IMEKO TC8, TC11 and TC24 Joint Conference
October 11-13, 2023, Madeira, Portugal

PREPARATION OF MULTICOMPONENT MIXTURES TO SUPPORT CARBON METROLOGY

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Abstract:
The Reference Gas Laboratory (LGR) of IPQ is participating in the project MetCCUS - Metrology for Carbon Capture Utilization and Storage under the new EPM (European Partnership on Metrology) Program.

The goal of this project is to develop a metrological infrastructure that enables monitoring and detection of carbon dioxide leaks in energy and industrial processes, in transport networks and also allow the support of a better understanding of the life cycle of carbon dioxide.

The contribution of LGR involves the preparation of certified reference materials (CRM) to allow the metrological traceability, providing support for the calibration and validation of instrumentation used in carbon capture processes.

Keywords: carbon metrology, multicomponent mixtures, gravimetric method, certification

1 INTRODUCTION

In recent years, the growing concern surrounding climate change has driven a substantial increase in environmental monitoring efforts. As a result, the demand for measurements with traceability has surged, aiming to ensure the reliability of data and minimize measurement uncertainties.

The Reference Gas Laboratory (LGR) at IPQ plays a pivotal role in this domain, responsible for producing, maintaining, and advancing national primary standard gaseous mixtures in strict accordance with ISO 17034 [1]. These mixtures are meticulously prepared using a gravimetric approach, following an internal procedure aligned with the international standard ISO 6142-1 [2], thereby guaranteeing the utmost accuracy. The certification of these gas mixtures adheres to the international standard ISO 6143 [3], leveraging analytical techniques such as gas chromatography (GC), paramagnetic moment, non-dispersive infrared spectroscopy (NDIR), and non-dispersive ultraviolet spectroscopy (NDUV).

The quality control of these measurements is fortified through active participation in projects and international comparisons. Furthermore, recognition and inclusion in the Bureau International des Poids et Mesures (BIPM) database of calibration and measurement capabilities (CMC) solidify their commitment to quality [4].

The LGR's latest contribution focuses on preparing multicomponent gaseous mixtures aimed at enhancing the accuracy, reliability, and traceability of carbon metrology measurements. Specifically, this paper outlines the work undertaken by LGR as part of the MetCCUS project. This project started on October 1, 2022, with the participation of 21 partners and will lasts for 36 months.

Under the MetCCUS project, the contribution of LGR involves the preparation of certified reference materials (CRM) to allow the measurement of impurities in CO2 with metrological traceability, providing support for methods validation and the calibration of instrumentation used in carbon capture processes. LGR had prepared the following bicomponent mixtures: SO_2 in CO_2 matrix and H_2S in CO_2 matrix; and two multicomponent mixtures SO_2+CO+O_2 in CO_2 and H_2S+CO+CH_4+O_2 in CO_2 matrix. This study successfully characterized four polluting gases and oxygen in CO_2 matrix within a cylinder under a pressure of approximately 40 bar, and it entailed an in-depth analysis of interferences and a stability study [5].

2 GAS MIXTURES PREPARATION

As previously mentioned, reference gas mixtures are prepared according to an internal procedure based on the gravimetric method outlined in ISO 6142-1 [2].

This section of ISO 6142 applies specifically to mixtures of gaseous or completely vaporized components, which can be introduced into the cylinder in either the gaseous or liquid state. The mixtures to be prepared can be either bicomponent or multicomponent.

This method describes the calculation of uncertainty associated with the molar fraction of each component. This uncertainty calculation requires the evaluation of contributions stemming from factors such as the weighing process, component purity, mixture stability, and final mixture verification.

During the preparation of gas mixtures, aluminium cylinders with a special coating are used to prevent the adsorption of mixture components on the inner walls.

Following the cylinder selection, a rigorous cleaning process is performed to ensure that any potential residues inside the cylinder do not impact the uncertainty of the composition of the final mixture. This step is particularly important when preparing mixtures with very low concentrations.

Another critical step in the filling process is the transfer of gases from the parent cylinder, for each component, to the cylinder where the mixture is being prepared. The addition of each gas is carried out at a filling station equipped with electronically polished tubes, valves, vacuum and pressure meters, and oil-free turbo molecular vacuum pumps. The amount of gas added to the cylinder is carefully controlled using a balance (Figure 1).

