrological traceability to all impurity classes critical for safe and efficient CO_2 transport and storage across Europe.

4 Conclusion

This work demonstrates the successful development, validation and long-term assessment of Primary Reference Materials (PRMs) for a broad range of impurities relevant to the CO_2 value chain. Binary and multicomponent mixtures were prepared in accordance with ISO 6142-1 and verified through repeated measurements over a period of up to two years. The stability studies show that several key impurities, most notably SO_2, H_2S, N_2O, ethanol and dimethyl sulfide, remain stable within their expanded uncertainties, confirming their suitability as long-term calibration materials for industry. In contrast, strongly reactive species such as NO_2, NO and, to a lesser extent, H_2O exhibit significant instability and cylinder-surface interactions, highlighting the need for careful selection of cylinder treatments, regular re-verification, or alternative dynamic preparation methods.

The comparison of dynamic dilution systems developed by VSL and NPL with static gravimetric PRMs demonstrates that dynamic generation can provide traceable mixtures within 1–5 % agreement, offering a robust route for impurities that cannot be stabilised in cylinders. The validation of a portable trace gas generator further expands metrological capabilities to highly reactive compounds such as NH_3, which are increasingly relevant for amine-based capture technologies.

Overall, the PRMs developed within MetCCUS provide a solid metrological foundation for impurity measurements in CO_2 streams and directly support industrial compliance with European CO_2 quality specifications. While the work successfully addresses most major impurity classes, gaps remain for certain highly reactive species, underscoring the need for continued research, improve measurement technologies and further development of dynamic reference methods.

References

1. EU Commission Carbon Capture and Geological Storage. [Online] https://energy.ec.europa.eu/topics/carbon-management-and-fossil-fuels/industrial-carbon-management_en.

2. European Commission A European Green Deal. [Online] https://ec.europa.eu/info/strategy/priorities-2019-2024/european-green-deal_en..

3. *ISO/TR 27921:2020 Carbon dioxide capture, transportation, and geological storage — Cross Cutting Issues — CO2 stream composition.* 2020.

4. *Framework for CO2 impurity monitoring in CCUS infrastructure.* Simonsen, Kenneth René, Hansen, Dennis Severin and Pedersen, Simon. s.l. : Carbon Capture Science & Technology, 2025, Vol. 16.

5. *The Challenge of Monitoring Impurity Content of CO2 Streams.* Morland, Bjørn H., Svenningsen, Gaute and Dugstad, Arne. 570, s.l. : Processes, 2021, Vol. 9.

6. Porthos. *Standard CO2 TRANSPORT AND STORAGE CONDITIONS.* 2022.

7. Lights, Northern. *Liquid CO2 Quality Specifications.* 2024.

8. TAQA. [Online] https://www.commissiemer.nl/projectdocumenten/00007536.pdf.

9. zeroemissionsplatform. [Online] https://zeroemissionsplatform.eu/publication/a-trans-european-co2-transportation-infrastructure-for-ccus-opportunities-challenges/.

10. [Online] https://www.decarbgrid.eu/app/uploads/sites/19/2022/03/Report-A2.1.1-Literature-review-on-hydrogen-and-carbon-dioxide-for-primary-reference-materials-for-decarbonised-gas-grids..pdf.

11. NPL. [Online] https://eprintspublications.npl.co.uk/8258/1/ENV23.pdf.

12. ISO 27913:2024 - Carbon dioxide capture, transportation and geological storage — Pipeline transportation systems. [Online] https://www.iso.org/standard/84840.html.

13. e East Coast Cluster Projects. [Online] https://northernendurancepartnership.co.uk/wp-content/uploads/2025/04/PES-NEP00-EN-SPE-000-00001-Public-B02.pdf.

14. HyNet CCUS. [Online] https://assets.publishing.service.gov.uk/media/629535b2e90e07039ba54e46/HyNet_CCUS_Pre-FEED_KKD_WP4_-_Onshore_CO2_Pipeline_Design_Study_Report.pdf.

15. *Integrated band intensities in N2O4 in the infrared range.* Hurtmans, D., Herman, M. and Auwera, J. Vander. 6, s.l. : Journal of Quantitative Spectroscopy and Radiative Transfer, 1993, Vol. 50, pp. 595-602.

16. *Preparation of multicomponent mixtures to support carbon metrology.* Dias, Florbela A., Palma, Cristina and Costa, Carlos J. s.l. : Measurement, 2025, Vol. 239.

17. 21NRM04 BiometCAP - Protocol for SI-traceable validation of methods for biomethane conformity assessment, project website:. [Online] https://www.euramet.org/research-innovation/search-research-projects/details/project/protocol-for-si-traceable-validation-of-methods-for-biomethane-conformity-assessment.

18. *Dynamic calibration method for reactive gases.* Saxholm, Sari, et al. 3, s.l. : Measurement Science and Technology, 2019, Vol. 31.

19. Arrhenius, Karine, et al. *Report A3.1.2: Literature survey on commercially available cylinders for the preparation of PRMs for CCUS.* s.l. : Zenodo, 2023.

20. *ISO 6142-1:2015 – Gas analysis — Preparation of calibration gas mixtures — Part 1: Gravimetric method for Class I mixtures.*

21. *ISO 6143:2001 – Gas analysis — Comparison methods for determining and checking the composition of calibration gas mixtures.*

22. 16ENV01 MercOx - Metrology for oxidised mercury. [Online] https://www.euramet.org/research-innovation/search-research-projects/details/?tx_eurametctcp_project%5bproject%5d=1485.

23. 16ENG05 Biomethane - Metrology for biomethane, project website. [Online] https://www.euramet.org/research-innovation/search-research-projects/details/project/metrology-for-biomethane.

24. 21GRD05 Met4H2 - Metrology for the hydrogen supply chain, project website. [Online] https://www.euramet.org/technical-committees/tc-projects/details/project/metrology-for-the-hydrogen-supply-chain.

25. 21GRD10 quantiAGREMI - On farm quantification of ammonia and greenhouse gas emissions from livestock production. [Online] https://www.euramet.org/research-innovation/search-research-projects/details/project/on-farm-quantification-of-ammonia-and-greenhouse-gas-emissions-from-livestock-production.

Annex

Annex A – Overview of specifications for impurities in CO_2

Table A. 1 - Specifications for impurities in CO_2 from different sources and guidelines

	Porthos (6)	**TAQA** (8) (CO_2 delivery specifications)	**ZEP** (9)	**Decarb WP 2,1,1** (10)	**ENV23 NPL Report** (11) (Saline reservoir sequestration)	**ENV23 NPL Report** (Unmineable coal seams)	**ENV23 NPL Report** (Oil and gas recovery)	**ISO 27913** (12)	**CCUS Specifications Summary (NPL)**	**ECC** (13) **(East Coast Cluster)**	**LBA** (14) **(Liverpool Bay Area)**	**Amount fraction**
component	**all percentages are mole %**											
Carbon dioxide (CO_2)	≥ 95 %	≥ 95 %	not defined	not defined				≥95%		≥96%	≥95%	≥96%
water (H_2O)	≤70	≤40	≤30	≤20	≤300	≤300	≤300	≤50 ppm	≤20-50 ppm	≤50 ppm	≤50 ppm	≤50 ppm
Sum [H_2+N_2+Ar+CH_4+CO+O_2]	≤4%	≤4%										≤4%
H_2	≤0.75%	≤0.75%	≤50	≤0.3%	≤4%	≤4%	≤1%	≤1%	≤0.005-2%	≤0.75%	≤0.75%	≤0.75%
N_2	≤2.4%	≤2%						≤4%	≤1-4%	≤4%	≤4%	≤1-4%
Ar	≤0.4%	≤1%	not defined					≤4%	≤1-4%	≤4%	≤4%	≤1-4%
CH_4	≤1%	≤1%	not defined					≤4%	≤1-4%			≤1-4%
CO	≤750 ppm	≤750 ppm	≤100 ppm					≤0.2%	≤0.01-0.2%	≤0.2%	≤0.2%	≤750 ppm
O_2	≤40 ppm	≤40 ppm	≤10 ppm	≤100 ppm	≤4%	≤4%	≤100 ppm	≤10 ppm	≤10-20 ppm	≤10 ppm	≤10 ppm	≤10 ppm
total sulfur-contained compounds (incl. mercaptan)	≤20 ppm							CS_2: ≤20 ppm				≤20 ppm
COS		≤0.1 ppm						≤100 ppm			COS and CS_2:≤5 ppm	≤5 ppm

