Stability Study of Multicomponent Mixtures to Support Carbon Metrology

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Abstract. The European project EPM SRT-v01 - MetCCUS (Metrology for Carbon Capture Utilization and Storage) is the first metrology project within the scope of CCUS (Carbon Capture Utilization and Storage), which, in the European ecological pact, European Commission's Green Deal, is listed as one of the priority areas to achieve a reduction in greenhouse gas emissions by 55 % by 2030 and carbon neutrality by 2050. This project, financed by EURAMET, aims to respond to the metrological challenges identified by the industry and aims to provide the primary standards, methods, good practice guides that will support the necessary measurements. This study successfully characterized four bicomponent mixtures: SO_2 in CO_2 matrix (two mixtures) and H_2S in CO_2 matrix (two mixtures) and four multicomponent mixtures SO_2+CO+O_2 in CO_2 (two mixtures) and H_2S+CO+CH_4+O_2 in CO_2 matrix (two mixtures) within a cylinder under a pressure of approximately 40 bar, and it entailed a stability study. The stability study was conducted over one year, employing statistical evaluation using the Normalized Error (E_n) function in accordance with the international standard ISO 13528:2022 for statistical methods.

1 Introduction

The European initiative EPM (European Partnership on Metrology) SRT-v01 - MetCCUS (Metrology for Carbon Capture Utilization and Storage) [1] represents the first metrology project dedicated to CCUS (Carbon Capture Utilization and Storage) in Europe. This initiative is a key element of the European Commission's Green Deal, an ambitious plan outlined in the European ecological pact. CCUS is identified as one of the priority areas for achieving the overarching goals of a 55 % reduction in greenhouse gas emissions by 2030 and achieving carbon neutrality by 2050. The project, funded by EURAMET, addresses significant metrological challenges faced by industry stakeholders. It aims to develop primary standards, methodologies and best practice guidelines to ensure precise and reliable measurements essential to support CCUS projects.

A critical aspect of this initiative lies in the preparation and use of primary gas mixtures, which plays a key role in environmental monitoring and decarbonization research. Reliable gas mixtures are essential for calibrating instruments that measure atmospheric pollutants and greenhouse gases, ensuring accuracy and consistency in data collection. Decarbonization itself refers to the process of significantly reducing carbon dioxide (CO_2) emissions resulting from human activities, with the goal of transitioning to a low-carbon or carbon-neutral economy. This transformation is a key strategy for mitigating climate change by directly reducing greenhouse gas concentrations in the atmosphere.

As part of the MetCCUS project, the Reference Gas Laboratory (LGR) at the Portuguese Institute for Quality (IPQ) is collaborating in the development of gas metrological capabilities. Specifically, the laboratory is preparing Certified Reference Materials (CRMs) to enable precise measurement of impurities in CO_2 with full metrological traceability [1, 2]. These materials are vital for validating analytical methods and calibrating the instruments used in carbon capture and storage processes.

To date, the LGR has prepared eight gas mixtures. These include four bicomponent mixtures (two consisting of SO_2 in a CO_2 matrix and two of H_2S in a CO_2 matrix) and four multicomponent mixtures (two containing SO_2, CO, and O_2 in a CO_2 matrix, and two with H_2S, CO, CH_4, and O_2 in a CO_2 matrix). These mixtures were successfully characterized to measure four pollutant gases and oxygen in a CO_2 matrix under high pressure, approximately 40 bar. The certification of these mixtures required an extensive stability study.

The stability of these mixtures was evaluated over one year using statistical methods. The Normalized Error (E_n) function, as specified by the ISO 13528 standard for statistical analysis, was employed to ensure accuracy and reliability in the results [3]. This rigorous approach underscores the project's commitment to providing industry and research sectors with robust and reliable metrological solutions.