Figure 12: Filling station and comparative balance

The accurate mass of each gas component added to the cylinder is determined using a mass comparator, utilizing calibrated masses that are traceable to the national standard. The traceability of the gas composition to the international system of units (SI) is ensured through the use of calibrated instrumentation.

By utilizing the results from the purity analysis certificates of the initial gases and the data obtained through the weighing process, the exact composition of the mixture and the associated uncertainties (relating to the various molar fractions obtained) can be calculated.

IPQ prepared a bicomponent gas mixture and a multicomponent gas mixture in a carbon dioxide matrix using the gravimetric method, with the following nominal molar fractions: SO_2 (20×10^{-6} mol/mol), H_2S (10×10^{-6} mol/mol) CO (750×10^{-6} mol/mol), CH_4 (2×10^{-2} mol/mol) and O_2 (1×10^{-2} mol/mol).

Once prepared, the gas mixture underwent a homogenization process. The cylinder containing the mixture was placed in a rolling system for approximately an hour (Figure 2).

Figure 2: Rolling cylinder system

3 GAS MIXTURES CERTIFICATION

The composition of the gas mixture is determined through an individual analysis of the molar fraction of each component. The procedure for determining the molar fraction is described in the international standard ISO 6143 [3]. The analytical method used is a comparative method, as it employs primary reference standards to establish the calibration curve. The specific analytical methods used are gas chromatography (GC), paramagnetic moment, non-dispersive infrared spectroscopy (NDIR), and non-dispersive ultraviolet spectroscopy (NDUV). The final results are presented together with their respective uncertainties in accordance with the Guide to the Expression of Uncertainty in Measurement [6].

The produced gas mixtures are certified using specific analysers for SO_2, H_2S, CO, CH_4 and O_2. In each certification, the molar fraction of each component in the prepared mixture is determined by comparing the equipment's response to the standards used, in accordance with the gas under analysis, within appropriate measurement intervals.

The certification process takes place using an automated multichannel sampling system, to which all the cylinders to be analysed are connected (Figure 3).

Figure 3: Certification of Gas Mixtures Facility

During the analysis, the cylinders are automatically selected, enabling the individual circulation of gas through the analyser. This system employs the purpose-built IPQAnaliseQui software, which manages the sampling process and records all measurements taken by the analyser. Ultimately, all the gathered data, including records of standard and sample analyses, are entered into a spreadsheet and adjusted with zero and pressure measurements.

The calibration function determination is carried out using the XGENLINE program developed by the NPL - National Physical Laboratory. This software calculates the most suitable low-degree polynomial calibration function (1, 2, 3 or 4) for a set of measurement data (X, Y), considering the uncertainties and covariances associated with the data. Hence, the determined calibration function is employed to derive estimates of the molar fraction values for the samples under analysis and their corresponding associated uncertainties.

4 INTERFERENT STUDY

The study of interferents was conducted using certified reference material (Table 1).

Table 7: PSM / CRM used for the study of interferents

Interferent Gas	PSM /CRM (mol/mol)	Analytical method
H_2S	CRM412061 (9,2±0,5) x10^{-6}	NDUV
SO_2	VSL4910 (25,00±0,37) x10^{-6}	NDIR
CO	CRM034916 (823±4) x10^{-6}	NDIR
O_2	VSL8612 (1,003±0,019) x10^{-2}	Paramagnetic
CH_4 / ar	CRM015377 (2,49±0,02) x10^{-2}	NDIR
CO_2	CRM034907 (20,01±0,05) x10^{-2}	NDIR
CH_4 / N_2	PSM202534 (2,501±0,012) x10^{-2}	NDIR

SO_2 Analyser

Measurements of SO_2, H_2S, CO, CH_4, O_2, and CO_2 standards were conducted on the SO_2 analyser. The results obtained during the SO_2 analyser tests are presented in Table 2. *Zero* is the reading of the analyser when the zero cleaning gas is passing, which is nitrogen. *Reading* is the value when the sample gas is passing. *S* is the standard deviation of the measurements.

