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EVALUATION OF MEASUREMENT STANDARDS

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1 - INTRODUCTION

Centro Español de Metrología (CEM), Spanish Metrological Institute, as part of its activity, has started to prepare primary reference gas mixtures using gravimetrical method.
As a consequence of this new work, a comparison of some primary reference gas mixtures prepared by CEM has been carried out with three of the gas mixtures manufacturers established in Spain.
CEM has coordinated this comparison with the manufacturers in order to assure traceability in equipments for the automotive exhaust gas field.
The objetive of this comparison is double:

- to compare the analytical results with the gravimetric value of Primary Standard Material (PSM) preparation,
- to compare the measurement capabilities between laboratories in measuring the amount of substance fractions of carbon dioxide in nitrogen.

2 - PARTICIPANTS

Four laboratories have participated in this comparison, three gas mixture manufacturer laboratories and CEM.
In order to maintain confidentiality, a number has been given to each laboratory.

3 - DESIGN OF THE COMPARISON

Two gas mixtures were prepared by means of primary methods (gravimetry) at the pilot laboratory (CEM). The method used in the preparation of the gas mixtures was in accordance with ISO 6142:2001 Gas analysis. Preparation of calibration gas mixtures. Gravimetric method.
These gas mixtures were analysed by CEM to check their composition before sending the cylinders to the participants. Analysis were made in accordance with ISO 6143:2000 Gas Analysis – Comparison methods for determining and checking the composition of calibration gas mixtures.
The nominal amount of substance ratios of CO_2 in nitrogen, as used in this comparison, are summarised in table 1:

TABLE 1: Nominal amount of substance ratios

Cylinder code	x (mmol/mol)
51837	60
51863	140

4 - MEASUREMENT METHODS AND CALIBRATION PROCEDURES

The following methods of measurement have been used (table 2).

TABLE 2: Measurement and calibration methods

Laboratory	Measurement method
1	CG (TCD)
2	CG (TCD)
3	NDIR
4	NDIR

5 - EVALUATION OF RESULTS

A target of 1% is manteined for the required agreement between a laboratory and the comparison reference value.
Furthermore, the difference observed between the value of a laboratory and the comparison reference value should not exceed the combined expanded uncertainty of this difference.
In order to evaluate the differences between the participating laboratories, the value x_{grav} is taken as the reference value for each cylinder.
The degree of equivalence of each laboratory with respect to the reference value is given by a pair of numbers for each cylinder:

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

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

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

Compatibility index is defined as:

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

6 - COMPUTATION OF DEGREES OF EQUIVALENCE AND ASSOCIATED UNCERTAINTIES

The degree of equivalence between two laboratories is defined as:

$$D_{ij} = D_i - D_j = x_i - xj \quad (4)$$

The uncertainty in the degree of equivalence can be expressed as:

$$U_{ij}^2 = k^2\left(u_i^2 + u_j^2 + 2u_{grav}^2\right) \quad (5)$$

Compatibility index is defined as:

$$CI_{ij} = \frac{D_{ij}}{U_{ij}} \quad (6)$$

7 - RESULTS

On the following pages, all results of this comparison are presented. The tables 3, 4, 5 and 6 contains the following information:

CylinderIdentification code of the cylinder

x_i	Result of measurement carried out by laboratory i
u_i	Combined standard uncertainty of x_i
x_{igrav}	Gravimetric value of the amount of substance fraction in the cylinder received by laboratory i
u_{igrav}	Combined standard uncertainty in x_{igrav}
D_i	Degree of equivalence of laboratory i with respect to the reference value
U_i	Expanded uncertainty in D_i
D_{ij}	Degree of equivalence between laboratories i and j
U_{ij}	Expanded uncertainty in D_{ij}
CI_{ij}	Compatibility index

TABLE 3: Results for Cylinder 51837

Lab i	x_i	u_i	x_{grav}	u_{grav}	D_i	D_i %	U_i	U_i %	CI_i
1	60,01	0,132	59,995	8,96E-05	0,012	0,020	0,264	0,440	0,046
2	60,02	0,155	59,995	8,96E-05	0,025	0,042	0,310	0,517	0,081
3	59,90	0,050	59,995	8,96E-05	-0,095	-0,158	0,100	0,167	0,949
4	60,10	0,20	59,995	8,96E-05	0,105	0,175	0,400	0,667	0,263

TABLE 4: Results for Cylinder 51863

Lab i	x_i	u_i	x_{grav}	u_{grav}	D_i	D_i %	U_i	U_i %	CI_i
1	147,55	0,081	147,594	4,52E-05	-0,045	-0,030	0,162	0,109	0,275
2	147,52	0,420	147,594	4,52E-05	-0,075	-0,051	0,840	0,569	0,089
3	147,80	0,200	147,594	4,52E-05	0,206	0,139	0,400	0,271	0,514
4	147,30	0,400	147,594	4,52E-05	-0,294	-0,200	0,800	0,542	0,368

