EURAMET 1080
Comparison of measurement standards

"Bilateral comparison of CO_2 in N_2 and in air at automotive emission level"

Final report

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Field

Amount of substance

Summary

The objective of this EURAMET project is to confirm INRIM (Istituto Nazionale di Ricerca Metrologica, Italy) measurement capabilities in the preparation of primary gravimetric gas mixtures of carbon dioxide (CO_2) at percent level in matrices of nitrogen (N_2) and of synthetic air by means of their analytical verification.

INRIM operated as coordinating laboratory in this comparison. The selected primary gas mixtures were individually prepared using gravimetry and their stability was investigated. The other laboratory that participated in this bilateral comparison was NPL (National Physical Laboratory, UK).

The results of the present comparison show data which are in agreement within the declared uncertainties. Furthermore there is not any bias between the performances of the two institutes that took part in the comparison. The obtained degrees of equivalence with respect to the reference gravimetric value, are a confirmation of INRIM capabilities in preparing primary gas mixtures.

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1 Introduction

The objective of this EURAMET project is to confirm INRIM (Istituto Nazionale di Ricerca Metrologica, Italy) measurement capabilities in the preparation of primary gravimetric gas mixtures of carbon dioxide (CO_2) at percent level in matrices of nitrogen (N_2) and of synthetic air. This verification was carried out by analysing the gas mixtures used in this comparison by infrared non-dispersive spectroscopy (NDIR).

INRIM operated as coordinating laboratory in this comparison. The selected primary gas mixtures were individually prepared using gravimetry and their stability was investigated. The other laboratory that participated in this bilateral comparison was NPL (National Physical Laboratory, UK).

2 Participants

The following institutes participated in this comparison (in alphabetical order).

Table 1: List of participants

Institute	City	Country
INRIM	Torino	Italy
NPL	Teddington	United Kingdom

3 Design of the comparison

Two gas mixtures of CO_2 in matrices of N_2 and of synthetic air were prepared by means of a primary method (gravimetry) by the coordinating laboratory INRIM, that then analysed them by NDIR spectroscopy against standards purchased by an accredited laboratory. Their stability for about 12 months was also evaluated.

Both mixtures were sent to NPL that analysed them via NDIR spectroscopy as well, against NPL standards. The cylinders were shipped back to INRIM that analysed them again in order to check their stability.

The nominal amount of substance ratios of CO_2 are summarised in table 2.

Table 2 : Nominal amount of substance ratios

Cylinder	CO_2 (% mol/mol)	Matrix gas
D37 0669	12.00	Nitrogen
D20 6708	12.00	Synthetic air

The cylinders were shipped to NPL in November 2007. A formal deadline for submission of results was not set. NPL results were received in December 2007.

4 Evaluation of results

4.1 Uncertainty evaluation of the gravimetric values

The reference values used in this comparison are based on gravimetry. The two mixtures were prepared at INRIM following the International Standard ISO 6142. The cylinders were weighted after each preparation step according to the double substitution weighing scheme (ABBA). Calibrated mass standards were added on the lighter cylinder to minimize, within 1 g, the mass difference between the two cylinders. For each weighing the above scheme was repeated three times and for each mass reading the environmental data of temperature, pressure and relative humidity were recorded for the calculation of the air density.

To evaluate the combined standard uncertainty, u_{grav}, the following sources were taken into account: weighted masses, molar masses and purity of parent gases, covariance between the CO_2 and N_2 molar fractions in the parent gases. The various contributions were combined according to the uncertainty propagation law. The major contribution were due to the molar masses of parent gases, declared by IUPAC.

4.2 Degrees of equivalence

In the current comparison, measurements were performed by the participating laboratories on gas mixtures individually prepared by INRIM with the gravimetric method. As it is typical for international comparisons in the gas analysis field, the individual gravimetric values calculated by the coordinating laboratory, can be adopted as reference values. Consequently to evaluate the differences between the two laboratories, the value x_{grav} is taken as the reference value.

