

SIM.8.S1

**SIM.QM-S1**

**SIM.8.1.S**

**Analysis of ten binary mixtures  
(CO, CO<sub>2</sub>, NO and C<sub>3</sub>H<sub>8</sub>)**

**BILATERAL COMPARISON NIST-CENAM**

**1.0 Subject:** Ten compressed gas cylinders from NIST containing binary mixtures with propane, carbon monoxide, carbon dioxide, or nitric oxide, all of them with nitrogen balance, were shipped to CENAM for bilateral comparison purpose between CENAM and NIST.

CENAM utilized its own gravimetrically prepared Primary Reference Materials (PRM), to measure the respective concentrations and reported to NIST. The cylinders were shipped back to NIST for their value verification. This Supplementary Comparison SIM.8.S.1 was designed as subsequent comparison of CCQM-K-1a, b, and c including propane..

**2.0 Analytical Methods:** CENAM employed Gas Chromatography with FID and Ni catalytic reactor to Propane/N<sub>2</sub>, CO/N<sub>2</sub> and CO<sub>2</sub>/N<sub>2</sub>, and the use was made also of specific gas analyzers such as NDIR to analyze CO/N<sub>2</sub> and CO<sub>2</sub>/N<sub>2</sub>, chemiluminescence to NO/N<sub>2</sub>.

### 3.0 Sample description:

Cylinders identifications and composition levels for each analyte are summarized in table 1.

**Table 1. Sample description. Nitrogen balance**

Cylinders number	Nominal composition
XF001077B	50 µmol/mol CO
XF001009B	1000 µmol/mol CO
CAL1582	5000 µmol/mol CO
CAL2132	10000 µmol/mol CO
CAL1484	80000 µmol/mol CO
FF18058	70000 µmol/mol CO <sub>2</sub>
FF17222	100 µmol/mol NO
FF20511	1500 µmol/mol NO
XF003823B	250 µmol/mol C <sub>3</sub> H <sub>8</sub>
XF001034B	1000 µmol/mol C <sub>3</sub> H <sub>8</sub>

### 4.0 Reference Methods

Relevant measurement conditions employed by CENAM are described for respective analyte and concentration level as follows

#### 4.1 CO (50 – 1000 µmol/mol)

##### 4.1.1 GC-FID (Method 1)

The measurements were performed with one GC HP-6890 Series (S/N US00010745), equipped with Ni catalyst methanalyzer, EPC split/splitless injector, capillary column Poraplot Q, 30 m, 0,530 mm OD, 20 µm, carrier gas He flow at 11.6 ml/min, FID at 250 °C, Injector at 250 °C, Oven program: 200 °C, initial time 3.0 min, make-up Nitrogen

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flow 30 ml/min; valve box 140 °C; sample volume 1 ml, time table: 0.05 VGS-ON, 0.3 VGS-OFF.

#### **4.1.2 Specific Analyzers (Method 2)**

The analytical method was performed with one Specific Analyzer Thermo Environmental Instruments Inc. Model 48C Serial Number 48C-59612-5207081281CO. The operation principle is NDIR and was used an automatic sampler.

### **4.2 CO (5000 – 80000 µmol/mol)**

#### **4.2.1 GC-TCD (Method 1)**

The analytical method was performed with one GC HP-6890 Series (S/N US00010745), equipped with EPC split/splitless injector, capillary column Poraplot Q, 30 m, 0,530 mm OD, 20 µm, carrier gas He flow at 3.9 ml/min, TCD at 180 °C, Injector at 250 °C, Oven program: 125 °C, initial time 6.5 min, make-up He flow 3.0 ml/min; valve box 140 °C; sample volume 1 ml, time table: 0.05 VGS-ON, 0.3 VGS-OFF.

#### **4.2.2 Specific Analyzers (Method 2)**

To analyze carbon monoxide use was made of a specific analyzer of HORIBA INSTRUMENTS INC., Model VIA-510 Serial Number 4146198002 with operation principle NDIR and manual sampler.

### **4.3 CO<sub>2</sub> (70000 µmol/mol)**

#### **4.3.1 GC-TCD (Method 1)**

To analyze carbon dioxide, use was made of one GC HP-6890 Series (S/N US00010745), equipped with EPC split/splitless injector, capillary column Poraplot Q, 30 m, 0,530 mm OD, 20 µm, carrier gas: He flow at 3.9 ml/min, TCD at 180 °C, Injector at 180 °C, Oven program: 100 °C, initial time 4.0 min, make-up He flow 3.0 ml/min; valve box 140 °C; sample volume 1 ml, time table: 0.05 VGS-ON, 0.3 VGS-OFF.

#### **4.3.2 Specific Analyzers (Method 2)**

To analyze carbon dioxide a specific analyzer of LISTON SCIENTIFIC CORPORATION Model ENVIROMAX Serial Number 371 was used, with NDIR operation principle and an automatic sampler.

### **4.4 C<sub>3</sub>H<sub>8</sub> (250 – 1000 µmol/mol)**

#### **4.4.1 GC-FID (Method 1)**

To analyze propane, use was made of one GC HP-6890 equipped with FID, EPC packed injector, column made of SS, Porapak Q, mesh 80/100, 6 feet long, 1/8" OD. He gas carrier flow with 22 ml/min, Detector at 250 °C, Injector at 200 °C, Oven program: 2 minutes isothermally at 145 °C; make-up Nitrogen flow 25 ml/min; Temperature auxiliary (valve box) 140 °C; sample volume 1 ml; time table: 0.05 VGS-ON, 0.3 VGS-OFF. The flow was controlled with one OMEGA rotameter model FL-1807 in the injector

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valve outlet.

