# International Comparison

## Final Report

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## Field

Amount of substance

## Subject

Comparison of measurements of carbon monoxide, carbon dioxide, and propane in nitrogen (car exhaust gas measurements)

## Participants

CZ (CMI-CHMI), IT (IMGC), NL (NMi VSL), PO (GUM), PT (IPQ), SA (CSIR-NML), SK (SMU)

## Organising body

EUROMET

## Rationale

Following-up the CCQM-K3 key comparison on "automotives", EUROMET accepted the project proposal for the organisation of a regional key comparison. The objective of this EUROMET key comparison are essentially the same as for the CCQM-K3 comparison: to compare the measurement capabilities of national metrological institutes (NMIs) in measuring amount of substance fractions of carbon monoxide, carbon dioxide, and propane in nitrogen.

## Introduction

NMi Van Swinden Laboratorium operated as pilot laboratory both in CCQM-K3 and in this comparison. The selected PSMs for this comparison were individually prepared using gravimetry and thoroughly studied for their chemical composition and stability. A long-term experience in the behaviour of these mixtures and the technical challenges in preparing batches of very similar mixtures is available at the pilot laboratory.

A target of 1% is maintained for the required agreement between a national metrology institute and the key comparison reference value. The 1% target had a direct impact on the choice of the analytical reference methods and it was decided that the preferred analytical methods for gas analysis in general would be:

- High accuracy mass spectroscopy,
- Isotope dilution mass spectroscopy,
- Gas chromatography,
- Chemiluminescence and Fluorescence,
- Non dispersive infrared spectroscopy

Furthermore, the difference observed between the value of a national metrology institute and the key comparison reference value should not exceed the combined expanded uncertainty of this difference.

The uncertainty calculations used during this comparison are based on the experience gained in CCQM-K3. All calculations made are fully compliant to the principles of the "Guide to the expression of uncertainty in measurement" (GUM), and represent state of the art in gas analysis.

## Measurement standards

The design of the comparison was adopted from CCQM-K3. The gas mixtures were prepared by means of primary methods (gravimetry) at the pilot laboratory NMi VSL and in order to do the whole comparison in a limited time frame, a batch of 6 mixtures was produced. There are small differences in the actual property values of these mixtures, which makes working with a single reference value undesirable. The differences in the compositions are of the same order of magnitude as the (expected) differences between laboratories, so that these two aspects are interfering.

Apart of the time frame in this set-up, there is another practical consideration to use a batch of very similar mixtures. From previous experience as well as from logistic problems in this key comparison, it is known that there are sometimes problems with customs or other authorities. These problems may in the worst case eventually lead to the loss of a gas mixture. Obviously, this has dramatic consequences if it is *the* mixture that is lost, rather than if it is 'only' one mixture out of the batch. For the participating national metrology institute, the latter case is still quite unsatisfactory, but in the design used, a new cylinder could be shipped without having a dramatic impact on the whole key comparison.

The nominal amount of substance ratios of CO, $CO_2$ and $C_3H_8$ in nitrogen, as used in this key comparison, are summarised in table 1.

**Table 1 : Nominal amount of substance ratios**

| Component | x (mmol/mol) |
|---|---|
| CO | 32 |
| $CO_2$ | 135 |
| $C_3H_8$ | 2,05 |
| $N_2$ | Balance |

## Schedule

The cylinders were shipped November 1999. A formal deadline for submission of results was not set. The measurements were carried out in the period January and May 2000. Reports were received until September 2000.

## Measurement protocol

The measurement protocol requested each laboratory to perform at least 3 measurements, with independent calibrations. The replicates, leading to a measurement, were to be carried out under repeatability conditions. The protocol informed the participants about the nominal concentration ranges, given as 2 – 4 mmol/mol carbon monoxide, 100 – 140 mmol/mol carbon dioxide, and 1,8 – 2,2 mmol/mol propane, and nitrogen as balance. The laboratories were also requested to submit a summary of their uncertainty evaluation used for estimating the uncertainty of their result.

## Measurement equation

The preparation of the gas mixtures has taken place using the substitution method. The model used to describe the preparation reads as follows. The basic equation for the weighing of the reference cylinder reads as follows

$$C + ep - V_c \rho^{air} = R + W - V_R \rho^{air} - W \frac{\rho^{air}}{\rho^S} \tag{1}$$

and that for the sample cylinder

$$C + eq - V_c \rho^{air} = S + M - V_S \rho^{air} - M \frac{\rho^{air}}{\rho^S} \tag{2}$$

where the symbols have the following meaning
$C$      weight contra mass (comparator)
$R$      weight reference cylinder
$S$      weight sample cylinder
$W$      total mass of added mass pieces to reference cylinder
$M$      total mass of added mass pieces to sample cylinder
$e$      calibration factor (reading → mass)
$p$      reading reference cylinder
$q$      reading sample cylinder
$V_C$      volume contra mass
$V_R$      volume reference cylinder
$V_S$      volume sample cylinder
$\rho^{air}$      density of air
$\rho^S$      density of mass pieces

The basic equation for the difference between reference and sample cylinder is given by

$$w_j = e_j(q_j - p_j) + (W_j - M_j)\left(1 - \frac{\rho_j^{air}}{\rho^S}\right) + \rho_j^{air}(V_{S,j} - V_R) \tag{3}$$

which follows from subtracting (2) from (1). The subscripts $j$ denote the variables that are determined in every cycle $j$, where $j = 0..n$ ($n$ is the number of parent gases the mixture).