DMS		≤1.1 ppm										≤1ppm
H_2S	≤5 ppm	≤5 ppm	≤9	≤20 ppm	≤5 ppm	≤5 ppm	≤5 ppm	≤5 ppm	≤5-20 ppm	≤5 ppm	≤5 ppm	≤10 ppm
SO_x		≤50 ppm	≤10	≤10 ppm	≤0.5 ppm	≤0.5 ppm	≤0.5 ppm	≤10 ppm	≤10-100 ppm	≤20 ppm	≤10 ppm	≤20 ppm
Total NO_x	≤5 ppm	NO ≤2,5 ppm, NO_2 ≤2.5 ppm, NO_x ≤5 ppm	NO_X: ≤10	NO_X: ≤20 ppm	NO_x: 0.5 ppm	NO_x: 0.5 ppm	NO_x: 0.5 ppm	NO_x: ≤10 ppm	NO_x: ≤10-100 ppm	≤10 ppm	≤10 ppm	≤10 ppm (NO2/NO)
Total aliphatic hydrocarbons (C2 to C10)	≤1200 ppm	≤1200 ppm						≤4.15%	≤1.15-6%		≤8.15%	≤1200 ppm
total aromatic hydrocarbons (C6 to C10, incl. BTEX)	≤0.1 ppm	≤0.1 ppm						BTEX: ≤15 ppm, Naphthalene: ≤100 ppb			BTEX: ≤15 ppm, Naphthalene: ≤100 ppb	≤0.1 ppm
Total volatile organic compounds (excl. methane, total aliphatic HC (C2 to C10), methanol, ethanol, and aldehydes)	≤10 ppm	≤350 ppm						≤48 mg/m^3	≤20-60 ppm		≤48 mg/m^3	≤10 ppm
total aldehyde compounds	≤10 ppm		acetaldehyde: ≤20 ppm formaldehyde: ≤20 ppm									≤10 ppm ≤20 ppm
ethanol	≤20 ppm									≤500 ppm		≤20 ppm
methanol	≤620 ppm							≤350 ppm		≤500 ppm	≤350 ppm	≤350 ppm
hydrogen cyanide (HCN)	≤2 ppm	≤20 ppm		≤5 ppm	≤0.9 ppm	≤0.9 ppm	≤0.9 ppm					≤2 ppm
total amine compounds	≤1 ppm		≤10	not defined				≤100 ppb	≤0.08-10 ppm		≤100 ppb	≤1 ppm
total glycol compounds	follow dew point specification								≤0.025-0.05 ppm			≤0.025-0.05 ppm

ammonia (NH_3)	≤3 ppm		≤10	≤50 ppm	≤25 ppm	≤25 ppm	≤25 ppm	≤10 ppm	≤10-1500 ppm	≤10 ppm	≤10 ppm	≤50 ppm
total carboxylic acid and amide compounds	≤1 ppm											≤1 ppm
total phosphorus-contained compounds	≤1 ppm											≤1 ppm
ethylene (etheen) (C_2H_4)		≤1 ppm										
Cadmium (Cd)/Titanium (Ti)			≤0.03 (sum)									
Mercury (Hg)			≤0.03		≤0.002	≤0.002	≤0.002					
Solid particulates								≤1 mg/m^3	≤1 ppm	≤1 mg/m^3	≤1 mg/m^3	
Toxic metal								≤0.15 mg/m^3			≤0.15 mg/m^3	
Acid forming compounds								≤150 mg/m^3	≤10-70 ppm		≤150 mg/m^3	
Nitrosamines and nitramines								≤3 µg/m^3			≤3 µg/m^3	
Dioxins and furans								≤0.02 ng/m^3			≤0.02 g/m^3	
He												

Annex B- Stability studies of binary PRMs

Reference gas mixtures were prepared in compliance with ISO 6142-1. This standard ensures high accuracy, full traceability to the SI, and international comparability through validated methods, uncertainty evaluation, and stability testing. Table 1 summarizes the impurities and mixtures prepared the participants. The results of the stability studies are described in this section.

Sulfur dioxide (SO_2)

VSL, IPQ and SINTEF prepared mixtures of 20 ppm SO_2 in CO_2. VSL prepared 2 mixtures (VSL503664 and VSL753627) and two mixtures of SO_2 in CO_2 by IPQ, labelled as PRM408326 and PRM108593, were also carefully assembled. SINTEF prepared two mixture labelled as CGM018707 and CGM018708.

The SO_2 amount fraction in VSL503664 and VSL753627 was verified against a suite of VSL PRMs of SO_2 in N2 according to ISO 6143. The analyser showed an offset for the CO_2 matrix, to correct for the offset, the response of pure CO_2 was recorded and the responses of VSL503664 and VSL753627 were corrected with the pure CO_2 response. VSL503664 was analysed 6 times over a period of 600 days and VSL753627 was analysed 7 times over a period of 750 days (Figure 1). The verification results for both PRMs show a decrease in the SO_2 fraction in the first 6 months after preparation. After that the composition of the mixture is stable over the measurement period within the measurement uncertainty of 1%. On average the fraction decreased with 0.2 µmol mol-1 (1%). This initial loss can be taken into account as an uncertainty source leading to an increased expanded uncertainty of 0.3 µmol mol-1 (1.5%) for the SO_2 in CO_2 PRMs.

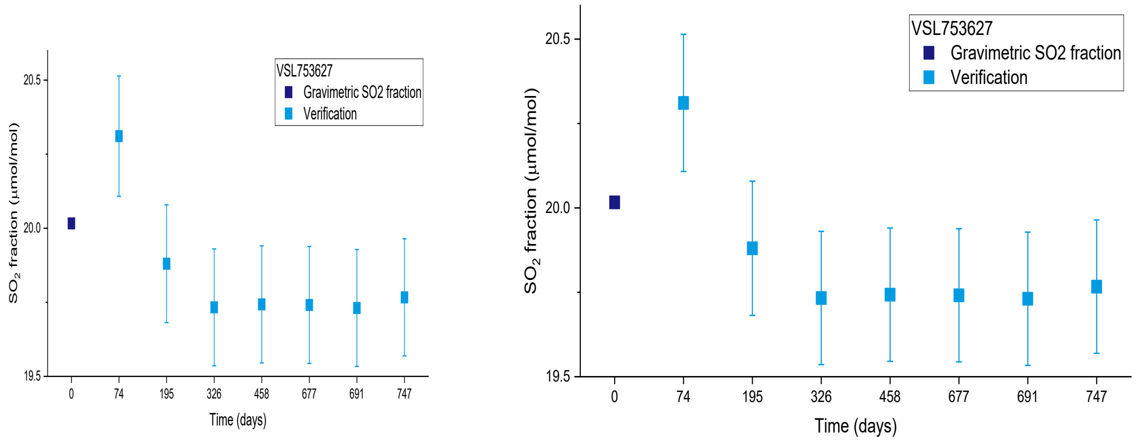
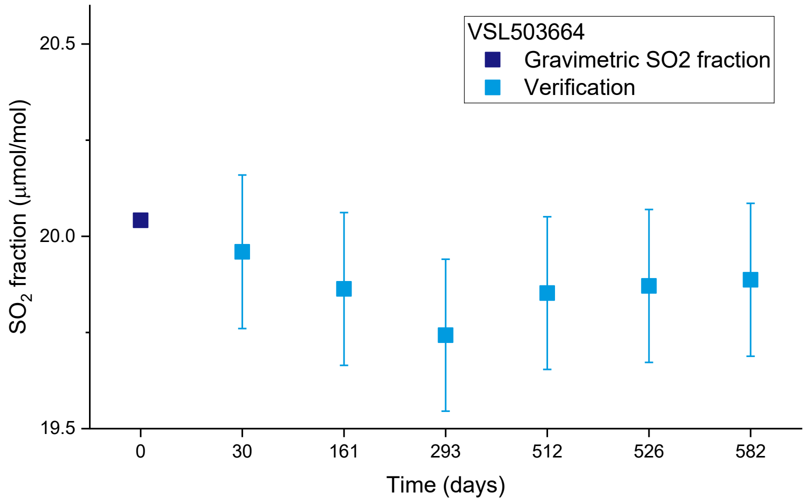


Figure 1 Verification results of VSL503664 and VSL753627. The first point represents the gravimetric fraction calculated based on the preparation of the PRM according to ISO 6142-1. The other points represent the verifications with error bars for the relative measurement uncertainty of 1% (k=2)



Two binary mixtures (PRM408326 and PRM108593) of SO_2 in CO_2 were prepared and analysed by IPQ to evaluate their long-term stability. The binary mixtures were certified using the SO_2 analyser with the calibration standards. The results for SO_2 in these mixtures are presented in Table 3. Stability was assessed using the normalized error (En), where values of |En| ≤ 1 indicate that no significant change has occurred. For PRM408326, the SO_2 concentration remained close to the initial value, with En values ranging from 0.31 to 0.84, confirming satisfactory stability throughout the study period. For PRM108593, the concentration showed no relevant variation, with En values between –0.19 and 0.00, demonstrating excellent stability. Overall, both SO_2/CO_2 mixtures analysed by IPQ were stable over the measurement period, confirming their suitability as reference materials.

Table 3 Results of the stability study for the prepared binary mixtures of SO2/CO2

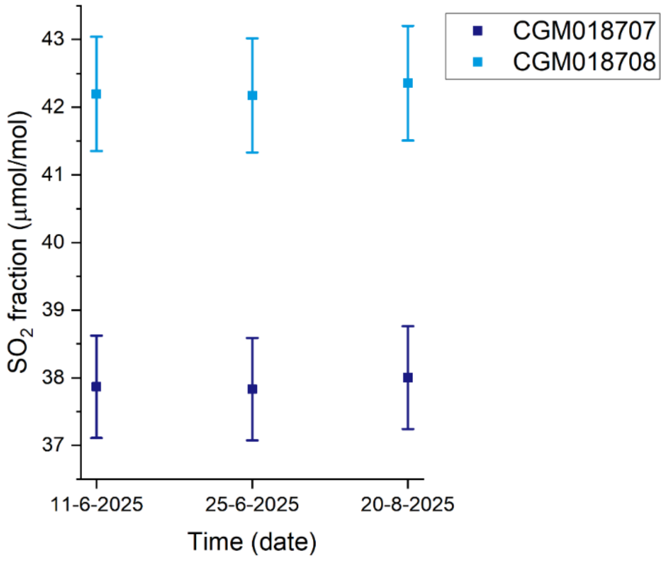
PRM408326	**SO_2/CO_2**		
Date	***x*** **µmol/mol**	***U*** **µmol/mol**	***E_n***
2023-09-04	19,52	0,51	-
2024-04-18	20,16	0,57	0,84
2024-11-18	19,9	1,1	0,31

PRM108593	**SO_2/CO_2**		
Date	***x*** **µmol/mol**	***U*** **µmol/mol**	***E_n***
2023-09-04	20,71	0,50	-
2024-04-18	20,71	0,58	0,00
2024-11-18	20,5	1,0	-0,19

The long-term stability of the SO_2 cylinders CGM018707 and CGM018708 by SINTEF, was evaluated through repeated verification measurements performed at VSL in 2025. Both mixtures were originally prepared in 2023, meaning the measurements presented here provide insight into their behaviour more than one year after preparation. Across three verification measurements performed in 2025, the observed amount fractions for both cylinders remained constant within their expanded uncertainties (k = 2) (see Table 4).