#### 4.4.2 GC-TCD (Method 2)

To analyze propane alternatively, use was made of one GC HP-5890 equipped with TCD, EPC SPLIT/SPLITLESS injector, column made of Silica, Porapak U, 25 m long X 0.53µm X 20µm. He gas carrier flow at 16 ml/min, Detector at 180 °C, Injector at 180 °C, Oven program: 4minutes isothermally at 90 °C; make-up flow He10 ml/min, reference flow He 25 ml/min; auxiliary temperature (valve box) with 140 °C; sample volume 1 ml; time table: 0.05 VGS-ON, 0.3 VGS-OFF. The flow was controlled by one OMEGA rotameter model FL-1807 in the injector valve outlet.

#### 4.5 NO (100 – 1500 µmol/mol)

To analyze nitric oxide, use was made of one specific analyzer of ROSEMOUNT ANALYTICAL INC., Model 951A Serial Number 0102177 with chemiluminescence operation principle and also an automatic sampler was used.

### 5.0 Measurement Results

#### 5.1 CARBON MONOXIDE (CO)

##### 5.1.1 CARBON MONOXIDE (CO) DATA

Measurement No. 1 (Method 1)	Date	Result CO (µmol/mol)	Standard Uncertainty (µmol/mol)	Number of sub-Measurements
XF001077B	07/06/01	49,287	0,12959	4
XF001009B	19/06/01	969,38	1,8214	4
CAL1582	11/07/01	4650,6	8,8836	4
CAL2132	11/07/01	9626,7	12,055	5
CAL1484	23/07/01	77670	66,859	4
Measurement No. 1 (Method 2)	Date	Result (µmol/mol)	Standard Uncertainty (µmol/mol)	Number of sub-Measurements
XF001077B	01/08/01	50,356	0,10639	3
XF001009B	01/08/01	963,01	5,3737	3
CAL1582	15/08/01	4664,58	14,316	4
CAL2132	15/08/01	9576,6	19,654	4
CAL1484	20/08/01	76873,7	83,506	3

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Measurement No. 2 (Method 1)	Date	Result ( $\mu\text{mol/mol}$ )	Standard Uncertainty ( $\mu\text{mol/mol}$ )	Number of sub-Measurements
XF001077B	11/06/01	49,198	0,10026	4
XF001009B	26/06/01	970,39	0,83727	5
CAL1582	12/07/01	4670,0	8,0080	5
CAL2132	12/07/01	96202	9,9338	5
CAL1484	24/07/01	76450	31,159	4
Measurement No. 2 (Method 2)	Date	Result ( $\mu\text{mol/mol}$ )	Standard Uncertainty ( $\mu\text{mol/mol}$ )	Number of sub-Measurements
XF001077B	01/08/01	49,599	0,15616	3
XF001009B	01/08/01	958,13	4,6132	3
CAL1582	16/08/01	4673,2	14,767	3
CAL2132	16/08/01	9578,8	16,474	3
CAL1484	21/08/01	76868,3	123,28	3

Measurement No. 3 (Method 1)	Date	Result ( $\mu\text{mol/mol}$ )	Standard Uncertainty ( $\mu\text{mol/mol}$ )	Number of sub-Measurements
XF001077B	21/06/01	49,342	0,27648	5
XF001009B	27/06/01	973,24	0,39578	5
CAL1582	13/07/01	4673,3	8,9657	5
CAL2132	13/07/01	9580,2	10,422	5
CAL1484	25/07/01	76386	74,584	5
Measurement No. 3 (Method 2)	Date	Result ( $\mu\text{mol/mol}$ )	Standard Uncertainty ( $\mu\text{mol/mol}$ )	Number of sub-Measurements
XF001077B	01/08/01	48,996	0,18751	3
XF001009B	01/08/01	959,97	4,4382	3
CAL1582	17/08/01	4673,83	14,718	3
CAL2132	17/08/01	9572,6	16,368	3
CAL1484	22/08/01	76950,3	13,295	3

### 5.1.2 CARBON MONOXIDE (CO) RESULTS WITH UNCERTAINTY

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Gas components Carbon Monoxide	Result (Assigned Value) ( $\mu\text{mol/mol}$ )	Coverage factor	Expanded Uncertainty ( $\mu\text{mol/mol}$ )
XF001077B	49,5	2	0,5
XF001009B	965,7	2	9,7
CAL1582	4667,6	2	46,7
CAL2132	9592,5	2	95,9
CAL1484	76866	2	768

## 5.2 CARBON DIOXIDE ( $\text{CO}_2$ )

### 5.2.1 CARBON DIOXIDE ( $\text{CO}_2$ ) DATA

Measurement No. 1 (Method 1)	Date	Result ( $\mu\text{mol/mol}$ )	Standard Uncertainty ( $\mu\text{mol/mol}$ )	Number of sub- Measurements
FF18058	28/08/01	68815,5	57,6	5

Measurement No. 1 (Method 2)	Date	Result ( $\mu\text{mol/mol}$ )	Standard Uncertainty ( $\mu\text{mol/mol}$ )	Number of sub- Measurements
FF18058	22/06/01	67218,0	202	5