The expression in equation (3) forms the basis for the computation of the uncertainty in the assigned value. The assignment of the amount of substance fractions is based on the mass brought in, and the compositions of the parent gases. In the case of propane, a pre-mixture has been used, which has been prepared in a similar way as the cylinders used for the key comparison.

The complete process involves 5 weighings, a weighing for each of the four components, and for the evacuated cylinder (= $w_0$). The results of a typical cylinder are given in tables 2-5.

**Table 2 : Uncertainty evaluation $w_{CO}$**

| Parameter | Estimate | u | sensitivity coefficient | uncertainty contribution (mg) | degrees of freedom |
|---|---|---|---|---|---|
| e (g) | 1.000 | $1.947\ 10^{-3}$ | $8.340\ 10^{-1}$ | 1.62 | 2 |
| $\Delta q$ (g) | $8.340\ 10^{-1}$ | $1.477\ 10^{-3}$ | 1.000 | 1.48 | 3 |
| $\Delta W$ (g) | $7.300\ 10^{1}$ | $2.956\ 10^{-5}$ | $9.999\ 10^{-1}$ | 0.03 | $\infty$ |
| $\rho^{air}$ (g/dm$^3$) | 1.187 | $6.706\ 10^{-4}$ | $9.605\ 10^{-3}$ | 0.01 | $\infty$ |
| $\Delta V$ (dm$^3$) | $4.800\ 10^{-4}$ | $3.000\ 10^{-3}$ | 1.187 | 3.56 | 1 |
| $\rho^{S}$ (g/dm$^3$) | $8.000\ 10^{3}$ | $2.000\ 10^{-3}$ | $1.354\ 10^{-6}$ | 0.00 | $\infty$ |
| w(j) | | | | 4.18 | |

**Table 3: Uncertainty evaluation of $w_{CO2}$**

| Parameter | Estimate | u | sensitivity coefficient | uncertainty contribution | degrees of freedom |
|---|---|---|---|---|---|
| e (g) | 1.000 | $1.080\ 10^{-3}$ | $8.605\ 10^{-1}$ | 0.93 | 2 |
| $\Delta q$ (g) | $8.605\ 10^{-1}$ | $8.165\ 10^{-4}$ | 1.000 | 0.82 | 3 |
| $\Delta W$ (g) | $9.300\ 10^{1}$ | $2.678\ 10^{-5}$ | $9.999\ 10^{-1}$ | 0.03 | $\infty$ |
| $\rho^{air}$ (g/dm$^3$) | 1.187 | $6.719\ 10^{-4}$ | $1.285\ 10^{-2}$ | 0.01 | $\infty$ |
| $\Delta V$ (dm$^3$) | $1.227\ 10^{-3}$ | $3.000\ 10^{-3}$ | 1.187 | 3.56 | 1 |
| $\rho^{S}$ (g/dm$^3$) | $8.000\ 10^{3}$ | $2.000\ 10^{-3}$ | $1.724\ 10^{-6}$ | 0.00 | $\infty$ |
| w(j) | | | | 3.77 | |

**Table 4: uncertainty evaluation of $w_{C3H8}$**

| Parameter | Estimate | u | sensitivity coefficient | u(w) mg | degrees of freedom |
|---|---|---|---|---|---|
| e (g) | 1.000 | $7.905\ 10^{-4}$ | $6.247\ 10^{-1}$ | 0.49 | 2 |
| $\Delta q$ (g) | $6.247\ 10^{-1}$ | $6.048\ 10^{-4}$ | 1.000 | 0.60 | 3 |
| $\Delta W$ (g) | $1.260\ 10^{2}$ | $3.284\ 10^{-5}$ | $9.999\ 10^{-1}$ | 0.03 | $\infty$ |
| $\rho^{air}$ (g/dm$^3$) | 1.186 | $6.726\ 10^{-4}$ | $1.902\ 10^{-2}$ | 0.01 | $\infty$ |
| $\Delta V$ (dm$^3$) | $3.273\ 10^{-3}$ | $3.000\ 10^{-3}$ | 1.186 | 3.56 | 1 |
| $\rho^{S}$ (g/dm$^3$) | $8.000\ 10^{3}$ | $2.000\ 10^{-3}$ | $2.335\ 10^{-6}$ | 0.00 | $\infty$ |
| w(j) | | | | 3.64 | |

