EURAMET Project 1084
Bilateral comparison of standards of CO (in nitrogen), NO (in nitrogen), NO$_2$ (in air) and SO$_2$ (in air) at ambient levels

Final report

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1   BACKGROUND

Pollutants such as nitrogen monoxide (NO), nitrogen dioxide (NO_2), carbon monoxide (CO) and sulphur dioxide (SO_2) are regulated in the directive 2008/50/CE on ambient air quality. Consequently, measurements of the amount fractions of these 4 pollutants in ambient air shall be accurate to fulfil the requirements given in this directive. In general, the primary element of quality assurance for field instruments is regular calibration using certified gas mixtures.

National Metrology Institutes have developed methods for certifying reference gas mixtures used on site for calibrating analysers and some of them are accredited. One of the requirements for accreditation is to participate in comparisons to demonstrate the accuracy of values carried by national reference materials and measurement methods over the time. As the previous comparisons (CCQM-K26a on NO and CCQM-K26b on SO_2) have been organized in 2004 there was a need to plan a new comparison on the 4 regulated pollutants (NO, NO_2, CO and SO_2).

2   OBJECTIVES

This document describes the protocol for a comparison for:

- Carbon monoxide (CO) in nitrogen at the nominal amount-of-substance fraction of 10 µmol/mol,
- Nitrogen monoxide (NO) in nitrogen at the nominal amount-of-substance fraction of 200 nmol/mol,
- Nitrogen dioxide (NO_2) in air at the nominal amount-of-substance fraction of 200 nmol/mol,
- Sulfur dioxide (SO_2) in air at the nominal amount-of-substance fraction of 270 nmol/mol.

The objective of this analytical comparison is to compare analytical results of the receiving laboratory on the respective gas mixtures to their reference values provided by the circulating laboratory for SO_2, CO, NO_2 and NO gas mixtures.

The comparison is aimed at typical amount fractions used to calibrate analysers carrying out automatic measurements of NO, CO and SO_2 in ambient air. The NO_2 composition is typical to verify the converter efficiency of the NO/NO_x analyser.

It is proposed that this comparison can be used to support CMC claims for CO, NO, NO_2 and SO_2 over the amount fraction ranges shown in Table 1.

Table 1: "How far the light shines" statement

Component	Amount Fraction Range (µmol/mol)
CO	10-1000
NO	0,2-10
NO_2	0,2-10
SO_2	0,2-10

3   PARTICIPANTS

LNE acted as pilot laboratory for this comparison which was led in the EURAMET framework.

The national Metrology Institutes which participated in this comparison are : NPL and LNE. VSL was added as independent third party for the NO_2 comparison because the difference between the reported NPL and LNE values was unexpectedly large.

4   COMPLETION DATE

The completion date of this comparison is : May 2013.

5   COMPARISON PROTOCOL

This comparison involves 5 gas mixtures:
- A commercial gas mixture of sulphur dioxide (SO_2) in air at a nominal amount fraction of 270 nmol/mol from Air Liquide circulated by NPL,
- A gravimetric gas mixture of carbon monoxide (CO) in nitrogen prepared by NPL at a nominal amount fraction of 10 µmol/mol circulated by NPL,
- Two commercial gas mixtures of nitrogen dioxide (NO_2) in air at a nominal amount fraction of 200 nmol/mol from Air Liquide and Messer circulated by LNE,
- A commercial gas mixture of nitrogen monoxide (NO) in nitrogen at a nominal amount fraction of 200 nmol/mol from Air Liquide circulated by LNE.

The commercial gas mixture of SO_2 in air and the gravimetric standard of CO in nitrogen were calibrated by NPL before being dispatched to LNE for analysis.
The commercial gas mixtures of NO_2 in air and NO in nitrogen were calibrated by LNE before being dispatched to NPL (and VSL) for analysis.

The participating laboratories made at least three measurements of the amount fraction of the component in the gas mixtures. The results of these measurements were combined to provide the final result. The expanded uncertainties reported for the analysis by each participant include the estimated uncertainties from the analysis and the reference standards used.

6   ANALYSIS METHODS USED BY PARTICIPATING LABORATORIES

The analytical methods and the reference standards used by the participating laboratories to analyse the gas mixtures are summarized in Table 2 and Table 3, respectively.