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2 Production of reference gas mixtures

The production of reference gas mixtures is done according to ISO 17034 [4] that specifies the requirements for the production of Certified Reference Materials (CRMs), ensuring high-quality and reliable standard gas mixtures. The process involves detailed documentation, and rigorous quality control to ensures high accuracy and traceability to the International System of Units (SI) [5, 6]. Producers must validate methods, assess uncertainties, and conduct stability studies to guarantee accuracy over time. Compliance with ISO 17034 ensures CRMs meet international standards for calibration, testing, and analytical measurements.

2.1 Preparation of gas mixtures

The preparation of gas mixtures following the ISO 6142-1 standard involves gravimetric methods, which are based on the precise weighing of components [7]. The process starts with the selection of a suitable gas cylinder, which must be thoroughly cleaned and evacuated to prevent contamination. The cylinder is then filled with the desired gas components, introduced sequentially, starting with the minor components (trace gases) and finishing with the balance gas, often nitrogen (N_2) or carbon dioxide (CO_2).

The mixture is prepared by gravimetric addition of each component. The mole fractions of the components in the final mixtures are calculated using the following equation [7]:

$$x_i = \frac{\sum_{A=1}^{P}\left(\frac{x_{i,A}\cdot m_A}{\sum_{i=1}^{n} x_{i,A}\cdot M_i}\right)}{\sum_{A=1}^{P}\left(\frac{m_A}{\sum_{i=1}^{n} x_{i,A}\cdot M_i}\right)} \quad (1)$$

Where: x_i is the mole fraction of the component i in the final mixture, i = 1,…., n; P is the total number of the parent gases; n is the total number of the components in the final mixture; m_A is the mass of parent gas A determined by weighing, A= 1,……, P; M_i is the molar mass of the component i; $x_{i,A}$ is the mole fraction of the component i.

Each gas is added using a high-precision mass comparator balance capable of measuring mass with a very low uncertainty. The mass of each component is calculated, considering the buoyancy effect of the surrounding air on the balance. Once all components are added, the total composition of the mixture is determined from the masses of the individual components and their respective molar masses.

After preparation, the mixture undergoes a homogenization process, which typically involves rotating the cylinder to ensure uniform distribution of gases within the cylinder. Finally, the prepared gas mixture is calibrated with others gas standards, by a suitable analytical method, to confirm its composition and validate the gravimetric calculations.

The traceable gas mixtures are widely used in calibration, environmental monitoring, and industrial applications.

Fig. 1. Filling Station and the mass comparator balance.

2.2 Certification of gas mixtures

The ISO 6143 standard provides a systematic framework for the calibration of gas mixtures using a multi-point method [8]. This approach involves comparing the response of an analytical instrument to a set of calibration gas mixtures with known compositions, referred to as reference standards. The goal is to establish a reliable relationship between the instrument's response and the concentrations of the target components in the mixture being analysed.

Fig. 2. Certification of Gas Mixtures Facility.

The process begins by selecting reference gas mixtures that cover the range of concentrations expected in the sample. These reference standards must be traceable to SI and prepared with high accuracy, often using gravimetric methods according to ISO 6142-1 [7]. The instrument response to each reference mixture is recorded, typically using signals such as peak areas or voltages, depending on the type of analyser is used.

A mathematical model, such as a linear or polynomial regression, is then applied to describe the relationship between the instrument response and the concentration of the analyte. ISO 6143 [8] emphasizes the evaluation of uncertainties for both the reference mixtures and the instrument response, ensuring the calibration curve is accurate and reliable.

Finally, the established calibration curve is used to determine the composition of unknown gas mixtures by measuring their instrument response and interpolating within the range of the calibration standards. This process is essential for applications requiring high precision, such as environmental monitoring and industrial quality control.

3 Stability Study

The stability study of the eight bi-component and multi-component mixtures prepared was conducted over approximately one year. The analysed parameters included H_2S, CO, O_2, CH_4, and SO_2 in a CO_2 matrix. This research aimed to assess the chemical interactions and long-term stability of these gas combinations. Understanding their behaviour is crucial for industrial applications, storage, and transportation safety.