**Table 5: Uncertainty evaluation of $w_{N2}$**

| Parameter | Estimate | u | sensitivity coefficient | uncertainty contribution | degrees of freedom |
|---|---|---|---|---|---|
| e (g) | 1.000 | $1.225\ 10^{-3}$ | $4.502\ 10^{-1}$ | 0.55 | 2 |
| $\Delta q$ (g) | $4.502\ 10^{-1}$ | $9.428\ 10^{-4}$ | 1.000 | 0.94 | 3 |
| $\Delta W$ (g) | $2.590\ 10^{2}$ | $5.921\ 10^{-5}$ | $9.999\ 10^{-1}$ | 0.06 | $\infty$ |
| $\rho^{air}$ (g/dm$^3$) | 1.186 | $6.725\ 10^{-4}$ | $4.737\ 10^{-2}$ | 0.03 | $\infty$ |
| $\Delta V$ (dm$^3$) | $1.500\ 10^{-2}$ | $3.000\ 10^{-3}$ | 1.186 | 3.56 | 1 |
| $\rho^{S}$ (g/dm$^3$) | $8.000\ 10^{3}$ | $2.000\ 10^{-3}$ | $4.800\ 10^{-6}$ | 0.00 | $\infty$ |
| w(j) | | | | 3.72 | |

From these evaluations, it has become apparent that the largest uncertainty contribution is coming from the volume expansion $\Delta V$; it has been assumed in the calculations to be 15 ml, with an uncertainty of 3 ml. In the calculation of $\Delta V$, it is assumed that the dependence of $\Delta V$ on the internal pressure is linear. Part of the uncertainty of 3 ml deals with this aspect; another component contained is the uncertainty in the evaluation of $V_S$ anyway.

For all cylinders of the batch, the values for the uncertainty components given in tables 4-7 are representative. The differences for the estimates (the values of the parameters) are relevant though. For the computation of the uncertainty of the components, a combined standard uncertainty of 4 mg for all components in all mixtures has been used.

In the uncertainty from preparation, furthermore the uncertainty from purity verification/composition of the parent gases is contained. The component of uncertainty hardly plays any role at all. The data from the purity verification/composition of the parent gases has been used for computing the gravimetric composition, as an amount of substance fraction.

A second main contributor to the uncertainty of the reference value is the uncertainty from verification. The verification process is used to confirm the gravimetric value. The uncertainty estimation of the verification is complex, and in view of the discussions of the incorporation of correlations in the estimation process, not yet complete. In order to keep in the time frame of this key comparison, a value for the uncertainty from verification has been derived from stability data. In stability data on the components, in principle, the following uncertainty components are contained
– stability of the reference material
– uncertainty from (different suites of) PRMs/PSMs used for calibration
– calibration model
– position of the "unknown" on the curve
– lack of fit
– repeatability of measurement
– number of replicates
Apart from the first component, for a single verification, all other components are relevant. As it is reasonable to expect that the stability of the components of interest ($CO_2$, CO, and $C_3H_8$) in nitrogen is not an issue, the stability data form a valuable source of information.

**Stability data for CO**
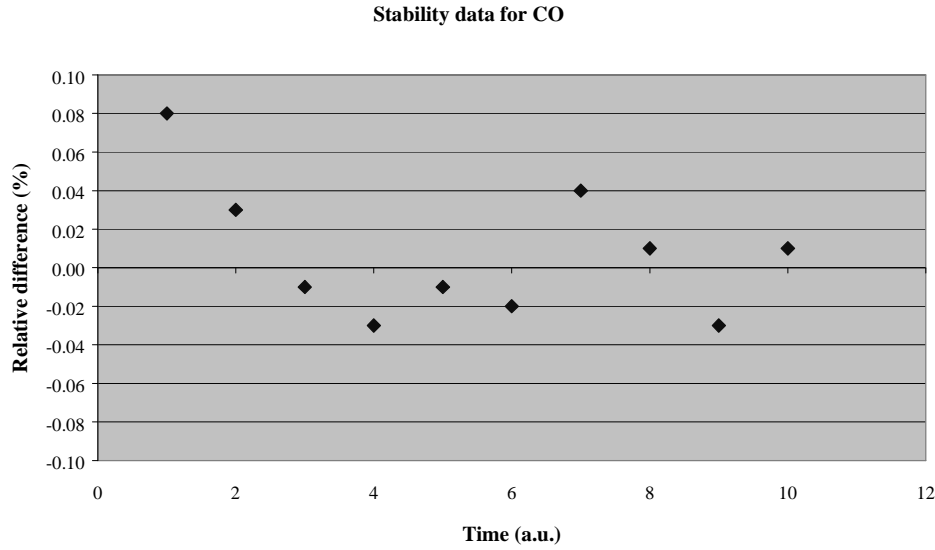
**Figure 1: Stability data of CO in nitrogen**

From the stability data, it becomes apparent that there is no drift, and it is also observed that the mean observed value is very close to the gravimetric value. Otherwise, an extra bias component in the uncertainty calculation had to be accounted for. In the stability data, 'reproducibility' components like calibration, operator etc. is contained, so that no "extras" are needed. A typical stability chart is shown in figure 1.From the theory of analysis of variance (ANOVA), the following expressions can be obtained for $MS_{among}$, the mean square "among groups"