The degree of equivalence D_i of each laboratory with respect to the reference value is given by a pair of numbers:

$$D_i = (x_i - x_{grav}) \quad (1)$$

and U_i , its expanded uncertainty ($k=2$),

$$U_i^2 = 2^2(u_i^2 + u_{igrav}^2) \quad (2)$$

A compatibility index is defined as :

$$CI_i = \frac{D_i}{U_i} \quad (3)$$

5 Results

In figures 1 and 2 the degrees of equivalence for the participating laboratories for each mixture are given, together with the expanded uncertainties (k=2) given for a confidence level of about 95 %.

Figure 1: Results for CO_2 in N_2

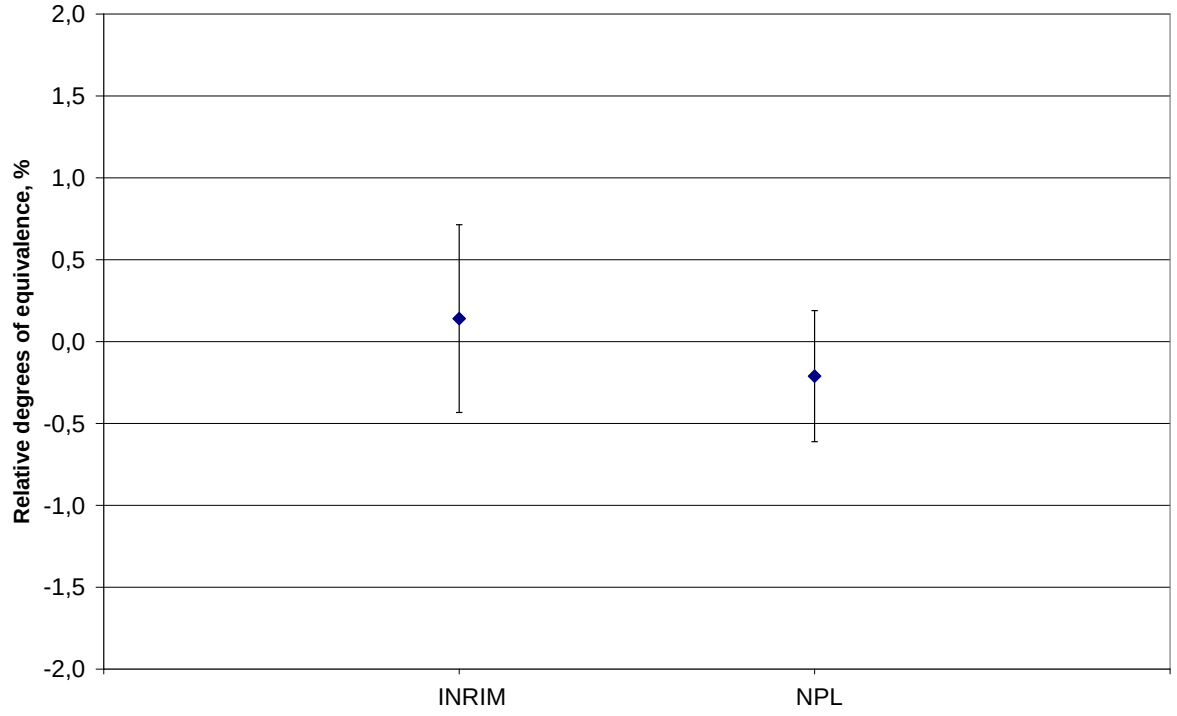
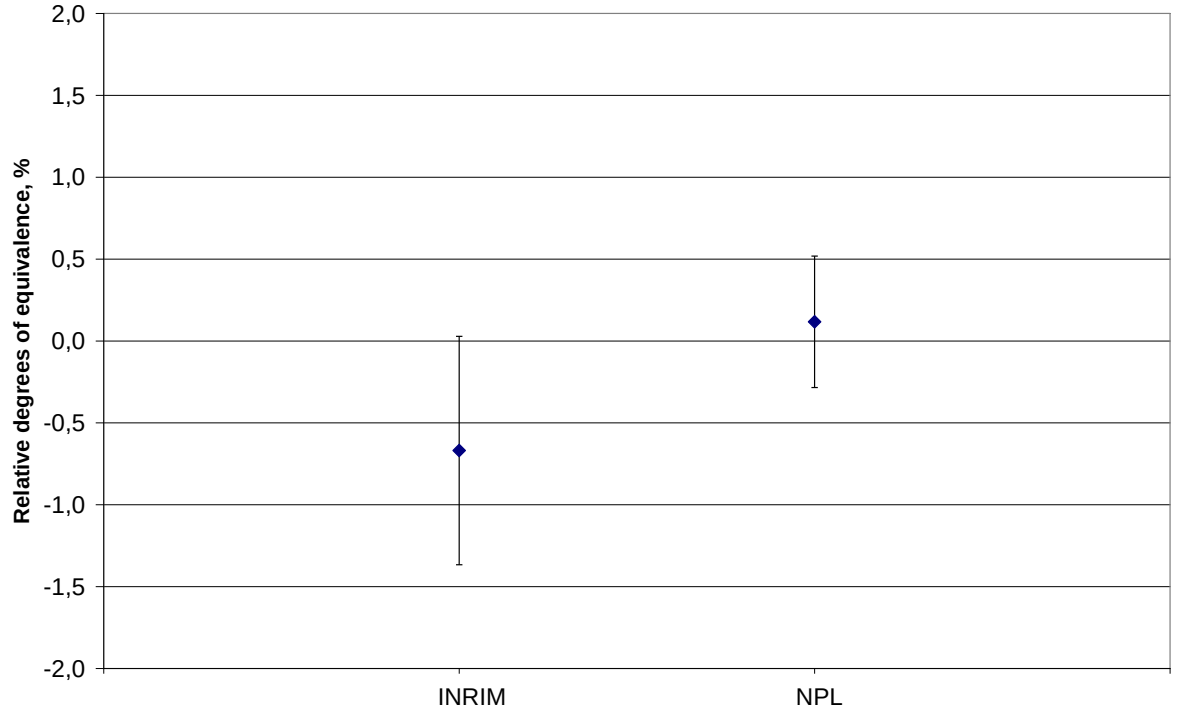