This study was conducted using Primary Reference Material (PRM) of several multicomponent mixtures (Table 1, Table 2, Table 3, Table 4, Table 5). All these reference gas mixtures were prepared in carbon dioxide matrix. The calibration curves were done using primary standards in nitrogen matrix. With these primary standards we can have traceability to the standards of these impurities in CO_2. In this case, the matrix will not influence the analysis because the analysers in question do not detect CO_2 just as they do not detect nitrogen. Each of them detects only the respective gas.

The purpose is to determine the shelf life of this type of mixtures, that is, the actual period during which a mixture can be considered stable concerning its original metrological specifications.

The study was conducted according to ISO 13528 standard [3], which provides various statistical evaluation methods that can be used in specific tests or measurements and for monitoring the ongoing performance of laboratories. In this context, it will be used to compare two concentrations: the concentration resulting from the initial certification and the concentration obtained in subsequent certifications according to the international standard ISO 6143 [8], over the lifetime of the standard.

In this study, we used the normalized error (*En*) statistical tool that is typically applied in comparison of measurement systems, calculated according to the following equation:

$$\boldsymbol{E_n} = \frac{x_{\text{cer1}} - x_{\text{cern}}}{\sqrt{{U_{\text{cer1}}}^2 + {U_{cern}}^2}} \quad (2)$$

Where x_{Cer1} is the concentration value from the first certification and x_{Cern} is the concentration value resulting from the n^{th} certification. U_{Cer1} represents the uncertainty associated with x_{Cer1} while U_{Cern} is the expanded uncertainty associated with x_{Cern}. With this statistical tool, the results are considered satisfactory if $|E_n| \leq 1$ and unsatisfactory if $|E_n| > 1$.

4 Results

Four gas mixtures, Primary Reference Material (PRM), were carefully prepared for analysis, including two binary combinations of H_2S in a carbon dioxide matrix, designated as PRM108595, PRM108596 and two mixtures of SO_2 in CO_2, labelled as PRM408326 and PRM108593, were also carefully assembled. This study facilitated the comprehensive characterization of these four mixtures, each contained within individual cylinders maintained at an approximate pressure of 40 bar.

Furthermore, four multicomponent mixtures were prepared in a CO_2 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. No stability study was conducted on the PRM308978 because this cylinder was sent for analysis to one of the participants of the MetCCUS project.

Table 1. 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

Table 2. Results of the stability study for the prepared binary mixtures of SO_2/CO_2

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

Table 3. Results of the stability study for the prepared multicomponent mixture of SO_2+CO+O_2 / CO_2

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 4. Results of the stability study for the prepared multicomponent mixture of H_2S +CO+O_2+CH_4 / CO_2

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

Table 5. Results of the stability study for the prepared multicomponent mixture of H_2S +CO+O_2+CH_4 / CO_2

PRM302530	**H_2S+CO+O_2+CH_4 / CO_2**		
	H_2S		
Date	x µmol/mol	U µmol/mol	E_n
2023-12-04	9,92	0,40	-
2024-04-23	9,60	0,36	-0,59
2024-11-08	9,16	0,33	-1,5
	CO		
Date	x µmol/mol	U µmol/mol	E_n
2023-12-14	677,0	1,8	-
2024-04-17	674,3	1,5	-1,1
2024-11-22	666,5	1,6	-4,3
	O_2		
Date	x cmol/mol	U cmol/mol	E_n
2023-12-18	0,602	0,051	-
2024-04-16	0,591	0,058	-0,14
2025-01-23	0,585	0,017	-0,32
	CH_4		
Date	x cmol/mol	U cmol/mol	E_n
2023-12-05	1,915	0,015	-
2024-04-17	1,9270	0,0059	0,74
2024-11-28	1,9284	0,0060	0,83

5 Summary

In conclusion, 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.

Looking ahead, this research may be extended to mixtures containing additional components. Additionally, to enhance the scope of the project, these mixtures will be analysed using alternative analytical methods to gather more data for further characterization of the mixtures.

References

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