$$MS_{among} = ns_A^2 + s_r^2 \qquad (4)$$

and

$$MS_{among} = ns^2 \qquad (5)$$

where $s^2$ denotes the variance of the group means, $n$ the number of replicates in each group, $s_A^2$ the among group variance, and $s_r^2$ the repeatability variance. Each "group" represents a data point in time. The significance in these expressions is, that apparently the variance of the data points accounts for both the among-group effects as well as for the effects of repeatability of measurement. These among group effects include calibration, operator, suite of PSMs/PRMs etc..

The standard uncertainty in each of the data points of figure 1 can be expressed as

$$u_{stab}^2 = s_A^2 + \frac{s_r^2}{n} = s^2 = Var(\Delta y) \qquad (6)$$

where $\Delta y$ denotes the relative difference between measured and gravimetric value. For the evaluation of this uncertainty component, $y_{grav}$ can be taken as a constant. This approach only works if
– there is no drift
– there is no bias
– no additional variance component due to instability
– the number of calibrants in the curve and the number of replicate measurements are constant
– repeatability of measurement does not change
– concentration level of the stability cylinder is relevant to the mixture in question

–    the lack of fit, repeatability of measurement etc. of the measurement in question is in line with the relevant parameters in the measurement of the stability cylinder

These assumptions are very important. Failing to check any of them may completely invalidate the approach.

It should be noted that this approach does not provide, in itself, any positive evidence that the estimator obtained for the uncertainty from verification is valid for the present case. Therefore, it cannot substitute for the approach of evaluating the experiment. This method is –under the assumptions stated– valid as a counter check on the evaluation method of a single experiment, as there is obviously a relationship between the two. Finally, the method only works if on all intermediate levels the method is performing within specifications.

For a typical mixture, the following results have been obtained, whereby for $u_{ver}$ the standard deviation $s$ is used (table 6).

**Table 6: Uncertainty components for a typical automotive mixture**

|  | $u_{grav}$ (%,rel.) | $u_{ver}$ (%,rel.) |
|---|---|---|
| CO | 0,020 | 0,030 |
| $CO_2$ | 0,003 | 0,030 |
| $C_3H_8$ | 0,012 | 0,056 |

The results from table 6 have been used to compute the uncertainty in the assigned (reference) value

$$U_{gravR} = k u_{gravR} \tag{7}$$

where

$$u_{gravR} = \sqrt{u_{grav}^2 + u_{ver}^2} \tag{8}$$

and $k = 2$. The relative uncertainty $u_{gravR}$ has been used to compute the combined standard uncertainty of the reference value for all mixtures.

## Measurement methods

The following methods of measurement and calibration methods have been employed (table 7).

**Table 7 : Measurement and calibration methods**

| Laboratory | Measurement method | Calibration method |
|---|---|---|
| SMU | GC; FID ($C_3H_8$), TCD (CO, $CO_2$) | Linear regression (5 points), weighted |
| IMGC | GC; FID ($C_3H_8$), TCD ($CO_2$) | Linear regression (3 points) |
| IPQ | GC; TCD | Second order polynomial ($CO_2$); linear regression (CO and $C_3H_8$) |
| CSIR-NML | NDIR | Polynomial regression (6 points) weighted |
| GUM | GC; FID ($C_3H_8$), TCD (CO, $CO_2$) | Linear regression (3 points) |
| CMI-CHMI |  | No information provided |

# Results

Usually all participants perform analyses on the same artefact and the key comparison reference value is calculated from the mean of the individual results. In the current comparison on gas mixtures, measurements were performed on individually prepared gas mixtures with (slightly) different concentrations. Since the pilot laboratory prepared these mixtures using the same methods and materials, the individual gravimetric values can be adopted as reference values, despite of the small differences that exist. The problem is that these small differences are of the same order of the differences found between the national metrological institutes, and thus influencing the outcome of the key comparison if it would be operated with a single reference value.

In order to evaluate the differences between the participating national metrology institutes, the difference between the gravimetric and analysed values has been taken as starting point. The results are expressed as degree of equivalence, defined as

$$D_i = x_{lab} - x_{grav} \tag{9}$$

where on the right-hand side the index *i* has been dropped. The combined standard uncertainty of the degree of equivalence can be expressed as

$$u(D_i) = \sqrt{u_{lab}^2 + u_{gravR}^2} \tag{10}$$

and the expanded uncertainty, at a 95% confidence level

$$U(D_i) = 2\sqrt{u_{lab}^2 + u_{gravR}^2} \tag{11}$$

that is, $k = 2$.