Table 4 Mixtures prepared in 2023; verification measurements performed at VSL in 2025. Amount fractions with expanded uncertainty (k = 2).

Date (2025)	CGM018707 (µmol/mol)	U(*k*=2) (µmol/mol)	CGM018708 (µmol/mol)	U(*k*=2) (µmol/mol)
11-06-2025	37.87	0.38	42.20	0.42
25-06-2025	37.83	0.38	42.18	0.42
20-08-2025	38.00	0.38	42.36	0.42



Dimethylsulfide (DMS)

The DMS containing PRMs by NPL were analysed by developing method using gas chromatography (GC) technique fitted with sulphur chemiluminescence detector (SCD). During method development (selectivity, limit of detection (LOD), limit of quantification (LOQ), working range, linearity, bias, repeatability, intermediate precision, robustness and stability of the reference materials used were checked. Uncertainty budget for the developed method was calculated based on the GUM guidelines. The 1 µmol/mol DMS mixture (D610430) was analysed using the method developed by inverse analysis method at various instances. The stability of this mixture was also checked periodically as shown below against two freshly prepared standards at the age of month 25. The new, 1 and 10 µmol/mol standards, D228758 and D180313 (Table B4, Annex B) were prepared starting from different parents compared to the rest of the mixtures and were found to match with the PRMs developed confirming their stability. The validation results are given in the Table 4.

Table 5 Analytical amount fractions of the old 1 µmol/mol of DMS in CO_2 PRM with combined relative uncertainty (k=2) over a period of 25 months.

Number of months from date of preparation	3	3	3	3	4	7	7	12	17	25
Gravimetric amount fraction of DMS (µmol/mol) ±relative uncertainty (%, *k*=2)	1.03 (±0.37)									
Analytical amount fraction of DMS (µmol/mol)	1.04	1.12	1.00	1.06	1.07	1.04	1.06	1.05	1.02	0.95
Combined relative uncertainty (%, *k*=2)	3.91	7.83	4.55	5.23	5.28	7.71	3.20	2.62	3.85	4.10

Figure 2 below show the stability data (some of the data points in the figure are removed for clarity). The stability data shows that the old 1 µmol/mol DMS mixture (D610430) is stable over 25 months and the analytical amount fraction of the old with the new matching standard prepared at month-25 from a different parent chain validates and confirm the stability of the mixtures.

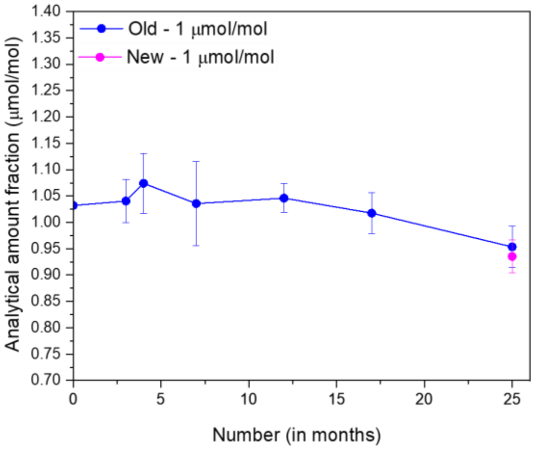


Figure 2 Stability data of the 1 µmol/mol DMS mixture (D610430) over 25 months compared with the new 1 µmol/mol DMS mixture (D180313).

Hydrogen sulfide (H_2S)

Two binary combinations of H_2S in a carbon dioxide matrix, designated as PRM108595, PRM108596 were prepared and analysed by IPQ. The binary mixtures were certified using the H_2S analyser and the calibration curves were done using primary standards in nitrogen matrix. Table 5 shows the results of the analysis of the H_2S component, in the two prepared binary mixtures.

Table 6 Results of the stability study for the prepared binary mixtures of H_2S/CO_2

PRM108596	**H_2S/CO_2**		
Date	***x*** **µmol/mol**	***U*** **µmol/mol**	***E_n***
2023-09-11	9,64	0,47	-
2024-04-23	10,22	0,42	0,92
2024-11-08	10,02	0,34	0,66

PRM108595	**H_2S/CO_2**		
Date	***x*** **µmol/mol**	***U*** **µmol/mol**	***E_n***
2023-09-11	9,97	0,48	-
2024-04-23	9,87	0,35	-0,17
2024-11-08	9,61	0,29	-0,64

Stability was assessed using the normalized error (En), where values of |En| ≤ 1 indicate that no significant change has occurred. For PRM108596, the H_2S concentration showed a slight increase during the first re-certification and a small decrease at the later point, with En values ranging from 0.66 to 0.92. These values remain within the acceptance limit, confirming satisfactory stability. For PRM108595, the H_2S concentration remained close to the initial value throughout the study, with En values between –0.64 and –0.17, also indicating good stability. Overall, both H_2S/CO_2 mixtures analysed by IPQ were stable over the measurement period and are suitable for use as reference materials

Water (H_2O)

At VSL, the H_2O amount fraction in VSL207088 and VSL207097 was verified against a suite of VSL PRMs of H_2O in N_2 according to ISO 6143. The PRMs were analysed 4 times over a period of 600 days (Figure 3). The verification results for VSL207088 show an initial decrease of the H2O fraction. The 4 verification results for VSL207088 are comparable within the measurement uncertainty of 4% and don’t show instability over time. The average loss when combining the 4 verification measurements is 1.24 µmol mol-1 which corresponds to 8% loss. For VSL207097 the verification results are not comparable within the measurement uncertainty.

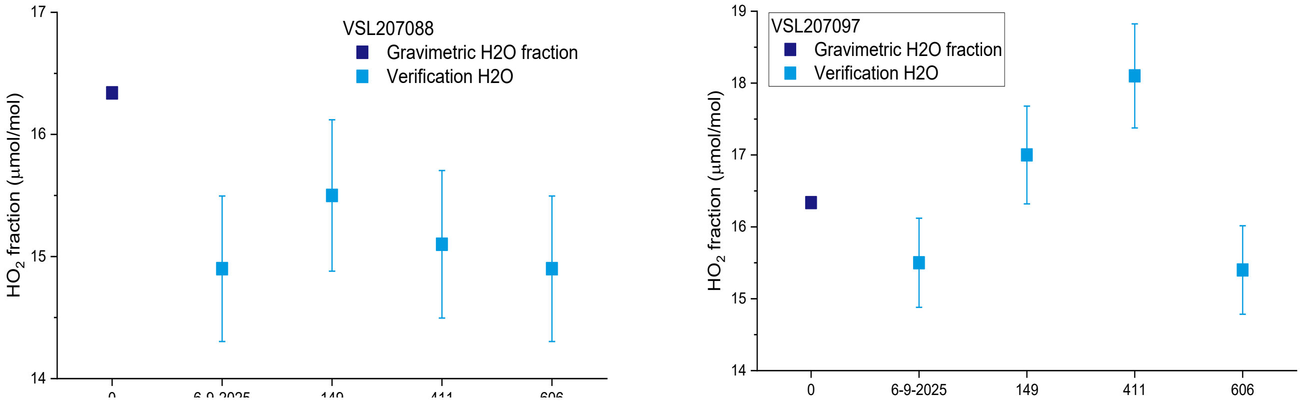


Figure 3 Verification results of VSL207088. The first point represents the gravimetric fraction calculated based on the preparation of the PRM according to ISO 6142-1. The other points represent the verifications with error bars for the relative measurement uncertainty of 4%((k=2)

Nitrogen dioxide (NO$_2$)

VSL prepared 4 mixtures of NO$_2$ in CO$_2$. The NO$_2$ amount fractions in VSL173849, VSL190518, VSL174101 and VSL174127 were verified against a suite of VLS PRMs of NO$_2$ in N$_2$ according to ISO 6143. The spectra were recorded against a nitrogen background and corrected with spectra from pure CO$_2$. The PRMs were analysed 3 times over a period of 600 days (Figure 4 and Figure 5)

Table 7 Results NO$_2$ and HNO$_3$ analysis.

PRM number	NO$_2$(ver) (μmol mol^{-1})	HNO$_3$(ver) (μmol mol^{-1})	NOx(ver) (μmol mol^{-1})	D (μmol mol^{-1})	D (%)
VSL173849	9.69	0.17	9.86	-0.14	-1.4
VSL190518	9.67	0.12	9.79	-0.21	-2.1
VSL174101	0.894	0.134	0.974	-0.05	5
VSL174127	0.915	0.598	1.028	0.04	4

After the last analysis, the HNO$_3$ fraction in the PRMs was determined and verified based on the absorption cross-section from the PNNL database (11) (Table 6, Figure 4 and Figure 5). The results for the NO$_2$ and HNO$_3$ verification were added together to obtain the NOx verification result. Those were used to calculate the deviation compared to the NOx gravimetric value (Table B1, Annex B).

The second verification results of the 10 µmol mol-1 PRMs VSL173849 and VSL190518 show a deviation larger than the measurement uncertainty of 2.6%. The other two verification measurements are within the measurement uncertainty. Nevertheless, the NO2 fractions show a decrease of 0.2 µmol mol-1 (2%) over a period of 600 days. The NOx verification results also show a decrease of the NOx fraction of 0.2 µmol mol-1.