Figure 2: Results for CO_2 in synthetic air



Tables 3 and 4 report the results, where:

Cylinder: identification code of the cylinder
x_{grav}: gravimetric value of CO_2 fraction in the cylinder
u_{grav}: combined standard uncertainty of x_{grav} (k=2)
x_{lab}: measurement result of laboratory i
u_{lab}: combined standard uncertainty of laboratory i
D_i: degree of equivalence of laboratory i with respect to the reference value
U_i: expanded uncertainty of D_i (k=2)
D_{irel}: relative degree of equivalence of laboratory i with respect to the reference value
U_{irel}: relative expanded uncertainty of D_i
CI: compatibility index

Table 3: Results and degrees of equivalence for CO_2 in N_2

Lab	Cylinder	x_{grav} 10^{-2} mol/ mol	u_{grav} 10^{-2} mol/ mol	x_{lab} 10^{-2} mol/ mol	u_{lab} 10^{-2} mol/ mol	D_i	U_i	D_{irel} %	U_{rel} %	CI
INRIM	D37 0669	11.99231	0.00027	12.009	0.034	0.017	0.069	0.14	0.57	0.24
NPL	D37 0669	11.99231	0.00027	11.967	0.024	-0.025	0.048	-0.21	0.40	-0.53

Table 4: Results and degrees of equivalence for CO_2 in synthetic air

Lab	Cylinder	x_{grav} 10^{-2} mol/ mol	u_{grav} 10^{-2} mol/ mol	x_{lab} 10^{-2} mol/ mol	u_{lab} 10^{-2} mol/ mol	D_i	U_i	D_{irel} %	U_{rel} %	CI
INRIM	D20 6708	11.96174	0.00027	11.878	0.042	-0.084	0.083	-0.70	0.70	-0.96
NPL	D20 6708	11.96174	0.00027	11.974	0.024	0.012	0.048	0.10	0.40	0.29

The evaluation of u_{lab} took into account the calibration curve, which represent the major uncertainty source, the uncertainty on the standards used to calibrate the NDIR analysers, the analyser resolution and its repeatability, the lack of fit of the mathematical model used to determine the calibration curve.

6 Conclusions

The results of the present comparison show data which are in agreement within the declared uncertainties. The participants used independent standards to assign the analytical values. Furthermore there is not any bias between the performances of the two institutes that took part in the comparison.

The obtained degrees of equivalence with respect to the reference gravimetric value, are a confirmation of INRIM capabilities in preparing primary gas mixtures.