In the tables 8-10, all results of this key comparison are presented. The tables contain the following information

| | |
|---|---|
| Cylinder | Identification code of cylinder |
| $x_{grav}$ | Assigned amount of substance fraction of a component |
| $U_{gravR}$ | Expanded uncertainty of the assigned value $x_{grav}$, $k = 2$ |
| $x_{lab}$ | Result as reported by the participant |
| $k_{lab}$ | Coverage factor as reported by participant |
| $U_{lab}$ | Expanded uncertainty as reported by participant |
| $D_i$ | Degree of equivalence, difference between laboratory value and the gravimetric value |
| $U(D_i)$ | Uncertainty of the degree of equivalence |

The differences between gravimetric and reported value are given as degree of equivalence, that is the difference between the value measured by the laboratory and the gravimetric value. All laboratories reported results within 1% of the gravimetric value, for all components.

The uncertainty of the degrees are given with $k = 2$ for all laboratories, taking into consideration both the uncertainty reported from the laboratory as well as the uncertainty from gravimetry (and validation). The combined standard uncertainty of a laboratory has been computed from $U_{lab}$ and $k_{lab}$. This implies that if a laboratory used a $k$ value deviating from $k = 2$, this information has been appreciated to obtain an estimate for the combined standard uncertainty of the result.

**Table 8: Results and degrees of equivalence for CO (mmol/mol)**

| Lab | Cylinder | $x_{grav}$ | $U_{gravR}$ | $x_{lab}$ | $k_{lab}$ | $U_{lab}$ | $D_i$ | $U(D_i)$ |
|---|---|---|---|---|---|---|---|---|
| SMU | VSL209534 | 31.016 | 0.022 | 31.030 | 2 | 0.093 | 0.014 | 0.096 |
| IPQ | VSL207381 | 31.033 | 0.022 | 31.060 | 2 | 0.110 | 0.027 | 0.112 |
| CSIR | VSL200601 | 31.040 | 0.022 | 30.780 | 2 | 0.460 | -0.260 | 0.461 |
| GUM | VSL207375 | 31.045 | 0.022 | 31.050 | 2 | 0.110 | 0.005 | 0.112 |
| CHMI | VSL207377 | 31.052 | 0.022 | 30.400 | 2 | 4.400 | -0.652 | 4.400 |

**Table 9: Results and degrees of equivalence for $CO_2$ (mmol/mol)**

| Lab | Cylinder | $x_{grav}$ | $U_{gravR}$ | $x_{lab}$ | $k_{lab}$ | $U_{lab}$ | $D_i$ | $U(D_i)$ |
|---|---|---|---|---|---|---|---|---|
| SMU | VSL209534 | 132.021 | 0.080 | 132.050 | 2 | 0.250 | 0.029 | 0.262 |
| IMGC | VSL200634 | 132.016 | 0.080 | 131.700 | 2 | 5.100 | -0.316 | 5.101 |
| IPQ | VSL207381 | 131.772 | 0.079 | 131.850 | 2 | 0.460 | 0.078 | 0.467 |
| CSIR | VSL103738 | 131.999 | 0.080 | 132.320 | 2 | 4.340 | 0.321 | 4.341 |
| GUM | VSL207375 | 132.143 | 0.080 | 132.350 | 2 | 0.110 | 0.207 | 0.136 |

**Table 10: Results and degrees of equivalence for $C_3H_8$ (mmol/mol)**

| Lab | Cylinder | $x_{grav}$ | $U_{gravR}$ | $x_{lab}$ | $k_{lab}$ | $U_{lab}$ | $D_i$ | $U(D_i)$ |
|---|---|---|---|---|---|---|---|---|
| SMU | VSL308509 | 2.0856 | 0.0024 | 2.0900 | 2 | 0.0110 | 0.004 | 0.011 |
| IMGC | VSL200634 | 2.0870 | 0.0024 | 2.0130 | 2 | 0.0720 | -0.074 | 0.072 |
| IPQ | VSL207381 | 2.0868 | 0.0024 | 2.0870 | 2 | 0.0050 | 0.000 | 0.006 |
| GUM | VSL207375 | 2.0876 | 0.0024 | 2.0870 | 2 | 0.0061 | -0.001 | 0.007 |
| CHMI | VSL207377 | 2.0881 | 0.0024 | 2.2100 | 2 | 0.1500 | 0.122 | 0.150 |