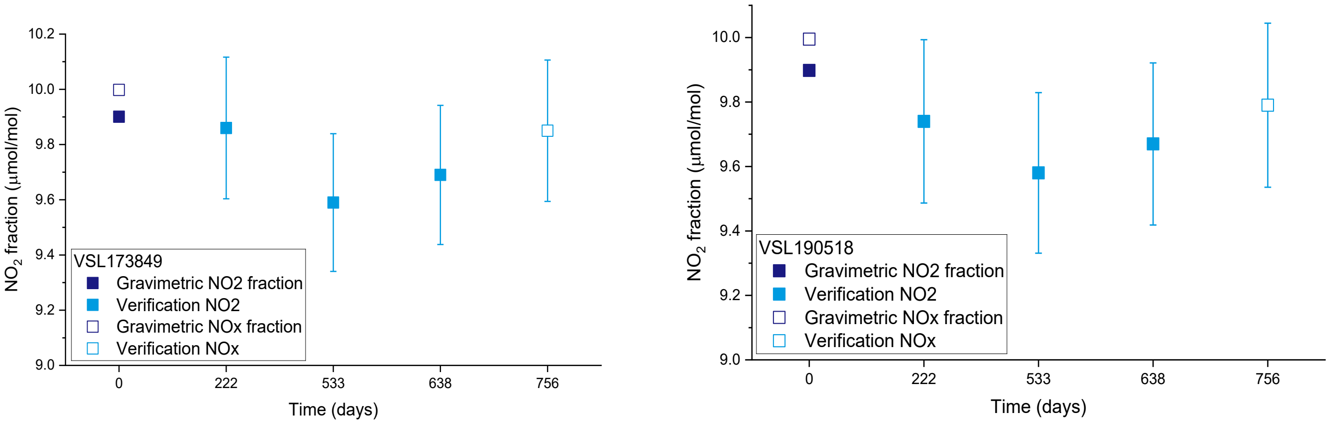


Figure 4 Verification results of VSL173849 and VSL190518. The first point represents the gravimetric NO2 and NOx fraction calculated based on the preparation of the PRM according to ISO 6142-1. The other points represent the verification results with error bars for the relative measurement uncertainty of 2.6% (k=2)

The verification results of the 1 µmol mol^{-1} PRMs VSL174101 and VSL 174127 show a decrease in NO_2 fraction over a period of 600 days. The average decrease is 0.1 µmol mol^{-1} (10%) which is larger than the measurement uncertainty of 5%. The deviation is smaller for the NOx verification results, VSL 174101 shows a decrease of 0.05 µmol mol^{-1} (5%) while the results for VSL174127 show a positive deviation of 0.04 µmol mol^{-1} (4%). These results are within the measurement uncertainty of 5%. More research is needed to demonstrate that the NO_2 in CO_2 PRMs are stable.

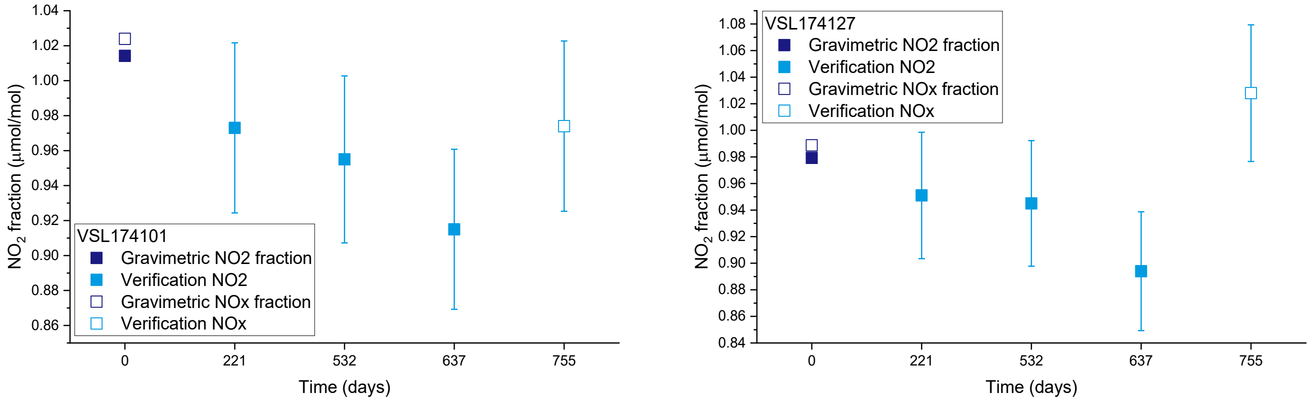


Figure 5 : Verification results of VSL174101 and VSL174127. The first point represents the gravimetric NO2 and NOx fraction calculated based on the preparation of the PRM according to ISO 6142-1. The other points represent the verification results with error bars for the relative measurement uncertainty of 5% (k=2)

At CMI, NO_2 mixtures were prepared in to two different types of cylinders. One type of cylinder was polished aluminium, second one was aluminium cylinder with internal treatment ACULIFE IV. All mixtures with similar composition were prepared into the cylinders with different internal surface.

Stability study was planned for two years. Analysing of mixtures was performed after preparation as an evaluation of mixtures, after 6 months from preparation, 12 months, last measurement will be performed 24 months since preparation (Table 7).

Table 8 Evaluation of stability of binary mixture with NO_2 in aluminum cylinder and Aculife treatment

Cylinder No. 579224	Internal surface: Aculife IV	
Binary NO_2 1	Concentration µmol/mol	Uncertainty k=2
Grav	25.9	1.4
M6	24.6	1.8
M12	20.1	1.9
M24	-	-

Cylinder No.002453	Internal surface: polished aluminium	
Binary NO_2 2	Concentration µmol/mol	Uncertainty k=2
Grav	26.3	2.0
M6	7.1	2.1
M12	0.3	1.8
M24	9.0	1.9

The stability study shows a clear dependence of NO_2 on the cylinder surface treatment. In the Aculife IV cylinder (No. 579224), the concentration decreased gradually from 25.9 µmol/mol (gravimetric) to 20.1 µmol/mol after 12 months, indicating moderate but ongoing instability. In contrast, the polished aluminium cylinder (No. 002453) exhibited severe losses, with the concentration dropping from 26.3 µmol/mol to 0.3 µmol/mol within 12 months, followed by a partial rebound to 9.0 µmol/mol at 24 months, likely due to re-desorption effects.

Nitrous oxide (N_2O)

N_2O Mixtures were prepared at CMI in to two different types of cylinders. One type of cylinder was polished aluminium, second one was aluminium cylinder with internal treatment ACULIFE IV. All mixtures with similar composition were prepared into the cylinders with different internal surface. Stability study was planned for two years.

Table 9 Evaluation of stability of binary mixture with N_2O in aluminum cylinder and Aculife treatment

Cylinder No. 579222	Internal surface: Aculife IV	
Binary N2O 1	Concentration µmol/mol	Uncertainty k=2
Grav	10.7	0.01
M6	10.6	0.12
M12	10.2	0.14
M24	10.8	0.13
Cylinder No. 925266	Internal surface: polished auminium	
Binary N2O 2	Concentration µmol/mol	Uncertainty k=2
Grav	10.4	0.01
M6	10.5	0.15
M12	10.6	0.13
M24	10.4	0.14

The stability study demonstrated that N_2O is highly stable in both Aculife IV (No. 579222) and polished aluminium (No. 925266) cylinders over 24 months. Concentrations remained within 10.2–10.8 µmol/mol, with variations well covered by the expanded uncertainties. Unlike NO_2, no significant losses or wall interactions were observed, confirming that N_2O can be reliably stored in both treated and untreated aluminium cylinders at the studied level.

Ethanol (EtOH)

At NPL, the EtOH based binary mixtures were analysed using GC-FID detector (Model:6890N; supplied by Agilent, UK). Method was developed to the accurate analysis and validation of the 20 µmol/mol EtOH in CO_2 using the hierarchy of the other amount fraction mixtures and various analytical parameters. The validation results are given in the Table 9.

Table 10 Analytical amount fractions of the old 20 µmol/mol of EtOH in CO_2 PRM (D050229) with combined relative uncertainty (k=2) over a period of 20 months.

Number of months from date of preparation	1	1	1	1	1	1	6	10	20	23
Gravimetric amount fraction of EtOH (µmol/mol) ± relative uncertainty (%, *k*=2)	20.02 (±0.24)									

Analytical amount fraction of EtOH (µmol/mol)	19.88	19.80	20.05	19.64	19.84	19.76	19.94	19.69	19.67	19.55
Combined relative uncertainty (%, *k*=2)	1.76	2.32	2.33	1.69	2.26	1.88	3.12	1.99	2.69	2.96

Figure 6 shows the analytical amount fraction of 20 µmol/mol of EtOH in CO_2 (D050229) measured against the other binary PRMs up to 23 months. Over a period of 23 months, the PRM showed stable composition ruling out any signs of degradation and all analytical amount fractions agree with the gravimetric amount fraction with less than 3.0 % uncertainty. The PRM's stability was also checked against an independent traceable in-house standard that agreed well with the amount fraction of the PRM with less than 3.0 % combined relative analytical uncertainty (*k*=2). The validation results with the combined analytical uncertainties are given in the Table 9 and Figure 6 (some of the data points are removed in the figure for clarity).