Measurement No. 2 (Method 1)	Date	Result ( $\mu\text{mol/mol}$ )	Standard Uncertainty ( $\mu\text{mol/mol}$ )	Number of sub- Measurements
FF18058	29/0801	68904,3	74,7	6

Measurement No. 2 (Method 2)	Date	Result ( $\mu\text{mol/mol}$ )	Standard Uncertainty ( $\mu\text{mol/mol}$ )	Number of sub- Measurements
FF18058	06/07/01	67080,0	145	5

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Measurement No. 3 (Method 1)	Date	Result (μmol/mol)	Standard Uncertainty (μmol/mol)	Number of sub-Measurements
FF18058	30/08/01	68308,0	83,3	5
Measurement No. 3 (Method 2)	Date	Result (μmol/mol)	Standard Uncertainty (μmol/mol)	Number of sub-Measurements
FF18058	30/08/01	66941,0	26	3

### 5.2.2 CARBON DIOXIDE (CO<sub>2</sub>) RESULT AND UNCERTAINTY

Gas components Carbon Dioxide	Result (Assigned Value) (μmol/mol)	Coverage factor	Expanded Uncertainty (μmol/mol)
FF18058	67890,0	2	679

### 5.3 PROPANE (C<sub>3</sub>H<sub>8</sub>)

#### 5.3.1 PROPANE (C<sub>3</sub>H<sub>8</sub>) DATA

Measurement No. 1 Method 1	Date	Result (μmol/mol)	Standard Uncertainty (μmol/mol)	Number of sub-Measurements
XF003823B	01/08/29	247,27	1,513	3
XF001034B	01/08/29	1015,1	0,985	4
Measurement No. 1 Method 2	Date	Result (μmol/mol)	Standard Uncertainty (μmol/mol)	Number of sub-Measurements
XF003823B	01/08/25	247,41	0,407	3
XF001034B	01/08/25	1002	1,707	3

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Measurement No. 2	Date	Result ( $\mu\text{mol/mol}$ )	Standard Uncertainty ( $\mu\text{mol/mol}$ )	Number of sub-Measurements
XF003823B	01/08/30	253,65	0,776	5
XF001034B	01/08/30	999,90	1,188	3
Measurement No. 2	Date	Result ( $\mu\text{mol/mol}$ )	Standard Uncertainty ( $\mu\text{mol/mol}$ )	Number of sub-Measurements
XF003823B	01/08/27	251,79	0,283	4
XF001034B	01/08/27	981,04	1,769	4

Measurement No. 3	Date	Result ( $\mu\text{mol/mol}$ )	Standard Uncertainty ( $\mu\text{mol/mol}$ )	Number of sub-Measurements
XF003823B	01/08/31	251,93	0,612	4
XF001034B	01/08/31	965,07	2,369	5
Measurement No. 3	Date	Result ( $\mu\text{mol/mol}$ )	Standard Uncertainty ( $\mu\text{mol/mol}$ )	Number of sub-Measurements
XF003823B	01/08/28	254,61	1,582	4
XF001034B	01/08/28	992,41	1,309	4

### 5.3.2 PROPANE ( $\text{C}_3\text{H}_8$ ) RESULTS AND UNCERTAINTIES

Gas components Propane	Result (Assigned Value) ( $\mu\text{mol/mol}$ )	Coverage factor	Expanded Uncertainty ( $\mu\text{mol/mol}$ )
XF003823B	251,1	2	2,5
XF001034B	992,6	2	9,9

### 5.4 NITRIC OXIDE (NO)

#### 5.4.1 NITRIC OXIDE (NO) DATA

Measurement No. 1	Date	Result ( $\mu\text{mol/mol}$ )	Standard deviation ( $\mu\text{mol/mol}$ )	Number of sub-Measurements
FF17222	26/07/01	99,32	0,7482	3
FF20511	18/07/01	1496,95	2,0533	4

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Measurement No. 2	Date	Result (µmol/mol)	Standard deviation (µmol/mol)	Number of sub-Measurements
FF17222	27/07/01	98,77	0,5816	3
FF20511	24/07/01	1497,88	1,9946	4

Measurement No. 3	Date	Result (µmol/mol)	Standard deviation (µmol/mol)	Number of sub-Measurements
FF17222	30/07/01	98,64	0,5704	3
FF20511	25/07/01	1498,55	2,1716	4

#### 5.4.2 NITRIC OXIDE (NO) RESULTS AND UNCERTAINTIES

Gas components Nitric Oxide	Result (Assigned Value) (µmol/mol)	Coverage factor	Expanded Uncertainty (µmol/mol)
FF17222	98,9	2	1,5
FF20511	1497,8	2	15

## 6. 0 Procedure

### 6.1 Calibration Curves

CO, C<sub>3</sub>H<sub>8</sub> and NO samples were analyzed using **multipoint calibration curves by comparing sample response with each other of the CENAM's PRM**, while CO<sub>2</sub> sample results were calculated by direct comparison, according ISO-11095.

The concentration was calculated comparing the sample response with each other of the CENAM's PRM using response ratios, by bracketing or **direct comparison to observe the repeatability, the reproducibility and the instrumental drift**. The range of the primary standards must bracket the concentration of the sample, a minimum of the 4 primary standards were used to calibrate the analyzers. The sample and standards were analyzed at least three times **each by triplicate**.