## Degrees of equivalence

The unilateral degree of equivalence has already been defined. For the bilateral degrees of equivalence, the model used for CCQM-K3 has been adopted. The degree of equivalence between two laboratories is defined as

$$D_{ij} = \left\{ x_{lab(i)} - x_{gravR(i)} \right\} - \left\{ x_{lab(j)} - x_{gravR(j)} \right\} \tag{12}$$

where $x_{lab(i)}$ denotes the amount of substance fraction of the laboratory $i$, $x_{grav(i)}$ the assigned value for laboratory $i$, and likewise for laboratory $j$. $x_{gravR(..)}$ is in value equal to x, but its uncertainty $u_{gravR(..)}$ is different (see equation (8)). The uncertainty in the degree of equivalence can be expressed as

$$u^2(D_{ij}) = u_{lab(i)}^2 + u_{gravR(i)}^2 + u_{lab(j)}^2 + u_{gravR(j)}^2 - 2u(x_{gravR(i)}, x_{gravR(j)}) \tag{13}$$

whereby $x_{grav}$ is defined as given in equation (8). Looking at the results of this key comparison, $u_{gravR}$ can generally not be neglected compared to $u_{lab}$. The degree of correlation between $x_{grav(i)}$ and $x_{grav(j)}$ has been assessed and lead to the following simplification

$$u^2(D_{ij}) = u_{lab(i)}^2 + u_{grav(i)}^2 + u_{lab(j)}^2 + u_{grav(j)}^2 \tag{14}$$

This simplification is the result of the establishment of $u_{ver}$ (see also equation (8)). From the verification measurements and the calibration of the equipment, it becomes clear

that $u_{ver}$ is a combined standard uncertainty from three main contributors: uncertainty of mixtures used, position of the "unknown(s)" on the curve, including lack of fit, and the repeatability of measurement. In formula, this expression reads as

$$u_{ver}^2 = u_{calibrants}^2 + u_{lof}^2 + u_r^2 \tag{15}$$

where $u_{calibrants}$ denotes the contribution from the mixtures used for calibrating the equipment, $u_{lof}$ denotes the contribution due to the fitting and interpolation procedure, and $u_r$ denotes the contribution due to repeatability of measurement. In this expression, $u_{lof}$ is by far the dominant factor. It is also a factor, that is the same for all mixtures prepared for this comparison. As a result, the covariance between $x_{grav(i)}$ and $x_{grav(j)}$ can be approximated by

$$u\left(x_{gravR(i)}, x_{gravR(j)}\right) \approx u_{lof}^2 \tag{16}$$

Substitution of (8) and the approximation for the covariance in (13) leads then to (14). These expressions have been used to calculate the matrix of equivalence for the three components (annex 1 to this report).

For the computation of the degrees of equivalence, it is necessary to compute the expanded uncertainty on the basis of a confidence interval with 95% level of confidence. Following the "Guide to the expression of uncertainty in measurement", there are two basic options, in fact

1. to assume the normal distribution, and using $k = 2$

2. to assume Student's $t$-distribution, and computing $k$ based on the effective number of degrees of freedom

In this key comparison, the first option has been chosen, although there are arguments to do otherwise. The arguments in favour for the first option are that

–   the whole system of preparing and measuring these mixtures is under proper statistical control, thus creating more inherent stability in the estimates of combined standard uncertainties than would be the case for just a single random sample

–   in this key comparison, all participants used a coverage factor of 2

–   the normal distribution by itself is already a conservative approach, as most statistical and true distribution functions are narrower

Some arguments against this approach are

–   the possible influence of the number of degrees of freedom is ignored in establishing the expanded uncertainty

–   the expanded uncertainty may be too optimistic for very small numbers of degrees of freedom

In this particular key comparison, the influence of this choice is relatively small. Furthermore, many participants have chosen option 1. as well.