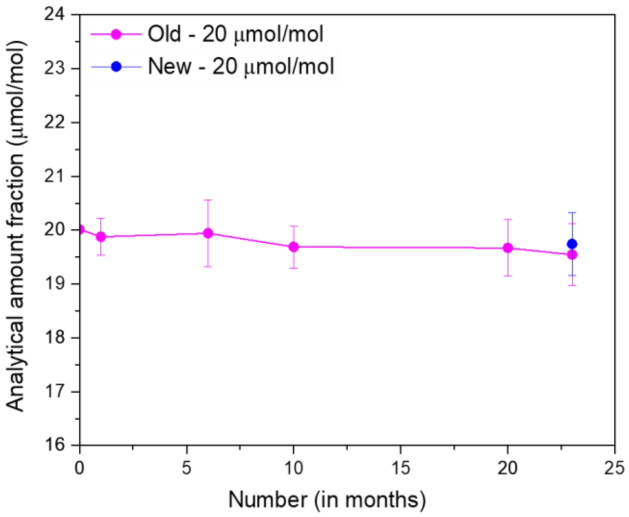


Figure 6 Stability data of the 20 µmol/mol EtOH mixture (D050229) over 23 months compared with the new 20 µmol/mol EtOH mixture (D310121).

B.1 Stability studies of multi-component PRMs

An overview of the prepared multi-component PRMs by the participants is provided in Table 2. In this section, the stability studies of these mixtures conducted by each NMI are presented.

NPL

Multicomponent PRMs containing impurities, N_2, H_2, Ar, CH_4, CO, O_2, NO and SO_2 of relevant amount fractions in CO_2 matrix were prepared and validated by comparing with in-house standard at NPL. Methods were developed in the due course to validate the amount fractions of the impurities in CO_2 matrix. The multicomponent PRMs containing the above impurities were prepared gravimetrically by either using diluting concentrated mixtures or by adding pure components to arrive at the target composition. Two sets of two matching standards were prepared and the gravimetric amount fractions with the uncertainty for all the components are shown below in Table C1 in the Annex C.

The four multicomponent PRMs prepared above were analysed using various analytical techniques such as GC-SCD, GC-NCD, GC-PDHID and GC-TCD/FID. The analytical amount fractions with the combined analytical uncertainties of the impurities on comparing with traceable in-house NPL PRMs are listed in Tabe 6. The stability of these mixtures were also checked during the 5th and the 11th month from the date of preparation and the results are also listed in Table E1 (Annex E). Analytical amount fractions for the components in the mixtures agreed well with the gravimetric amount fractions with quite low uncertainties (k=2 was <2 %) except for CO that showed (15 % – 20 %). Ar and O_2 showed up to 10 % relative analytical uncertainties due to the complexity in the analytical method that involved deconvolution of the Ar and O_2 peaks. SO_2 did show higher uncertainties during initial set of analysis, but with method development the uncertainties were brought down to about 6 %. Further experimental work is under progress to improve these methods to bring down the analytical uncertainty. The NO component in the mixtures during the month-5 and month-11 stability studies indicated that the NO has degraded during the period of study. The decay of the NO component in the multicomponent mixtures is shown in Figure 7. The mixtures containing 5 µmol/mol of initial NO concentration had about 77 % of its initial content decayed by month-5 and 92 % of its initial content decayed by month-11 respectively. However, the mixtures containing 10 µmol/mol initial NO concentration had about 52 % of its initial content decayed by month-5 and 93 % of its initial content decayed by month-11 respectively.

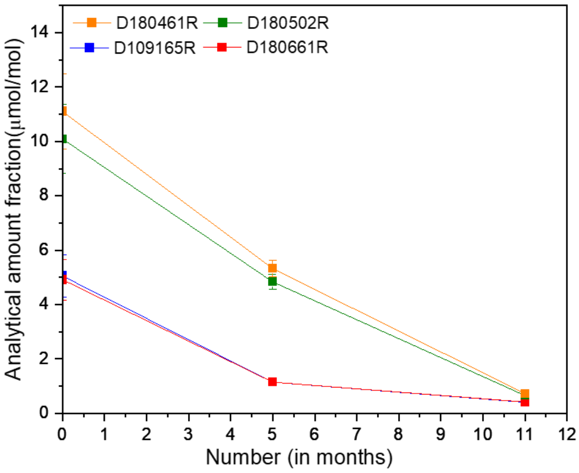


Figure 7 Analytical amount fraction of NO vs number of months since preparation of the multicomponent mixtures.

CMI

Two multicomponent mixtures containing N_2O, SO_2, NO_2, H_2, CH_4 and N_2 (Table 2) were prepared into different cylinder types to evaluate the effect of internal surface treatment on long-term stability. Cylinder No. 161481 was manufactured from polished aluminium, while Cylinder No. 964877 was an aluminium cylinder with ACULIFE IV treatment. Stability was monitored over a 24-month period with analyses performed after 6, 12 and 24 months, and compared to the gravimetric preparation values. Results are shown in Table 10 and Table 11.

In the polished aluminium cylinder (161481), the behaviour of the individual components was mixed. N_2O remained relatively stable during the first 12 months (9.5 µmol/mol at preparation vs. 9.6 µmol/mol at 6 months, and 8.6 µmol/mol at 12 months), but no result was available at 24 months. SO_2 showed moderate decreases over time, falling from 9.0 µmol/mol at preparation to 7.7 µmol/mol at 12 months and 6.6 µmol/mol at 24 months, indicating ongoing instability. NO_2, however, displayed inconsistent behaviour: a large decrease was observed at 6 months (8.8 µmol/mol vs. 23 µmol/mol gravimetric), followed by an increase at 12 months (31.5 µmol/mol), and a sharp drop again at 24 months (2.5 µmol/mol). These strong fluctuations point to instability and possible interaction with the cylinder walls. In contrast, the major components H_2, CH_4 and N_2 showed good consistency over the full measurement period, with only minor deviations from the gravimetric values within the range of uncertainty.

Table 11 Evaluation of stability of binary mixture with NO2 in aluminum cylinder

Cylinder No. 161481	**Internal surface: polished aluminium**					
Multicomponent 1	N2O	SO2	NO2	H2	CH4	N2
Grav	9.5	9.00	23	6986.4	35140.9	20611.9
Uncertainty *k* = 2	0.14	0.04	1.9	5.1	18	15
Anal 6M	9.6	9.6	8.8	7150.9	35359.2	20127.8
Uncertainty *k* = 2	0.5	1.0	2	14.4	44	19.6
Anal 12M	8.6	7.7	31.5	7078.2	35091.8	20331.1
Uncertainty *k* = 2	0.6	1.1	2.1	13.6	48	26
Anal 24M	-	6.6	2.5	6946.5	35219.4	20138.9
Uncertainty *k* = 2	-	1.0	2.1	12	25	14.6

In the ACULIFE IV treated cylinder (964877), the results were more complex. N_2O remained stable overall, fluctuating only slightly within the measurement uncertainty. SO_2 showed a dramatic decrease, from 8.7 µmol/mol at preparation to 6.8 µmol/mol at 6 months, 2.1 µmol/mol at 12 months, and 0.71 µmol/mol at 24 months, clearly indicating strong adsorption or reaction with the cylinder surface. NO_2 concentrations varied substantially: initially close to the gravimetric value (27.2 µmol/mol vs. 27.9 µmol/mol at 6 months), they rose sharply to 52.4 µmol/mol at 12 months before falling to 6.4 µmol/mol at 24 months. This non-linear behaviour again suggests instability and complex interactions with the internal surface. The matrix components H_2, CH_4 and N_2 remained largely unchanged, confirming their stability in both cylinder types.

Table 12 Evaluation of stability of binary mixture with NO2 in Aculife IV cylinder

Cylinder No. 964877	**Internal surface: Aculife IV**					
Multicomponent 2	N2O	SO2	NO2	H2	CH4	N2
Grav	9.4	8.7	27.2	7070.2	22552.8	19618.4
Uncertainty *k* = 2	0.26	0.04	2	6.3	21	21
Anal 6M	8.5	6.8	27.9	6907.9	22765.4	20171.7
Uncertainty *k* = 2	0.6	1	1.8	12.2	46	26
Anal 12M	9	2.1	52.4	6958.1	22234.5	19302.8
Uncertainty *k* = 2	0.7	0.95	1.9	11.1	36	22
Anal 24M	-	0.71	6.4	7080.1	22626.8	19556.2
Uncertainty *k* = 2	-	0.91	2.3	14.3	38	24

Overall, the study demonstrates that the stability of multicomponent mixtures strongly depends on the nature of the analyte and the cylinder material. Reactive species such as SO_2 and NO_2 were particularly unstable, with severe losses in both cylinder types, although SO_2 degradation was faster in the ACULIFE IV treated cylinder. N_2O remained relatively stable in both materials, and the major components H_2, CH_4 and N_2 showed no significant changes. These results underline that while ACULIFE IV treatment can reduce reactivity for some species, it does not guarantee stability for highly reactive impurities such as SO_2 and NO_2. Further optimisation of cylinder treatment or storage conditions may be required to improve the long-term suitability of these multicomponent reference mixtures.

IPQ

The multicomponent mixtures prepared by IPQ were certified using the SO_2, H_2S, CO, CH_4 and O_2 analysers as described (12). four multicomponent mixtures were prepared in a CO2 matrix, PRM608395 and PRM308978 with the impurities SO^2, CO and O^2; and two, PRM202557 and PRM302530, with the impurities H_2S, CO, O_2, and CH_4. These mixtures were contained within four cylinders at an approximate pressure of 40 bar each. The results are shown in Table 12 and Table 13. IPQ has demonstrated its ability to prepare and certify reference materials (CRM) for measuring impurities of H_2S, SO_2, CO, O_2 and CH_4 in CO_2, within the requested concentration with metrological traceability. The uncertainties obtained were as expected. The stability study has confirmed that, except for CO, all components remain stable for about one year within the associated uncertainties. To further refine our understanding, a longer study will be conducted to determine the stability period of each type of mixture.