Primary standards used in the calibration curve to 50 µmol/mol CO/N<sub>2</sub> in XF001077B cylinder:

**Table 2. CO/N<sub>2</sub> CENAM's PRM**

Reference Material	Cylinder number	Concentration (µmol/mol)
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CO/N <sub>2</sub>		
PRM-DMR-MPG-031	FF2220	9,94 ± 0,01
PRM-DMR-MPG-022	FF2225	24,94 ± 0,01
PRM-DMR-MPG-022	FF2251	24,97 ± 0,01
PRM-DMR-MPG-021	FF2076	49,94 ± 0,02
PRM-DMR-MPG-021	FF2119	49,47 ± 0,59
PRM-DMR-MPG-030	FF2196	99,87 ± 0,06
PRM-DMR-MPG-030	FF2174	100,68 ± 0,03

Primary standards used in the calibration curve to 1000 µmol/mol CO/N<sub>2</sub> in XF001009B cylinder:

**Table 3. CO/N<sub>2</sub> CENAM's PRM**

Reference Material	Cylinder number	Concentration (µmol/mol)
PRM-DMR-MPG-030	FF2196	99,87 ± 0,06
PRM-DMR-MPG-030	FF2174	100,68 ± 0,03
PRM-DMR-MPG-020	FF2231	249,56 ± 0,05
PRM-DMR-MPG-020	FF1949	250,07 ± 0,04
PRM-DMR-MPG-019	FF2193	500,56 ± 0,16
PRM-DMR-MPG-019	FF2163	495,64 ± 0,62
PRM-DMR-MPG-018	FF2018	1006,89 ± 0,24

Primary standards used in the calibration curve to 5000 µmol/mol CO/N<sub>2</sub> in CAL1582 cylinder:

**Table 4. CO/N<sub>2</sub> CENAM's PRM**

Reference Material	Cylinder number	Concentration (µmol/mol)
PRM-DMR-MPG-017	FF2239	2498,89 ± 0,28
PRM-DMR-MPG-017	FF2242	2492,25 ± 0,36
PRM-DMR-MPG-016	FF2292	4988,14 ± 1,53
PRM-DMR-MPG-016	FF2064	4985,69 ± 1,78
PRM-DMR-MPG-015	FF2262	10040,12 ± 2,23
PRM-DMR-MPG-015	FF1956	9991,28 ± 1,15
PRM-DMR-MPG-014	FF2079	19976,12 ± 1,51
PRM-DMR-MPG-014	FF2137	20000,80 ± 2,53

Primary standards used in the calibration curve to 80000 µmol/mol CO/N<sub>2</sub> in CAL1484 cylinder and 10000 µmol/mol CO/N<sub>2</sub> CAL 2132:

**Table 5. CO/N<sub>2</sub> CENAM's PRM**

Reference Material	Cylinder number	Concentration (µmol/mol)
PRM-DMR-MPG-013	FF2101	39970,29 ± 5,82
PRM-DMR-MPG-013	FF1978	39971,27 ± 4,94
PRM-DMR-MPG-032	FF1979	48029,88 ± 13,95
PRM-DMR-MPG-001	FF2142	60053,69 ± 12,28
PRM-DMR-MPG-001	FF1892	59962,66 ± 16,59

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PRM-DMR-MPG-011	FF2187	80049,12 ± 5,86
PRM-DMR-MPG-011	FF2063	80111,60 ± 9,68
PRM-DMR-MPG-011	FF1924	79990,59 ± 11,96

Primary standards used in the calibration curve to 70000 µmol/mol CO<sub>2</sub>/N<sub>2</sub> in FF17222 cylinder:

**Table 6. CO<sub>2</sub>/N<sub>2</sub> CENAM's PRM**

Reference Material	Cylinder number	Concentration (µmol/mol)
PRM-DMR-MPG-002	FF2001	78017,48 ± 16,00
PRM-DMR-MPG-001	FF2061	60200,83 ± 11,00

Primary standards used in the calibration curve to 250 µmol/mol C<sub>3</sub>H<sub>8</sub>/N<sub>2</sub> in XF003823B and 1000 µmol/mol C<sub>3</sub>H<sub>8</sub>/N<sub>2</sub> in XF001034B cylinders:

**Table 7. C<sub>3</sub>H<sub>8</sub>/N<sub>2</sub> CENAM's PRM**

Reference Material	Cylinder number	Concentration (µmol/mol)
PRM-DMR-MPG-010	FF2154	206,61 ± 0,10
PRM-DMR-MPG-010	FF2288	198,24 ± 0,12
PRM-DMR-MPG-009	FF2306	413,01 ± 0,13
PRM-DMR-MPG-008	FF1894	618,60 ± 0,19
PRM-DMR-MPG-007	FF2058	928,89 ± 0,43
PRM-DMR-MPG-007	FF1899	898,08 ± 0,55
PRM-DMR-MPG-011	FF2255	1103,52 ± 0,40

Primary standards used in the calibration curve to 100 µmol/mol NO/N<sub>2</sub> in FF17222 cylinder:

**Table 8. NO/N<sub>2</sub> CENAM's PRM**

Reference Material	Cylinder number	Concentration (µmol/mol)
PRM-DMR-MPG-029	FF2238	99,52 ± 0,13
PRM-DMR-MPG-028	FF2083	299,04 ± 0,37
PRM-DMR-MPG-027	FF2084	598,49 ± 0,83
PRM-DMR-MPG-026	FF2229	994,88 ± 1,28