TABLE 5: CI between laboratories for cylinder 51837

	Lab j							
Lab i	1		2		3		4	
	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}
1			-0,013	0,407	0,107	0,282	-0,093	0,479
2	0,013	0,407			0,120	0,326	-0,080	0,506
3	-0,107	0,282	-0,120	0,326			-0,200	0,412
4	0,093	0,479	0,080	0,506	0,200	0,412		
	CI_{ij}		CI_{ij}		CI_{ij}		CI_{ij}	
			0,032		0,379		0,194	
	0,032				0,368		0,158	
	0,379		0,368				0,485	
	0,194		0,158		0,485			

TABLE 6: CI between laboratories for cylinder 51863

	Lab j							
Lab i	1		2		3		4	
	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}
1			0,030	0,855	-0,250	0,431	0,250	0,816
2	-0,030	0,855			-0,280	0,930	0,220	1,16
3	0,250	0,432	0,280	0,930			0,500	0,894
4	-0,250	0,816	-0,220	1,160	-0,500	0,894		
	CI_{ij}		CI_{ij}		CI_{ij}		CI_{ij}	
			0,035		0,580		0,306	
	0,035				0,301		0,190	
	0,580		0,301				0,560	
	0,306		0,190		0,559			

8 - CONCLUSIONS

8.1 - Comparison of the analytical results with the gravimetric value of Primary Standard Material (PSM) preparation.

The results submitted by the four participants are shown in the tables 3 and 4. In the figures 1 and 3 , the results are plotted in terms of their deviation from the gravimetric value. Expanded uncertainties are calculated using a coverage factor k = 2, as an approximation of 95 % confidence intervals.

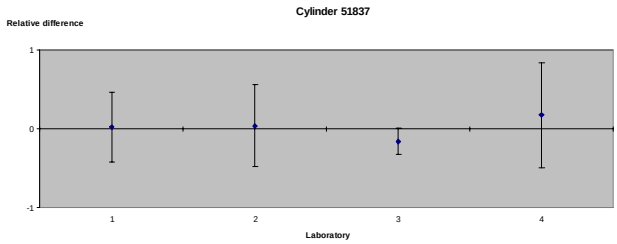

Fig. 1: Results for Cylinder 51837

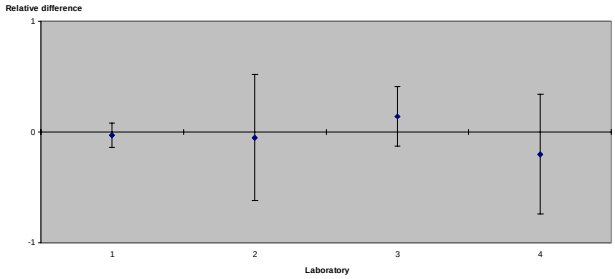

Fig. 3: Results for Cylinder 51863

In Figures 2 and 4 show for each cylinder the CI for each laboratory.

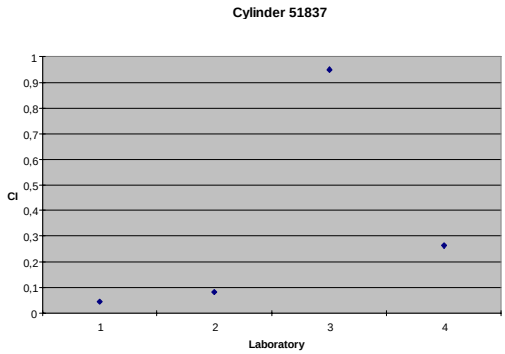

Fig. 2: Results for Cylinder 51837

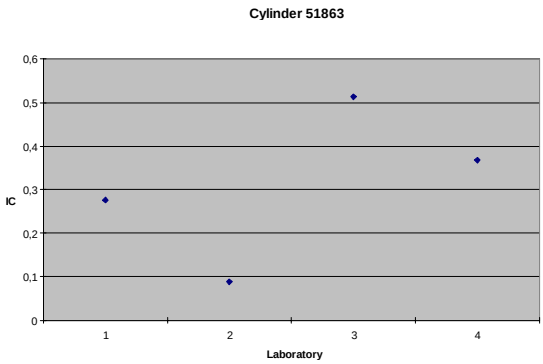

Fig. 4: Results for Cylinder 51863

The differences between gravimetric and reported value are given relative to the gravimetric value, allowing to check directly whether the result of the laboratory is within ±1 % relative to the gravimetric value.

The uncertainty bars in the graphs are given with k = 2 for all laboratories, taking into consideration both the reported uncertainty from the laboratory as well as the uncertainty from gravimetry. The uncertainty of a laboratory has been computed from u_i and k_i. All laboratories used a coverage factor of 2.

For both cylinders, the results of the four laboratories are within ±1 % relative to the gravimetric value (figures 1 and 3) and their uncertainties overlap with the zero axis. For every laboratories CI < 1 (figures 2 and 4).

8.2 - Comparison of measurement capabilities between laboratories in measuring the amount of substance fractions of carbon dioxide in nitrogen

In tables 5 and 6 is shown D_{ij}, U_{ij} and CI_{ij}.

For every laboratories CI < 1 (figures 5.1, 5.2, 5.3, 5.4, 6.1, 6.2, 6.3 and 6.4).