Table 13 Results of the stability study for the prepared multicomponent mixture of SO2+CO+O2 / CO2

PRM608395	**SO_2+CO+O_2 / CO_2**		
	SO_2		
Date	***x*** **µmol/mol**	***U*** **µmol/mol**	***E*****n**
2024-04-18	14,24	0,77	-
2024-11-18	14,1	1,3	-0,09
	CO		
Date	***x*** **µmol/mol**	***U*** **µmol/mol**	***E*****n**
2024-04-17	660,7	1,6	-
2024-11-22	653,5	1,6	-3,2
	O_2		
Date	***x*** **cmol/mol**	***U*** **cmol/mol**	***E*****n**
2024-04-16	0,568	0,048	-
2025-01-23	0,572	0,017	0,08

Table 14 Results of the stability study for the prepared multicomponent mixture of H2S +CO+O2+CH4 / CO2

PRM202557	**H_2S+CO+O_2+CH_4 / CO_2**		
	H_2S		
Date	***x*** **µmol/mol**	***U*** **µmol/mol**	***E*****n**
2023-09-20	9,83	0,48	-
2024-04-23	9,73	0,33	-0,17
2024-11-08	9,61	0,28	-0,40
	CO		
Date	***x*** **µmol/mol**	***U*** **µmol/mol**	***E*****n**
2023-09-15	669,5	2,7	-
2024-04-17	662,3	1,6	-2,3
2024-11-22	654,4	1,6	-4,8
	O_2		
Date	***x*** **cmol/mol**	***U*** **cmol/mol**	***E*****n**
2023-09-15	0,586	0,027	-
2024-04-16	0,582	0,048	-0,07
2025-01-23	0,586	0,017	0,00
	CH_4		
Date	***x*** **cmol/mol**	***U*** **cmol/mol**	***E*****n**
2023-09-14	1,9685	0,0060	-
2024-04-17	1,9686	0,0061	0,01
2024-11-28	1,9706	0,0062	0,24

B.2 Validation results of dynamic gas mixture system by VSL and NPL

VSL

VSL developed primary gas reference standards (PRMs) permanent gases (e.g. Ar, N_2, O_2, CH_4, H_2 and CO) in CO_2. The PRMs were prepared with two methods 1) static gas mixture preparation, according to ISO 6142-1, in high pressure cylinders with an internal passivation treatment and 2) dynamic gas mixture preparation, according to ISO 6145-7, using thermal mass flow controllers (MFC).

A gas mixture with permanent gases (N_2, O_2, CH_4, H_2 and CO) in CO_2 was ordered at Air Liquide the composition of the gas mixture was determined by verification of the of the mixture with and without dilution using the dynamic dilution system Table 14. The method of the dynamic dilution system is described in Annex D2.

Table 15 Composition of the GCM with and without dilution.

Dilution	**N_2 (%)**	**O_2 (µmol mol^{-1})**	**CH_4 (%)**	**H_2 (%)**	**CO (µmol mol^{-1})**	**CO_2 (%)**
Undiluted	2.510 ± 0.025	499 ± 5	2.510 ± 0.025	0.1250 ± 0.0013	503 ± 5	94.8 ± 0.9
1	1.022 ± 0.010	203.4 ± 2.1	1.022 ± 0.010	0.0509 ± 0.0005	204.9 ± 2.1	97.9 ± 1.0
2	0.516 ± 0.005	102.7 ± 1.0	0.516 ± 0.005	0.02568 ± 0.00026	103.3 ± 1.1	98.9 ± 1.0

For verification of the CGM a regression function was calculated, according to ISO 6143, using the PRMs. The response for the CGM were interpolated to determine the amount fraction (Figure 8). The fractions obtained with dilution 2 were outside the PRM calibration range save for CH_4. The results for dilution 1 and dilution 2 were multiplied with the dilution factor to obtain the CGM fraction.

The results obtained without and with dilution are comparable within the uncertainty calculated. There are two uncertainty sources 1) the verification uncertainty calculated according to ISO 6143 and 2) the dilution uncertainty for the dilutions (1%). The results are averaged and the certified values for the CGM are given in Table 15

Table 16 Verification results CGM

Component	**x_{ver}**	**U_{ver} (%, k = 2)**
N_2 (%)	2.47	0.04
O_2 (µmol mol^{-1})	482	20
CH_4 (%)	2.47	0.04
H_2 (%)	0.1259	0.0015
CO (µmol mol^{-1})	503	4
CO_2 (%)	94.76	0.20

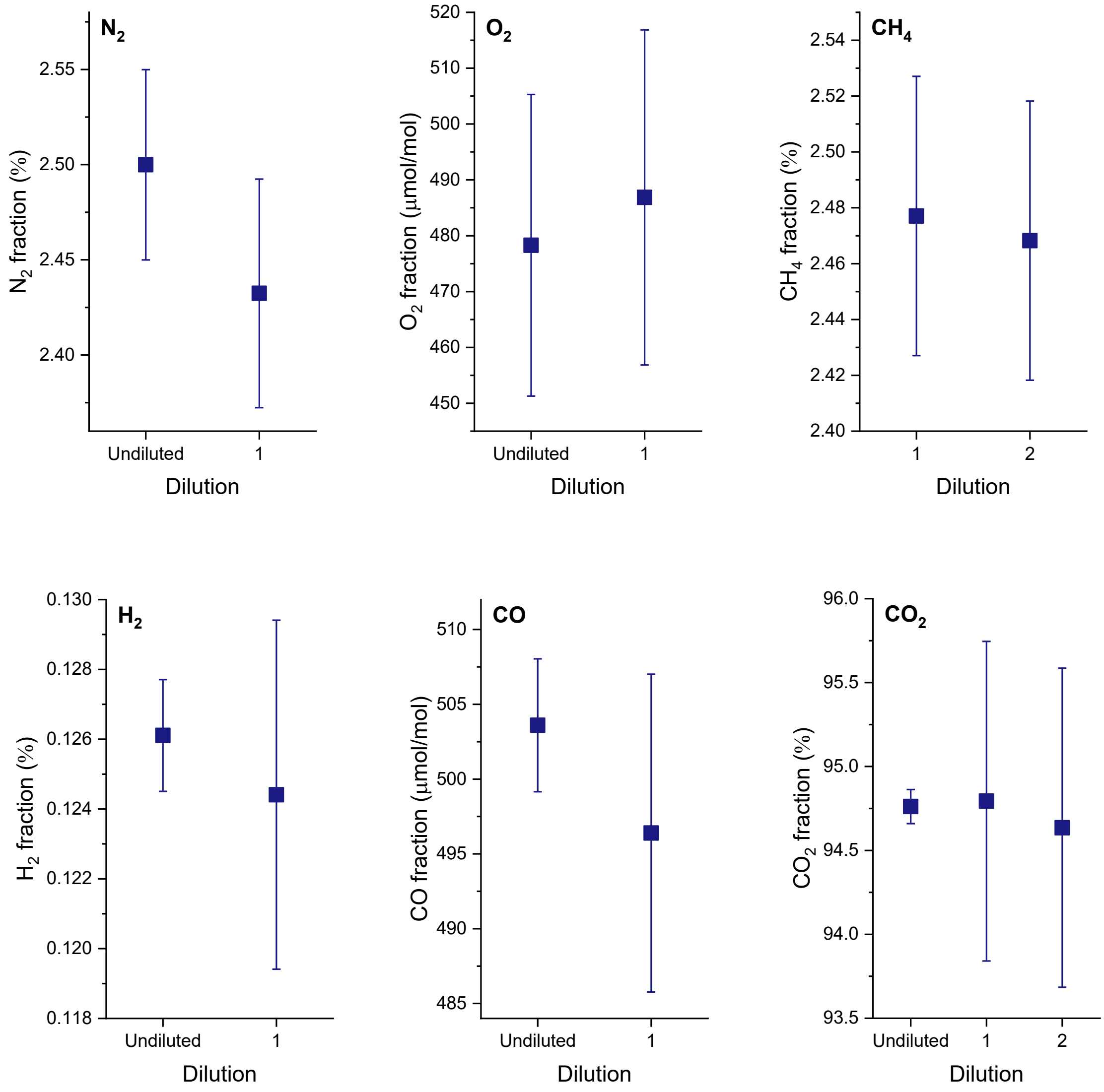


Figure 8 Interpolation results (xver) and deviation of the CGM.

NPL

NPL developed a dynamic gas PRMs starting from higher amount fraction static PRMs containing CO, CH_4, N_2 and Ar in CO_2. The gravimetric amount fractions and the analytical amount fractions with their relative uncertainty (k=2) of these precursor mixtures are given in Table D2 (Annex D). Each of these mixtures were used to prepare different dynamic gas mixtures using thermal mass-flow controllers based on ISO 6145-7. The new dynamic gas mixtures were compared against the static inhouse standards.

The static mixtures of CH_4, N_2 and Ar impurities in CO_2 were dynamically diluted to give mixtures of the target amount fractions given in Table 16. Additionally, the standards were diluted down to lower than the values reported in the Table 16. For example, N_2 was diluted down to 5 different amount fractions beginning from 4% to 0.4% and validated the dynamically generated 2% N_2 with the independent static 2% N_2 PRM. Similarly, CH_4 and Ar were diluted down to lower amount fraction values compared to the values listed in table 8 and validated against the static independent standard. On validation of the dynamically diluted standards with independent static NPL PRMs, the analytical amount fractions with the relative uncertainty (k=2) are also given in Table 16. All dynamically produced standards validated against NPL standards with less than 4.5 % bias.

Dynamic mixtures starting from CO in CO_2 static mixtures were not prepared and validated against NPL standards at this instance.

Table 17 The gravimetric amount fractions and the analytical amount fractions with their relative uncertainty (k=2) of the diluted mixtures containing Ar, CH4 and N2 in CO2.