Primary standards used in the calibration curve to 1500 µmol/mol NO/N<sub>2</sub> in FF20511 cylinder:

**Table 9. NO/N<sub>2</sub> CENAM's PRM**

Reference Material	Cylinder number	Concentration ( $\mu\text{mol/mol}$ )
PRM-DMR-MPG-026	FF2229	$994,88 \pm 1,28$
PRM-DMR-MPG-025	FF2098	$1495,47 \pm 1,86$
PRM-DMR-MPG-024	FF2148	$1792,24 \pm 2,24$

## 7. Sample preparation and sampling

The compressed gas samples were acclimated (thermal equilibrium between room and cylinder) and rolled prior analysis. The sampling systems to GC analysis consist of a regulator, a flow controller (rotameter) and a sampler line. Sampling system to specific analyzers was domestic automatic system sampler.

## 8. Uncertainty

There are potential sources that influence the uncertainty of the final measurement result. Depending on the equipment, the applied analytical method and the target uncertainty of the final result, they have to be taken into account or can be neglected.

To Describe in detail how the uncertainty components were estimated and how they were combined to calculate the overall uncertainty, a list of potential uncertainty sources is given. This list may not be complete and is compiled from draft ISO-Standards currently under development in ISO/TC158.

### 8.1 Uncertainty estimation

#### 8.1.1 Uncertainty of primary standard mixtures

The uncertainty of the primary standard mixtures has been calculated applying the Law of propagation of uncertainties to the equation 1 of the ISO/DIS 6142 (1999). Whose uncertainty sources are: the uncertainty in molar mass, the uncertainty on the weighing and the uncertainty in the purity analysis.

The uncertainty of weighing has been calculated using the Law of propagation of uncertainties to the model for single substitution weighing:

$$m_T = m_R + \rho_a \cdot (V_T - V_R) + \Delta I \omega / S$$

where:

$m_T$  = mass of the tested cylinder

$m_R$  = reference mass

$\rho_a$  = air density

$V_T$  = weights used in the tested cylinder

$V_R$  = weights used in the reference cylinder

$\Delta I\omega$  = difference in balance readouts

S = balance sensitivity

The uncertainty of molar masses has been taken as a type B evaluation of uncertainty from the IUPAC assuming a uniform distribution.

The next table summarizes the uncertainty sources and the way there were calculated or controlled.

**Table 10. Uncertainty sources and status**

Uncertainty source	Status	Type of evaluation
Uncertainty related to the balance and the weights:		
Resolution of balance	Controlled by weighing enough amount of each gas	-
Accuracy of balance including	Calibrated balance, but the accuracy comes from the weights used (see * below)	-
Linearity	Evaluated by weighing procedure	A
Incorrect zero point	Evaluated by weighing procedure	A
Drift (thermal and time effects)	Evaluated by weighing procedure	A
Instability due to draught	Evaluated by weighing procedure	A
Location of cylinder on the balance pan	Controlled by balance calibration procedure and using a bulldozer load plate	-
Uncertainties in the weights used *	Obtained from a calibration certificate	B
Buoyancy effects on the weights used	Evaluated with the environmental conditions and from a calibration certificate	A and B
Uncertainties related to the gas cylinder:		
Mechanical handling of cylinder: Loss of metal, paints or labels from surface of cylinder Loss of metal from threads of valve/fitting Dirt on cylinder, valves or associated fitting	Controlled by the cylinders clean procedure and carefully handling of them	-
Absorption/desorption effects on the external cylinder surface		
Buoyancy effects on the cylinder itself Cylinder temperature differs from surrounding air due to e.g. filling with gas Change of cylinder volume during filling Change of density of surrounding air due to changes in temperature, air pressure, humidity and carbon dioxide content	Controlled by temperature equilibrium between the reference cylinder and tested cylinder and their environment, using the temperature measurement of the external surface of the cylinder The cylinder expansion has been taken into account in the air buoyancy correction Changes in temperature, air pressure and humidity have been considered in the weighing procedure, but not carbon dioxide content, cause until now we have considered that air density is not a significant uncertainty source	-  A and B  A and B

Uncertainty in determination of external cylinder volume	In our measurements it is not considered cause we have used a reference cylinder from exactly the same shape (including the valve)	-
Uncertainties related to the component gases		
Residual gas in cylinder	Considered as a correction in balance gas, taken into account gotten vacuum as a previous purge with nitrogen	A and B
Leakage; Leakage of air into the cylinder after evacuation Leakage of gas from the cylinder valve during filling Escape of gas from cylinder into transport lines	Controlled by the filling procedure	-
Gas remaining in transfer system when weight loss method is used	Not apply	-
Absorption/reaction of components on internal cylinder surface	Controlled by the cylinder type and	-
Reaction between components	Controlled by permitted impurities in the parent gases and cautions taken in the preparation procedure	-
Impurities in the gases used	Evaluated by analytical verification of critical impurities	A and B
Impurities in the component gases	Evaluated by analytical verification of critical impurities	A and B
Impurities present in the balance gas (or in other components)	Evaluated by analytical verification of critical impurities	A and B
One or more of the mixture components present in other component gases	Evaluated by analytical verification of critical impurities	A and B
Insufficient homogenization	Rolling cylinders enough time	-
Uncertainty of molecular mass	Taken from IUPAC (reference data)	B

### 8.1.2 Uncertainties related to the analysis

- \* Repeatability and selectivity of the analyzer
- \* Selectivity was performed with gas chromatography, which separate the sample in each component and don't affect the background or interference of matrix.
- \* Appropriateness of the calibration curve (model and its residuals)
- \* The quantification method used to know the analytes concentration was bracketing method and direct comparison, using Reference Materials. In order to control the instrumental drift were used Reference Materials too.