The *Zero* value of the analyser does not have to be zero because the calculations are carried out with the zero correction and the analytical method is a comparative method according to ISO 6143.

Table 2: Results of interferents on the SO_2 analyser

Cylinder	Molar Fraction mol/mol	Zero mV	Reading mV	S mV
CRM412061 (H_2S)	9,2x10^{-6}	-2560,95	-2556,61	0,6686
VSL4910 (SO_2)	25,00x10^{-6}	-2553,19	-2249,54	0,6123
CRM034916 (CO)	823x10^{-6}	-2547,53	-2546,61	0,5344
VSL8612 (O_2)	1,003x10^{-2}	-2545,11	-2544,24	0,5266
CRM015377 (CH_4 / ar)	2,49x10^{-2}	***-2543,55***	***7314,06***	0,6940
CRM034907 (CO_2)	20,01x10^{-2}	-2531,41	-2540,10	0,8063
PSM202534 (CH_4 / N_2)	2,501x10^{-2}	---	---	---

We can observe that for the gases H_2S, CO, O_2 and CO_2, the zero in the table is similar to the reading. We consider that the values are similar when the difference between the reading and the zero is less than 10 mV. This indicates that these gases do not interfere with the SO_2 gas reading on the SO_2 analyser. On the other hand, we have CH_4 gas interfering with the SO_2 sensor.

H_2S Analyser

Measurements of SO_2, H_2S, CO, CH_4, O_2, and CO_2 standards were conducted on the H_2S analyser. The results obtained during the H_2S analyser tests are presented in Table 3.

Table 3: Results of interferents on the H_2S analyser

We can observe that for the gases CO, O_2, CH_4 and CO_2, the zero in the table is similar to the reading. This indicates that these gases do not interfere with the H_2S gas reading on the H_2S analyser. On the other hand, we have SO_2 gas interfering with the H_2S sensor.

CO Analyser

Measurements of SO_2, H_2S, CO, CH_4, O_2, and CO_2 standards were conducted on the CO analyser. The results obtained during the CO analyser tests are presented in Table 4.

Table 4 – Results of interferents on the CO analyser

Cylinder	Molar Fraction mol/mol	Zero mV	Reading mV	S mV
CRM412061 (H_2S)	$9{,}2x10^{-6}$	2180,90	2179,85	0,378
VSL4910 (SO_2)	$25{,}00x10^{-6}$	2179,17	2178,70	0,382
CRM034916 (CO)	$823x10^{-6}$	2179,00	7819,40	0,665
VSL8612 (O_2)	$1{,}003x10^{-2}$	2180,19	2178,71	0,419
CRM015377 (CH_4 / ar)	$2{,}49x10^{-2}$	*2179,03*	*2147,72*	0,459
CRM034907 (CO_2)	$20{,}01x10^{-2}$	2178,36	2170,43	0,356
PSM202534 (CH_4 / N_2)	$2{,}501x10^{-2}$	---	---	---

We can observe that for the gases SO_2, H_2S, O_2 and CO_2, the zero in the table is similar to the reading. This indicates that these gases do not interfere with the CO gas reading on the CO analyser. Methane gas interferes with the CO analyser (NDIR) however the interference is negligible within the measurement uncertainty.

O_2 Analyser

Measurements of SO_2, H_2S, CO, CH_4, O_2, and CO_2 standards were conducted on the O_2 analyser. The results obtained during the O_2 analyser tests are presented in Table 5.

Table 5 – Results of interferents on the O_2 analyser

Cylinder	Molar Fraction mol/mol	Zero mV	Reading mV	S mV
CRM412061 (H_2S)	$9{,}2x10^{-6}$	-1054,93	-548,592	4,8925
VSL4910 (SO_2)	$25{,}00x10^{-6}$	***-1036,35***	***781,121***	8,3786
CRM034916 (CO)	$823x10^{-6}$	-1030,93	-1028,56	6,3142
VSL8612 (O_2)	$1{,}003x10^{-2}$	-1027,85	-1025,05	7,1555
CRM015377 (CH_4 / ar)	$2{,}49x10^{-2}$	---	---	---
CRM034907 (CO_2)	$20{,}01x10^{-2}$	-1024,66	-1022,14	4,8874
PSM202534 (CH_4 / N_2)	$2{,}501x10^{-2}$	-2458,53	-2456,86	8,4032

We can observe that for the gases SO_2, H_2S, CO, O_2 and CO_2, the zero in the table is similar to the reading. This indicates that these gases do not interfere with the O_2 gas reading on the O_2 analyser.