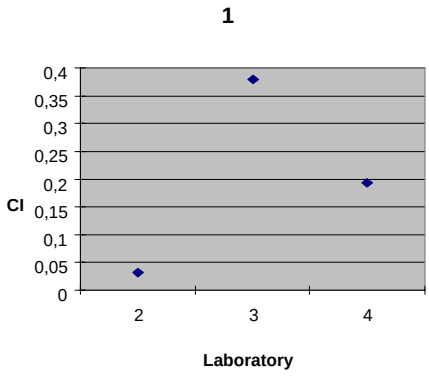

Fig. 5.1: CI between laboratories for cylinder 51837

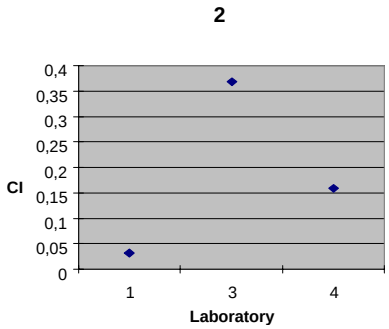

Fig. 5.2: CI between laboratories for cylinder 51837

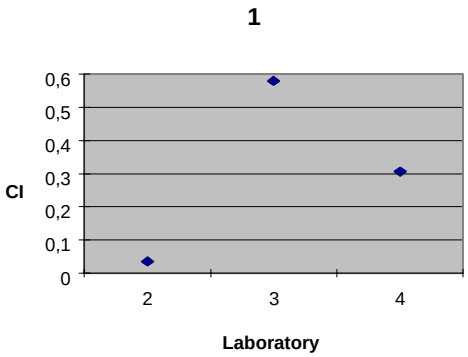

Figure 6.1: CI between laboratories for cylinder 51863

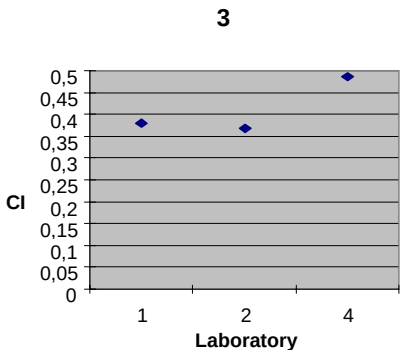

Figure 5.3: CI between laboratories for cylinder 51837

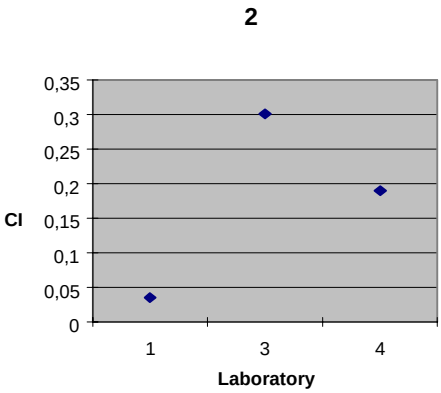

Figure 6.2: CI between laboratories for cylinder 51863

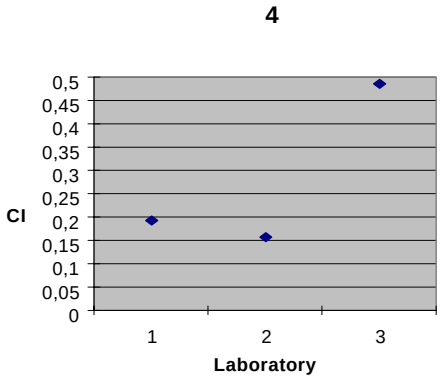

Figure 5.4: CI between laboratories for cylinder 51837

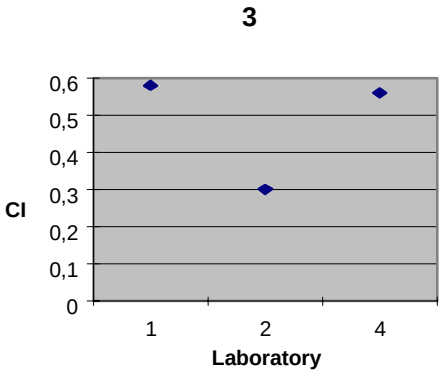

Figure 6.3: CI between laboratories for cylinder 51863

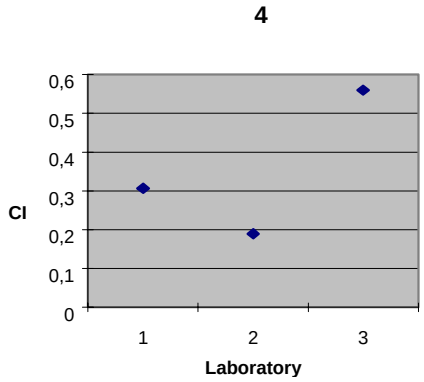

Figure 6.4: CI between laboratories for cylinder 51863

9 - REFERENCES

[1] ISO 6142:2001 Gas analysis. Preparation of calibration gas mixtures. Gravimetric method.

[2] ISO 6143:2000 Gas analysis. Comparison methods for determining and checking the composition of calibration gas mixtures.

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