Coverage factor:  $k = 2$

All calculations were made using B\_LEAST computer program. ISO/DIS 6143.2

To evaluate the true value we combined results from two methods used in each case.  
**Was used one data sheet based in the ISO GUM. J. of Research of the NIST, 105, 571**  
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**8.1.3 Expanded uncertainty:**

$$U = \sqrt{U_{\text{sample}}^2 + u_{\text{std1}}^2 + u_{\text{std2}}^2 + (s_{\text{std1divider}}^2/\sqrt{n}) + (s_{\text{std2divider}}^2/\sqrt{n})}$$

Where:

$u_{\text{sample}}^2$  = uncertainty of sample measurements mean

$u_{\text{std1}}^2$  = uncertainty of standard # 1 measurements mean

$u_{\text{std2}}^2$  = uncertainty of standard # 2 measurements mean

$s_{\text{std1divider}}^2/\sqrt{n}$  = uncertainty related with the gas divider including standard # 1

$s_{\text{std2divider}}^2/\sqrt{n}$  = uncertainty related with the gas divider including standard # 2

**9. CENAM and NIST results**

The concentration values reported by CENAM are the averages of both methods utilized except in the case of nitric oxide where only one method was used. NIST values are certified values

**Table 11. Reported concentration and Uncertainty data**

CYLINDER NUMBER	ANALYTE	CONCENTRATION, ( $\mu\text{mol/mol}$ )					
		CENAM $\pm$ U	$U_{\text{REL}}$ CENAM (%)	NIST $\pm$ U	$U_{\text{REL}}$ NIST (%)	DIFFERENCE IN CONCENTRATION ( $\mu\text{mol/mol}$ )	% DIFFERENCE
XF003823B	C <sub>3</sub> H <sub>8</sub>	251,1 $\pm$ 2,5	0,99	246,5 $\pm$ 1,0	0,41	4,9	2,0
XF001034B	C <sub>3</sub> H <sub>8</sub>	992,6 $\pm$ 9,9	0,99	979,1 $\pm$ 6,6	0,67	13,5	1,4
FF-17222	NO	98,9 $\pm$ 1,5	1,52	97,5 $\pm$ 0,8	0,82	1,4	1,4
FF-20511	NO	1497,8 $\pm$ 15	1,00	1487 $\pm$ 6	0,40	10,8	0,7
XF001077B	CO	49,5 $\pm$ 1,5	3,03	48,76 $\pm$ 0,31	0,64	0,74	1,5
XF001009B	CO	965,7 $\pm$ 9,7	1,00	970,0 $\pm$ 5,8	0,60	4,3	0,4
CAL-1582	CO	4667,6 $\pm$ 46,7	1,00	4680,0 $\pm$ 47	1,00	12,4	0,3
CAL-2132	CO	9592,5 $\pm$ 95,9	1,00	9600 $\pm$ 100	1,04	7,5	0,1
CAL-1484	CO	76866 $\pm$ 768	1,00	76800 $\pm$ 800	1,04	66	0,1

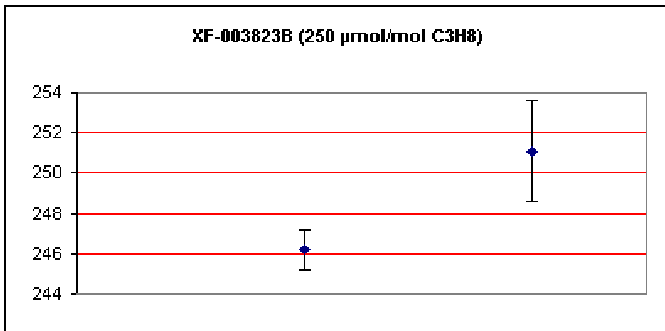
SIM.8.S1

FF-18058	CO <sub>2</sub>	67890 ± 679	1,00	68000 ± 300	0,44	110	0,2
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### 10. Graphical comparisons

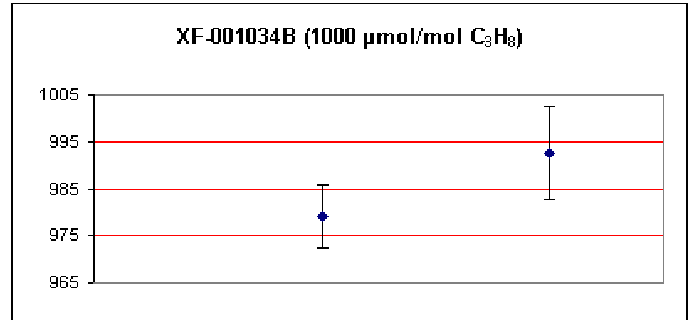
**XF-003823B (250 µmol/mol C<sub>3</sub>H<sub>8</sub>)**

Laboratory Name	Certified Value (µmol/mol)	Expanded Uncertainty (µmol/mol)	Difference (µmol/mol)	% Difference
NIST	246.2	1	4.9	2
CENAM	251.1	2.5		