**Results for Carbon Monoxide (nominal 32 mmol/mol)**
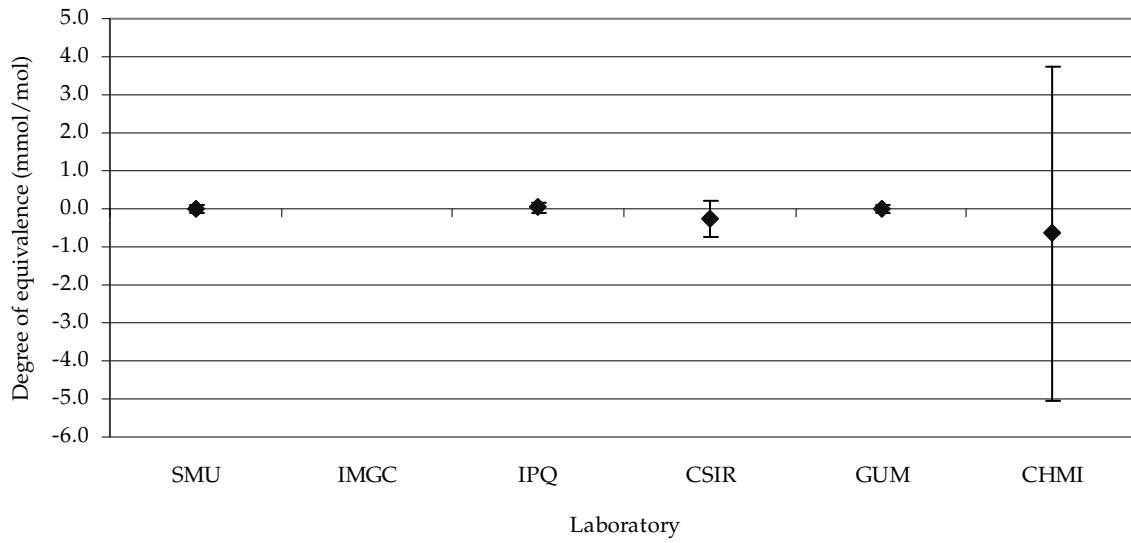


**Figure 2: Degree of equivalence for carbon monoxide**

**Results for Carbon Dioxide (nominal 135 mmol/mol)**
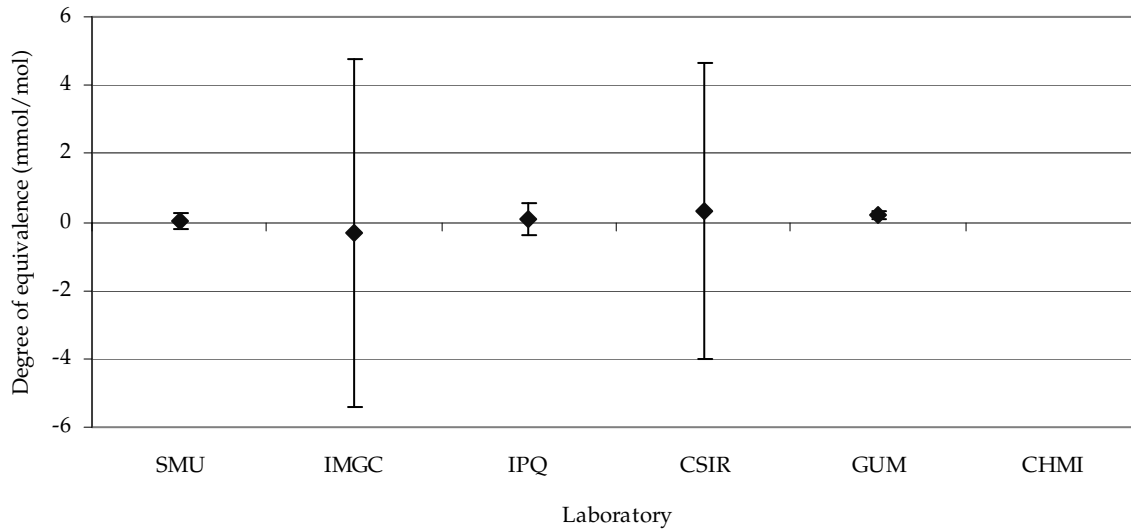


**Figure 3: Degree of equivalence for carbon dioxide**

**Results for Propane (nominal 2,05 mmol/mol)**
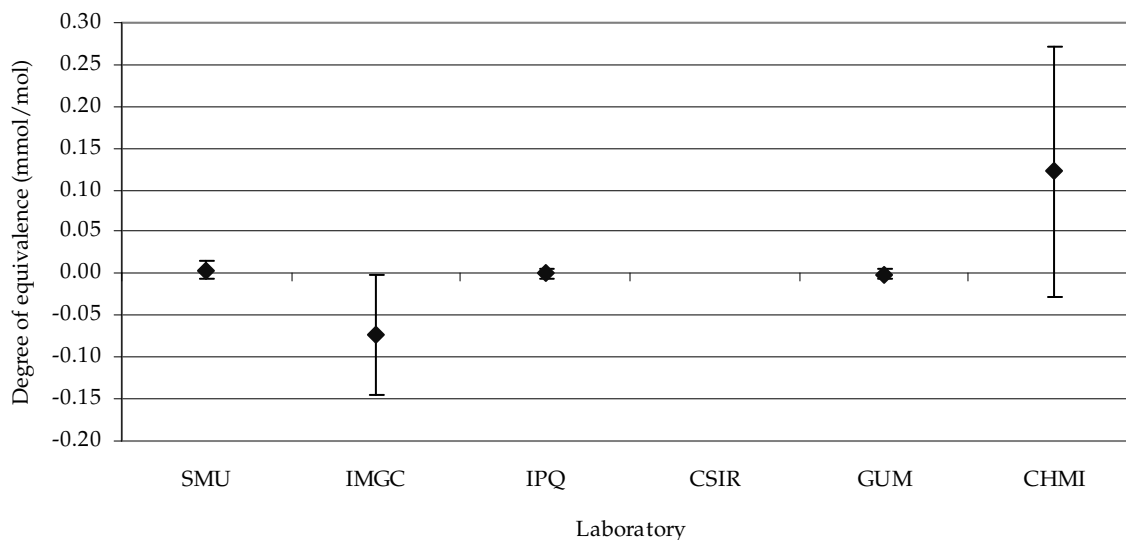


**Figure 4: Degree of equivalence for propane**

## Discussion and conclusions

The laboratories of SMU, IPQ, CSIR and GUM have shown on all analysed components to be able to assign values for all components within within ± 1% relative to the gravimetric value. Apart from propane, this is also true for IMGC. The results of CHMI show larger deviations from the gravimetric value, which are however covered by the reported uncertainty.

## Completion date

November 2000

# Annex 1: Proposal for degrees of equivalence

## Table 11: Degrees of equivalence for carbon monoxide

| | $D_i$ | $U_i$ | SMU $D_{ij}$ | $U_{ij}$ | IPQ $D_{ij}$ | $U_{ij}$ | CSIR-NML $D_{ij}$ | $U_{ij}$ | GUM $D_{ij}$ | $U_{ij}$ | CMI-CHMI $D_{ij}$ | $U_{ij}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| SMU | 0.014 | 0.096 | | | -0.013 | 0.145 | 0.275 | 0.470 | 0.009 | 0.145 | 0.666 | 4.401 |
| IPQ | 0.027 | 0.112 | 0.013 | 0.145 | | | 0.287 | 0.473 | 0.022 | 0.157 | 0.679 | 4.401 |
| CSIR-NML | -0.260 | 0.461 | -0.275 | 0.470 | -0.287 | 0.473 | | | -0.265 | 0.473 | 0.392 | 4.424 |
| GUM | 0.005 | 0.112 | -0.009 | 0.145 | -0.022 | 0.157 | 0.265 | 0.473 | | | 0.657 | 4.401 |