Impurity	**Ar**		**CH_4**	**N_2**
Cylinder No	**Mix-1**	**Mix-2**	**Mix-1**	**Mix-1**
Dynamically generated amount fraction (%)	8946.80	6529.16	19990.61	19834.46
u/c (%), *k*=2 (for dilution)	3.56	3.69	5.62	5.62
Analytical amount fraction	9183.73	6819.36	20201.80	20226.28
Analytical uncertainty (*k*=2)	3.60	3.95	5.70	5.71
Bias (%)	2.65	-4.26	1.06	1.98

Validation of trace gas generator (VTT)

Validation measurements of VTT trace gas generator were performed in another ongoing EURAMET funded project 21NRM04 BiometCAP "Protocol for SI-traceable validation of methods for biomethane conformity assessment" (13), where trace amounts of ammonia NH_3 was generated into biogas. Due to its operating principle based on injecting and vaporizing a water solution containing the impurity into a carrier gas stream, the generation method is insensitive to the carrier gas as long as no chemical reaction occurs, which is the case for a mixture of $CO_2(g)$, $NH_3(g)$ and $H_2O(g)$. This has been demonstrated for multiple gases (e.g. air, nitrogen, hydrogen and methane) in past and ongoing projects (11-14). To ensure reliable performance, it is important that the mass flow controller (MFC) is calibrated with the same gas used as used as carrier gas, because MFCs are known to be sensitive to gas type. The VTT trace gas generator gas flow is always calibrated prior to operation using a calibrated piston-cylinder flow meter (e.g. MesaLabs Bios Drycal), which is considered gas independent due to its volumetric operating principle.

To validate the performance of the VTT trace gas generator, a comparison against a static gas reference produced by NPL was performed using DTU far-UV analyser as a comparator. The NPL static gas reference was connected through a (uncoated) pressure regulator and Ø3 mm SilcoNert2000 coated SS tubing to the far-UV analyzer. The NPL reference gas was prepared gravimetrically to realize an ammonia concentration of (19.6 ± 1.1) ppm in methane. The concentration was verified by means of gas chromatography.

Measurements with the DTU far-UV analyser from the output of the NPL reference gas cylinder show a concentration around 20 $\mu mol\ mol^{-1}$, which corresponds well to the certified concentration of NPL reference gas (Figure 9). Vertical error bars show uncertainty of the NPL reference gas. A possible NH_3 desorption from the cylinder walls (vertical arrow) has been observed.

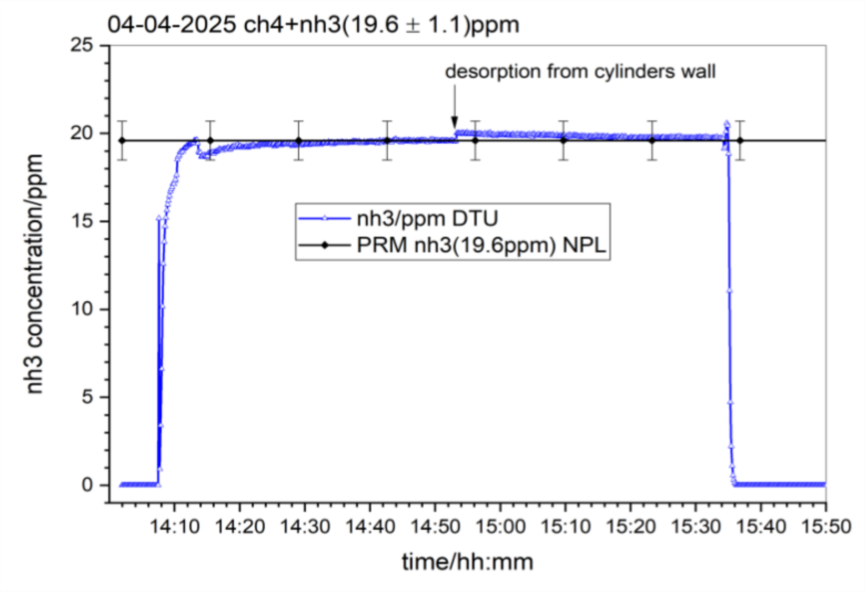


Figure 9 Ammonia concentrations measured with DTU far-UV analyser from NPL reference gas containing 19.6 µmol mol-1 (ppm) of ammonia in methane at about 1 bar pressure and 24°C in the analyser.

Figure 10 shows repeated after around 1½ months measurements from around 1 bar to around 18 bar pressure in the analyser. The measurements started and ended with N_2 reference gas in the analyser. No NH_3 losses in the NPL reference gas at 1 bar have been observed over a given time span. The NH_3 amount fraction in the gas phase, however, decreases by a few µmol mol^{-1} at pressures above 1 bar. This is caused by a forced surface NH_3 adsorption on the inner walls at elevated pressures.

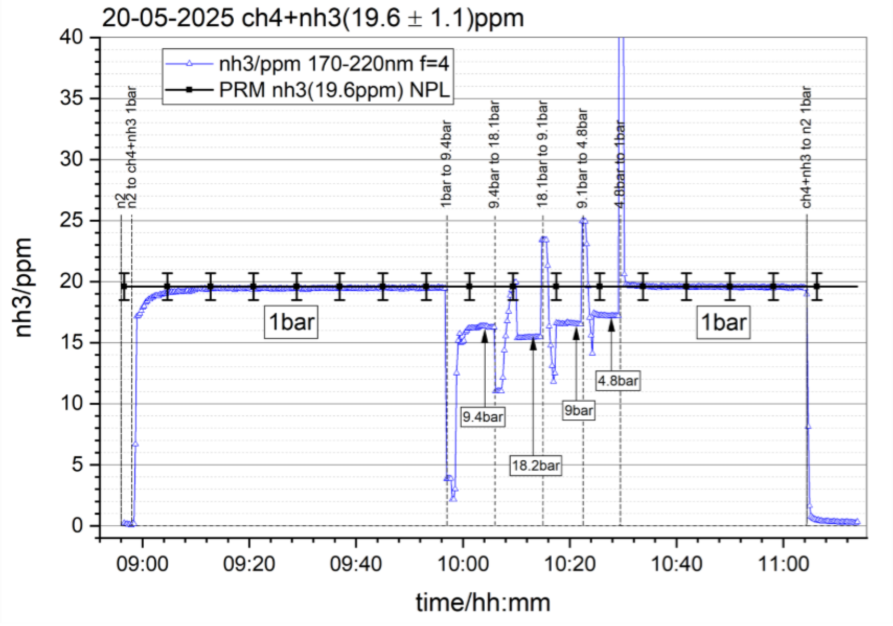


Figure 10 Ammonia concentrations measured with DTU far-UV analyser from NPL reference gas containing 19.6 µmol mol-1 (ppm) of ammonia in methane. The measurements were done around 1½ months after the measurements in Figure 3. Some measurements (marked by vertical

Measurements were repeated using the VTT trace gas generator as a source of ammonia to realize an output NH_3 concentration of 19.6 µmol mol^{-1}. The generator produces an H_2O+NH_3 gaseous mixture through a H_2O+NH_4OH solution evaporation. A commercial 5.0 M NH_4OH solution from Honeywell, traceable to NIST SRM was used. In house available milli-Q water was used to prepare a final H_2O+NH_4OH solution. The generator was connected through an unheated Ø6 mm PTFE tubing to the far-UV analyser. The results of the NH_3 measurements are shown in Figure 11.

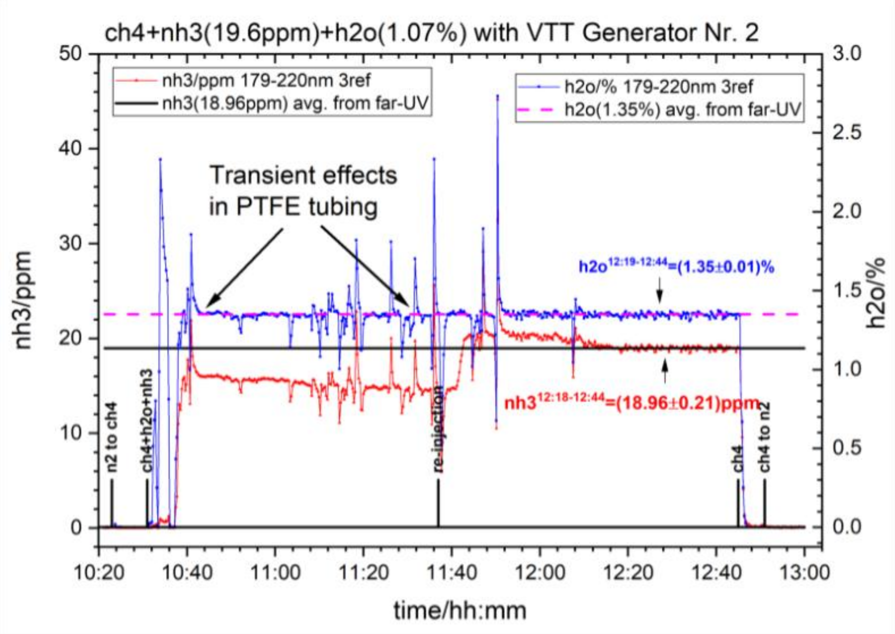


Figure 11 Ammonia (left) and water (right) concentrations measured with DTU far-UV analyser from the VTT trace gas generator Nr. 2 output with a nominal concentration of 19.6 ppm ammonia in methane-water-ammonia mixture at about 1 bar pressure and temperature of about 24°C.

As one can see from the Figure 11, a stable NH_3 and H_2O concentration is achieved after the second H_2O+NH_4OH solution injection in the syringe pump at about 11:38. The NH_3 steady-state concentration achieved was about 19 µmol mol^{-1} which is a bit lower than the nominal set point: 19.6 µmol mol^{-1}. This agreement (within 3%) between NH_3 measured and NH_3 set point can be considered as a very good one, considering the uncertainties of the methods as well as the complexity of the measurements at the low NH_3 concentrations.