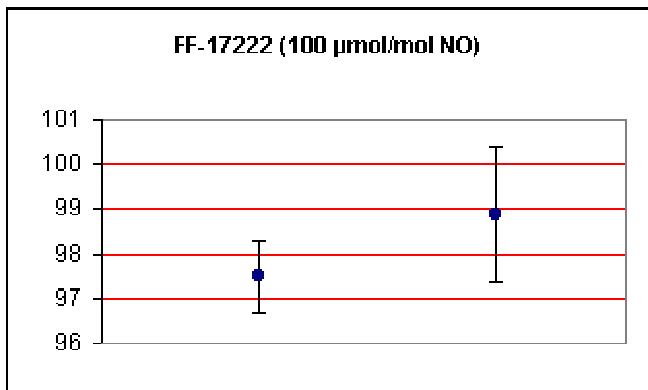
**XF-001034B (1000 µmol/mol C<sub>3</sub>H<sub>8</sub>)**

Laboratory Name	Certified Value (µmol/mol)	Expanded Uncertainty (µmol/mol)	Difference (µmol/mol)	% Difference
NIST	979.1	6.6	13.5	1.4
CENAM	992.6	9.9		



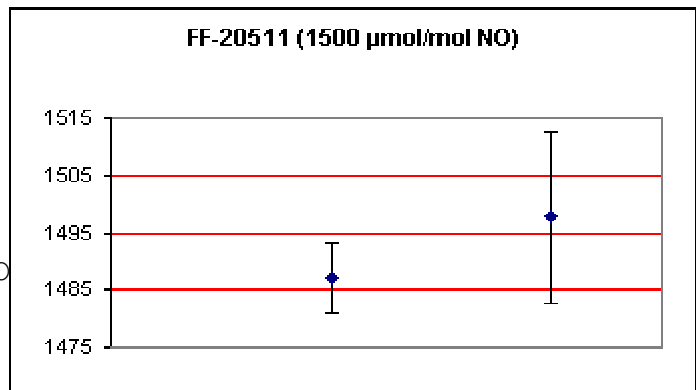
**FF-17222 (100 µmol/mol NO)**

Laboratory Name	Certified Value (µmol/mol)	Expanded Uncertainty (µmol/mol)	Difference (µmol/mol)	% Difference
NIST	97.5	0.8	1.4	1.4
CENAM	98.9	1.5		



**FF-20511 (1500 µmol/mol NO)**

Laboratory Name	Certified Value (µmol/mol)	Expanded Uncertainty (µmol/mol)	Difference (µmol/mol)	% Difference
NIST	1487	6	10.8	0.7
CENAM	1497.8	15		

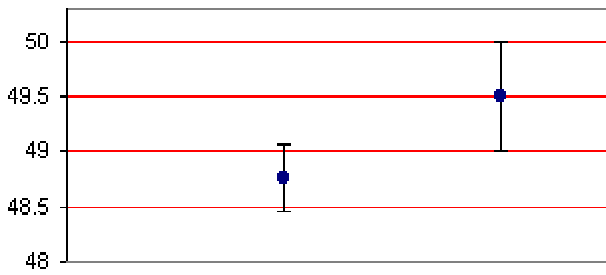


ISO

**XF-01077B (50 µmol/mol CO)**

Laboratory Name	Certified Value (µmol/mol)	Expanded Uncertainty (µmol/mol)	Difference (µmol/mol)	% Difference
NIST	48.76	0.31	0.74	1.5
CENAM	49.5	0.5		

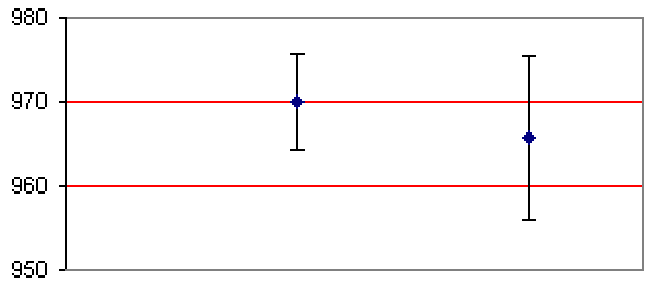
**XF-01077B (50 µmol/mol CO)**



**XF-01009B (1000 µmol/mol CO)**

Laboratory Name	Certified Value (µmol/mol)	Expanded Uncertainty (µmol/mol)	Difference (µmol/mol)	% Difference
NIST	970	5.8	4.3	0.4
CENAM	965.7	9.7		

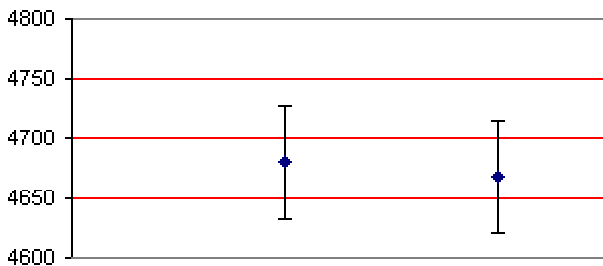
**XF-01009B (1000 µmol/mol CO)**



**CAL-1582 (5000 µmol/mol CO)**

Laboratory Name	Certified Value (µmol/mol)	Expanded Uncertainty (µmol/mol)	Difference (µmol/mol)	% Difference
NIST	4680	47	12.4	0.3
CENAM	4667.6	46.7		