| CMI-CHMI | -0.652 | 4.400 | -0.666 | 4.401 | -0.679 | 4.401 | -0.392 | 4.424 | -0.657 | 4.401 | | |

## Table 12: Degrees of equivalence for carbon dioxide

| | $D_i$ | $U_i$ | SMU $D_{ij}$ | $U_{ij}$ | IMGC $D_{ij}$ | $U_{ij}$ | IPQ $D_{ij}$ | $U_{ij}$ | CSIR-NML $D_{ij}$ | $U_{ij}$ | GUM $D_{ij}$ | $U_{ij}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| SMU | 0.03 | 0.26 | | | 0.34 | 5.11 | -0.05 | 0.52 | -0.29 | 4.35 | -0.18 | 0.27 |
| IMGC | -0.32 | 5.10 | -0.34 | 5.11 | | | -0.39 | 5.12 | -0.64 | 6.70 | -0.52 | 5.10 |
| IPQ | 0.08 | 0.47 | 0.05 | 0.52 | 0.39 | 5.12 | | | -0.24 | 4.36 | -0.13 | 0.47 |
| CSIR-NML | 0.32 | 4.34 | 0.29 | 4.35 | 0.64 | 6.70 | 0.24 | 4.36 | | | 0.11 | 4.34 |
| GUM | 0.21 | 0.14 | 0.18 | 0.27 | 0.52 | 5.10 | 0.13 | 0.47 | -0.11 | 4.34 | | |

**Table 13: Degrees of equivalence for propane**

| | $D_i$ | $U_i$ | SMU | | IMGC | | IPQ | | GUM | | CMI-CHMI | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | $D_{ij}$ | $U_{ij}$ | $D_{ij}$ | $U_{ij}$ | $D_{ij}$ | $U_{ij}$ | $D_{ij}$ | $U_{ij}$ | $D_{ij}$ | $U_{ij}$ |
| SMU | 0.0044 | 0.0113 | | | 0.0784 | 0.0728 | 0.0042 | 0.0121 | 0.0050 | 0.0126 | -0.1175 | 0.1504 |
| IMGC | -0.0740 | 0.0720 | -0.0784 | 0.0728 | | | -0.0741 | 0.0722 | -0.0734 | 0.0723 | -0.1959 | 0.1664 |
| IPQ | 0.0002 | 0.0055 | -0.0042 | 0.0121 | 0.0741 | 0.0722 | | | 0.0007 | 0.0079 | -0.1218 | 0.1501 |
| GUM | -0.0006 | 0.0066 | -0.0050 | 0.0126 | 0.0734 | 0.0723 | -0.0007 | 0.0079 | | | -0.1225 | 0.1501 |
| CMI-CHMI | 0.1219 | 0.1500 | 0.1175 | 0.1504 | 0.1959 | 0.1664 | 0.1218 | 0.1501 | 0.1225 | 0.1501 | | |