CH_4 Analyser

Measurements of SO_2, H_2S, CO, CH_4, O_2, and CO_2 standards were conducted on the CH_4 analyser. The results obtained during the CH_4 analyser tests are presented in Table 6.

Table 6 – Results of interferents on the CH_4 analyser.

Cylinder	Molar Fraction mol/mol	Zero mV	Reading mV	S mV
CRM412061 (H_2S)	$9{,}2x10^{-6}$	2079,21	2078,47	0,190
VSL4910 (SO_2)	$25{,}00x10^{-6}$	2079,33	2080,43	0,201
CRM034916 (CO)	$823x10^{-6}$	2079,44	2079,35	0,203
VSL8612 (O_2)	$1{,}003x10^{-2}$	2079,87	2079,67	0,222
CRM015377 (CH_4 / ar)	$2{,}49x10^{-2}$	2079,72	5944,30	0,292
CRM034907 (CO_2)	$20{,}01x10^{-2}$	2081,01	2078,70	0,208
PSM202534 (CH_4 / N_2)	$2{,}501x10^{-2}$	---	---	---

We can observe that for the gases SO_2, H_2S, CO, O_2 and CO_2, the zero in the table is similar to the reading. This indicates that these gases do not interfere with the CH_4 gas reading on the CH_4 analyser.

5 RESULTS

Four gas mixtures were carefully prepared for analysis, including two binary combinations of SO_2 in a carbon dioxide matrix, designated as PRM408326 and PRM108593. Furthermore, two mixtures composed of H_2S in CO_2, labelled as PRM108595 and PRM108596, 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, two multicomponent mixtures were prepared in a CO_2 matrix, PRM308978 with the impurities SO_2, CO and O_2; and PRM202557, with the impurities H_2S, CO, O_2, and CH_4 at the previously mentioned molar fractions. These mixtures were contained within two cylinders at an approximate pressure of 40 bar each.

a. Results for the SO_2 Mixtures

The binary mixtures PRM408326 and PRM108593 were certified using the SO_2 analyser with the standards presented in Table 7.

Table 7 – Standards used for SO_2 Component Certification.

Standards Used	*x* mol/mol	*U* mol/mol
VSL9159	2,554E-05	3,7E-07
VSL7897	2,992E-04	9,3E-07
VSL7886	1,001E-03	3,2E-06

Table 8 shows the results of the analysis of the SO_2 component, in the two prepared binary mixtures, PRM408326 and PRM108593.

Table 8 – Results of the analysis of the SO_2 component, in the prepared binary mixtures.

Results PRM408326 – SO_2		
Data	***x*** **10^{-6} mol/mol**	***U*** **10^{-6} mol/mol**
2023-09-04	19,52	0,51

Results PRM108593 – SO_2		
Data	***x*** **10^{-6} mol/mol**	***U*** **10^{-6} mol/mol**
2023-09-04	20,71	0,50

b. Results for the H_2S Mixtures

The binary mixtures PRM108595 and PRM108596 were certified using the H_2S analyser with the standards presented in Table 9.

Table 9 – Standards used for H_2S Component Certification.

Standards Used	*x* mol/mol	*U* mol/mol
NPL0274	4,610E-06	4,6E-06
VSL4408	5,000E-06	5,0E-06
VSL4982	1,001E-05	1,0E-05
VSL4427	5,000E-05	5,0E-05

Table 9 shows the results of the analysis of the H_2S component, in the two prepared binary mixtures, PRM108595 and PRM108596.

Table 10 – Results of the analysis of the H_2S component, in the prepared binary mixtures.