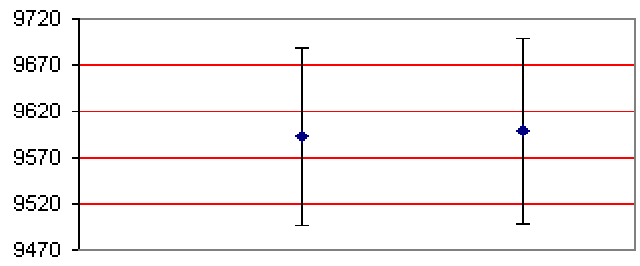
**CAL-1582 (5000 µmol/mol CO)**



**CAL-2132 (10000 µmol/mol CO)**

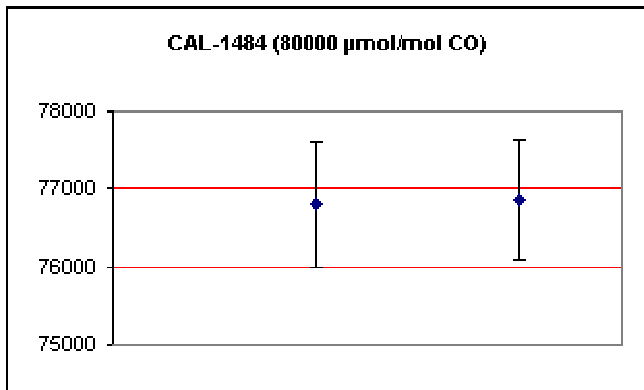
Laboratory Name	Certified Value (µmol/mol)	Expanded Uncertainty (µmol/mol)	Difference (µmol/mol)	% Difference
NIST	9592.5	95.9	7.5	0.1
CENAM	9600	100		

**CAL-2132 (10000 µmol/mol CO)**

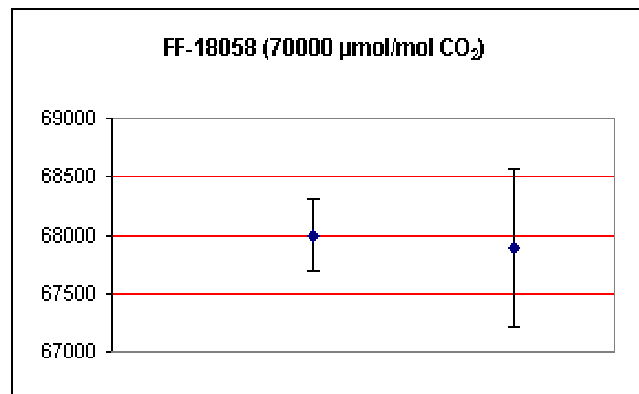


**CAL-1484 (80000 µmol/mol CO)**

Laboratory Name	Certified Value (µmol/mol)	Expanded Uncertainty (µmol/mol)	Difference (µmol/mol)	% Difference
NIST	76800	800	66	0.1
CENAM	76866	768		

**FF-18058 (70000 µmol/mol CO<sub>2</sub>)**

Laboratory Name	Certified Value (µmol/mol)	Expanded Uncertainty (µmol/mol)	Difference (µmol/mol)	% Difference
NIST	68000	300	110	0.2
CENAM	67890	679		



## 11. Equivalence table

CYLINDER NUMBER	ANALYTE	CONCENTRATION, (µmol/mol)					
		CENAM ± U	U <sub>REL</sub> CENAM (%)	NIST ± U	U <sub>REL</sub> NIST (%)	DIFFERENCE IN CONCENTRATION (µmol/mol)	D <sub>IJ</sub>
XF003823B	C <sub>3</sub> H <sub>8</sub>	251,1 ± 2,5	0,99	246,5 ± 1,0	0,41	4,9	1.82
XF001034B	C <sub>3</sub> H <sub>8</sub>	992,6 ± 9,9	0,99	979,1 ± 6,6	0,67	13,5	1.13
FF-17222	NO	98,9 ± 1,5	1,52	97,5 ± 0,8	0,82	1,4	0.82
FF-20511	NO	1497,8 ± 15	1,00	1487 ± 6	0,40	10,8	0.67
XF001077B	CO	49,5 ± 1,5	3,03	48,76 ± 0,31	0,64	0,74	0.48
XF001009B	CO	965,7 ± 9,7	1,00	970,0 ± 5,8	0,60	4,3	0.38
CAL-1582	CO	4667,6 ± 46,7	1,00	4680,0 ± 47	1,00	12,4	0.19
CAL-2132	CO	9592,5 ± 95,9	1,00	9600 ± 100	1,04	7,5	0.05
CAL-1484	CO	76866 ± 768	1,00	76800 ± 800	1,04	66	0.06
FF-18058	CO <sub>2</sub>	67890 ± 679	1,00	68000 ± 300	0,44	110	0.15

$$D_{ij} = \frac{X_i - X_j}{\sqrt{u_i^2 + u_j^2}}$$

SIM.8.S1

$X_i$  = Value of laboratory  $i$

$X_j$  = Value reference (laboratory  $j$ )

$u_i$  = uncertainty of laboratory  $i$

$u_j$  = uncertainty of reference laboratory

The present work was developed for CENAM's Gas Metrology Group, Carlos E. Carbajal-Alarcon, Francisco Rangel-Murillo, Carlos Ramirez-Nambo, Jorge Koelliker-Delgado with collaboration of Esther Castro-Galvan and Alejandro Perez –Castorena.