Other observation from the Figure 11 is that it takes around 1 hr and an additional solution injection to get a steady-state NH_3 concentration time-profile. This is because of transient effects in Ø6 mm PTEF tubing. Measurements under MetCCUS project when the original generator was connected via various stainless-steel coated and PTFE tubing to other DTU's UV-analyser have shown that the noisiness in NH_3/H_2O time-concentration profiles is mainly caused by tubing diameter and not the tubing material.

The spikes in NH_3/H_2O concentrations in the Figure 11 between 10:40 and 12:10 correspond to sudden NH_3/H_2O concentration variations in the gas phase and are not related either to an analyser noise or any other analyser operation artefacts. The (time-correlated) H_2O/NH_3 spikes reflect a non-homogeneous mist/aerosol generation in the generator from the operation start up at low solution dosing flow rate (0.04 ml min^{-1}) and seems to be smoothed out with time.

The generated NH_3 amount fractions were determined using the following measurement model and the operation parameters (Table F1).

$$x_{NH_3}[mol/mol] = \frac{n_{NH_3}[mol/min]}{n_{gas}[mol/min] + n_{H_2O}[mol/min]} = \frac{c_{NH_3}[mol/l] \bullet \frac{q_{m,H2O}[g/min]}{\rho_{H2O}[g/l]}}{\frac{q_{v,gas}[l/min]}{V_m[l/mol]} + \frac{q_{m,H2O}[g/min]}{M_{H2O}[g/mol]}} + \delta_{ev} + \delta_{rep}$$

The uncertainty of amount fraction of generated ammonia (NH_3) is given in Table 17 for the nominal amount fraction of 10 µmol·mol^{-1}. From the table it can be seen that the largest source of uncertainty is the concentration of the solution, which is mainly caused by the uncertainty of the micropipette used for preparing the solution. The uncertainty of pipetting is estimated as the maximum permissible error (mpe) as stated in the ISO8655 standard. Combining all uncertainty components results in a relative expanded uncertainty (k = 2) of 1.9 %. In the typical operational range of the generator, the relative values of the uncertainty components are considered constant, therefore the expanded uncertainty of 1.9 % can be applied in the whole operational concentration range.

Table 18 Uncertainty budget for generated trace concentration of ammonia (NH3).

symbol	quantity	unit	value	uncertainty	sensitivity coefficient	uncertainty / mol · mol^{-1}	type	probability distribution	divisor	contribution to standard uncertainty	
c_{NH3}	Concentration of NH_3 solution	mol · l^{-1}	3.48E-02	2.31E-04	2.87E-04	6.64E-08	B	normal	1	6.64E-08	
$q_{m,H2O}$	Liquid mass flow of syringe	g · min^{-1}	8.41E-02	5.05E-04	4.05E-07	2.04E-10	B	normal	2	1.02E-10	
$q_{v,gas}$	Volume flow at standard temperature (23 °C)	l · min^{-1}	7.01E+00	7.01E-02	-1.40E-06	-9.85E-08	B	normal	2	-4.92E-08	
δn_{ev}	Evaporation losses	mol · mol^{-1}	0	6.00E-08	1	6.00E-08	B	rectangular	1.73	3.47E-08	
δn_{rep}	Repeatability	mol · mol^{-1}	0	6.00E-08	1	6.00E-08	B	rectangular	1.73	3.47E-08	
	Molar fraction of NH_3 (x_{mol_NH3})		1.00E-05	mol · mol^{-1}					combined standard uncertainty	9.61E-08	
			10.0	**ppm**					**expanded uncertainty (*k*=2)**	1.92E-07	
										0.2	**µmol/mol**
										1.9	**%**

The complete evaporation of the gas-liquid mixture is critical to ensure reliable performance of the trace gas generator. The evaporation has to be complete and adsorption of the mixture to the generator surfaces need to be minimized. Evaporative losses were thoroughly investigated in previous research by Sari S. et al. (14) for oxidized mercury. This value can be used as a worst-case estimate of generation losses for ammonia (NH_3), because the relative influence of evaporative losses is minimal.

Annex C – Stability results of multi-component PRM (NPL)

Table E 1- Analytical amount fractions with combined relative uncertainty (k=2) of impurities in the multicomponent PRMs at month-0, month-5 and month-11.

D109165R									
Component	**CO_2**	**N_2**	**CH_4**	**Ar**	**H_2**	**CO**	**O_2**	**SO_2**	**NO**
Gravimetric amount fraction (µmol/mol)	959704.21	20270.83	9938.82	7538.60	2337.32	99.85	95.30	10.07	4.96
Gravimetric Uncertainty (%, k=2)	0.01	0.28	0.12	0.73	0.70	0.11	0.16	0.32	0.35
Month-0									
Analytical amount fraction (µmol/mol)	959545.90	20284.29	9930.75	7469.05	2332.97	98.23	94.42	10.11	5.03
Analytical Uncertainty (%, k=2)	0.32	0.63	0.80	6.55	0.72	7.79	2.64	6.04	5.70
Month-5									
Analytical amount fraction (µmol/mol)	960016.70	20279.84	9947.97	7290.62	2333.19	97.33	95.09	10.01	1.14
Analytical Uncertainty (%, k=2)	0.62	0.82	1.00	6.56	1.03	17.62	8.65	17.94	10.27
Month-11									
Analytical amount fraction (µmol/mol)	960508.47	20279.67	9946.18	7508.58	2332.56	97.06	94.00	10.11	0.36
Analytical Uncertainty (%, k=2)	0.47	0.77	0.70	6.92	1.10	8.90	5.15	6.04	0.04
D180661R									
Component	**CO_2**	**N_2**	**CH_4**	**Ar**	**H_2**	**CO**	**O_2**	**SO_2**	**NO**
Gravimetric amount fraction (µmol/mol)	959529.83	20336.58	9883.76	7577.00	2463.31	99.23	95.13	10.11	5.01
Gravimetric Uncertainty (%, k=2)	0.01	0.28	0.12	0.73	0.67	0.11	0.16	0.32	0.35
Month-0									
Analytical amount fraction (µmol/mol)	959688.16	20327.19	9889.80	7647.56	2468.09	100.27	96.01	10.07	4.93

Analytical Uncertainty (%, k=2)	0.32	0.63	0.63	6.85	0.73	9.81	2.64	6.04	5.70
Month-5									
Analytical amount fraction (µmol/mol)	959217.50	20327.55	9874.66	7628.52	2467.67	101.80	95.33	10.18	1.14
Analytical Uncertainty (%, k=2)	0.62	0.82	1.00	6.56	1.03	17.62	8.65	17.94	10.27
Month-11									
Analytical amount fraction (µmol/mol)	958726.39	20327.72	9876.44	7607.30	2468.34	102.10	96.44	10.07	0.37
Analytical Uncertainty (%, k=2)	0.47	0.77	0.70	6.92	1.10	8.90	5.16	6.04	0.05
D180502R									
Component	**CO_2**	**N_2**	**CH_4**	**Ar**	**H_2**	**CO**	**O_2**	**SO_2**	**NO**
Gravimetric amount fraction (µmol/mol)	962068.53	10219.11	14936.74	10165.86	2495.64	51.25	47.67	5.01	10.13
Gravimetric Uncertainty (%, k=2)	0.01	0.73	0.08	0.52	0.63	0.15	0.18	0.36	0.30
Month-0									
Analytical amount fraction (µmol/mol)	959919.00	10233.58	14957.73	10257.13	2476.31	49.51	45.59	4.99	10.09
Analytical Uncertainty (%, k=2)	0.63	1.20	0.54	7.86	0.91	8.51	9.31	6.46	12.55
Month-5									
Analytical amount fraction (µmol/mol)	961701.74	10222.65	14928.55	10180.63	2476.59	50.49	48.14	5.00	4.83
Analytical Uncertainty (%, k=2)	0.67	1.28	0.73	9.96	0.93	20.97	6.88	10.49	5.67
Month-11									
Analytical amount fraction (µmol/mol)	962744.16	10913.85	14939.76	9696.22	2477.66	50.79	48.10	5.33	0.60
Analytical Uncertainty (%, k=2)	0.53	1.19	0.64	7.66	0.93	16.63	10.09	6.66	0.06
D180461R									
Component	**CO_2**	**N_2**	**CH_4**	**Ar**	**H_2**	**CO**	**O_2**	**SO_2**	**NO**

Gravimetric amount fraction (µmol/mol)	961865.96	10559.98	14871.49	10103.34	2483.45	51.39	48.40	4.88	11.06
Gravimetric Uncertainty (%, k=2)	0.01	0.72	0.82	0.53	0.64	0.15	0.18	0.36	0.30
Month-0									
Analytical amount fraction (µmol/mol)	964019.80	10546.81	14851.66	10013.45	2502.88	53.52	50.61	4.90	11.10
Analytical Uncertainty (%, k=2)	0.63	1.16	0.44	7.86	0.91	5.98	9.31	6.46	12.55
Month-5									
Analytical amount fraction (µmol/mol)	962232.80	10556.33	14879.64	9890.40	2502.56	52.16	47.93	4.89	5.32
Analytical Uncertainty (%, k=2)	0.67	1.28	0.73	9.96	0.93	20.97	6.88	10.49	5.72
Month-11									
Analytical amount fraction (µmol/mol)	961190.94	9887.77	14868.47	13394.38	2501.47	51.86	47.97	4.59	0.68
Analytical Uncertainty (%, k=2)	0.53	1.19	0.64	8.37	0.93	16.63	10.09	6.66	0.03