Results PRM108595 – H_2S		
Data	***x*** **10^{-6} mol/mol**	***U*** **10^{-6} mol/mol**
2023-09-11	9,97	0,48

Results PRM108596 – H_2S		
Data	***x*** **10^{-6} mol/mol**	***U*** **10^{-6} mol/mol**
2023-09-11	9,64	0,47

c. Results for the Multicomponent Mixtures

The multicomponent mixtures PRM308978 and PRM202557 were certified using the SO_2, H_2S, CO, CH_4 and O_2 analysers with the standards presented in Table 11.

Table 11 – Standards Used for Certification of the Components.

Standards Used	*x* mol/mol	*U* mol/mol
SO_2		
VSL9159	2,554E-05	3,7E-07
PSM502546	5,005E-05	4,0E-07
VSL7897	2,992E-04	9,3E-07
VSL7886	1,001E-03	3,2E-06
H_2S		
NPL0274	4,610E-06	3,4E-07
VSL4408	5,000E-06	3,7E-07
VSL4982	1,001E-05	3,2E-07
VSL0536	2,000E-04	3,0E-06

PSM402577	5,0020E-04	5,0E-06
NMI8601	5,5010E-04	5,2E-06
NMI8622	7,0050E-04	2,0E-06
NMI3707	8,0030E-04	2,3E-06
NPL1720	9,9940E-04	3,7E-06
CH_4		
NPL273	4,999E-03	1,9E-05
VSL6039	5,001E-03	1,8E-05
PSM202534	2,501E-02	1,2E-02
VSL6037	5,006E-02	1,0E-04
O_2		
VSL3704	5,000E-03	4,3E-04
VSL8612	1,003E-02	1,9E-04
VSL8554	1,003E-01	2,6E-04

6 SUMMARY

Under the MetCCUS project, the contribution of LGR involves the preparation of certified reference materials (CRM) to allow the measurement of impurities in CO_2 with metrological traceability, providing support for the calibration and validation of instrumentation used in carbon capture processes.

We can conclude that methane gas interferes with the SO_2 sensor when using the NDIR analytical method. Also, SO_2 gas interferes with the H_2S sensor when using the NDUV analytical method. Methane gas interferes with the CO analyser (NDIR) however the interference is negligible within the measurement uncertainty. Therefore, two multicomponent mixtures were prepared taking this information into account. One mixture does not contain SO_2 and the other does not contain CH_4 and H_2S.

Four bicomponent and two multi-component mixtures in CO_2 matrix were prepared, with uncertainties within expectations.

The results of the molar fractions of the multicomponent mixtures PRM308978 (SO_2+CO+O_2 in CO_2) and PRM202557 (H_2S+CO+CH_4+O_2 in CO_2) are presented in Table 12.

Table 12 – Molar fractions of the multicomponent mixtures in CO_2

PRM308978 2023-09-19		
Component in a Carbon Dioxide Matrix.	***x*** **mol/mol**	***U*** **mol/mol**
SO_2	14,26 x 10^{-6}	0,46 x 10^{-6}
CO	666,1 x 10^{-6}	2,7 x 10^{-6}
O_2	0,594 x 10^{-2}	0,027 x 10^{-2}
PRM202557 2023-09-20		
Component in a Carbon Dioxide Matrix.	***x*** **mol/mol**	***U*** **mol/mol**
H_2S	9,83 x 10^{-6}	0,48 x 10^{-6}
CO	669,5 x 10^{-6}	2,7 x 10^{-6}
CH_4	1,9685 x 10^{-2}	0,0060 x 10^{-2}
O_2	0,586 x 10^{-2}	0,027 x 10^{-2}

A stability study will be carried out in order to have data to establish the shelf life of the different mixtures.

In the future, we intend to extend this study to mixtures with more components. To obtain more information regarding what is intended in the project, we intend to analyse these mixtures using other analytical methods to avoid the interferences.

7 REFERENCES

ISO/IEC 17034:2016 General requirements for the competence of reference material producers;

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

ISO 6143:2001 – Gas analysis – Comparison methods for determining and checking the composition of calibration gas mixtures;

https://www.bipm.org/kcdb/;

ISO 13528:2022 – Statistical methods for use in proficiency testing by interlaboratory comparisons;

Evaluation of measurement data – Guide to the expression of uncertainty in measurement JCGM 100:2008 (GUM 1995 with minor corrections).