Table 2: Analytical methods used by the participating laboratories

Participating laboratory	Analytical methods used			
	NO	NO$_2$	CO	SO$_2$
LNE	42C analyser (TEI) based on the principle of chemiluminescence	42C analyser (TEI) based on the principle of chemiluminescence	48C analyser (TEI) based on non dispersive infrared technique	43C analyser (TEI) based on the principle of UV fluorescence
NPL	CLD 66 analyser (Eco Physics) based on the principle of chemiluminescence	CLD 66 analyser (Eco Physics) based on the principle of chemiluminescence with a molybdenum catalyst to convert NO$_2$ to NO (determination of the efficiency using gas phase titration with ozone)	02020 analyser (ABB) based on non disperse infrared technique	43i analyser (TEI) based on the principle of UV fluorescence
VSL	-	17C analyser (TEI) based on the principle of chemiluminescence	-	-

Table 3: Reference standards used by the participating laboratories

Participating laboratory	Reference standards used			
	NO	NO$_2$	CO	SO$_2$
LNE	Generation of a reference gas mixture of NO in nitrogen at about 200 nmol/mol by dynamic dilution of a gravimetric gas mixture at 10 µmol/mol	Generation of a reference gas mixture of NO$_2$ in air at about 200 nmol/mol by the permeation method	Generation of a reference gas mixture of CO in nitrogen at about 10 µmol/mol by dynamic dilution of a gravimetric gas mixture at 500 µmol/mol	Generation of a reference gas mixture of SO$_2$ in air at about 280 nmol/mol by the permeation method
NPL	Generation of a reference gas mixture of NO in nitrogen at about 200 nmol/mol by dynamic dilution from a stable primary reference standard at 10 µmol/mol	Generation of reference gas mixtures of NO and NO$_2$ in air at about 200 nmol/mol by dynamic dilution from stable primary reference standards of the target compound at 10 µmol/mol in each case	Preparation of a reference gas mixture of CO in nitrogen at 10.766 µmol/mol by gravimetry	Generation of a reference gas mixture of SO$_2$ in air at about 280 nmol/mol by dynamic dilution from a stable primary reference standard at 5 µmol/mol
VSL	-	Generation of a reference gas mixture of NO$_2$ in nitrogen (at about 150, 200, 250 and 300 nmol/mol) by dynamic dilution from a stable primary reference standard at 5 µmol/mol	-	-

7 RESULTS

CO/N$_2$, NO/N$_2$ and SO$_2$/air

The results submitted by the participating laboratories for CO, NO and SO$_2$ are shown in Table 4 to 6. All of the uncertainties represent 95 % confidence intervals (expanded using a coverage factor k of 2).

Table 4: Results for SO$_2$ (December 2010)

| Component	Cylinder number	NPL		LNE	
		Reference value (nmol/mol)	Expanded uncertainty (k=2) (nmol/mol)	Analytical value (nmol/mol)	Expanded uncertainty (k=2) (nmol/mol)
SO$_2$	D611759 (Air Liquide)	275.6	5.5	269.6	3.0

Table 5: Results for CO (December 2010)

| Component	Cylinder number	NPL		LNE	
		Reference value (µmol/mol)	Expanded uncertainty (k=2) (µmol/mol)	Analytical value (µmol/mol)	Expanded uncertainty (k=2) (µmol/mol)
CO	163993SG (NPL)	10.867	0.043	10.903	0.082

Table 6: Results for NO (December 2010)

| Component	Cylinder number	LNE		NPL	
		Reference value (nmol/mol)	Expanded uncertainty (k=2) (nmol/mol)	Analytical value (nmol/mol)	Expanded uncertainty (k=2) (nmol/mol)
NO	D320208 (Air Liquide)	202.3	2.2	200.1	2.0

Figures 1 - 3 show the amount fractions submitted by the participating laboratories for CO, NO and SO$_2$.
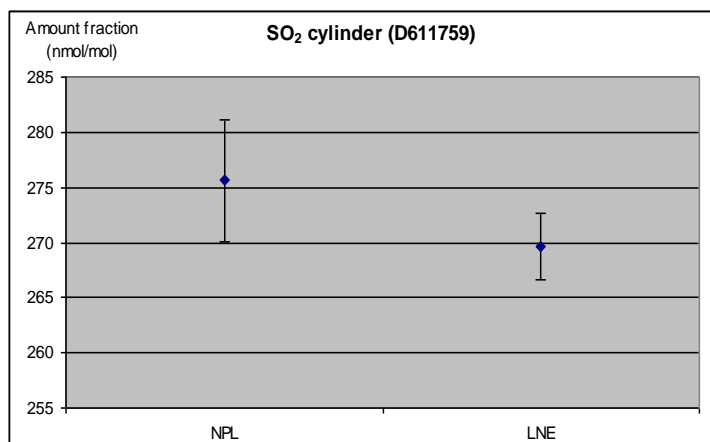
Figure 1: Representation of the amount fractions for SO_2
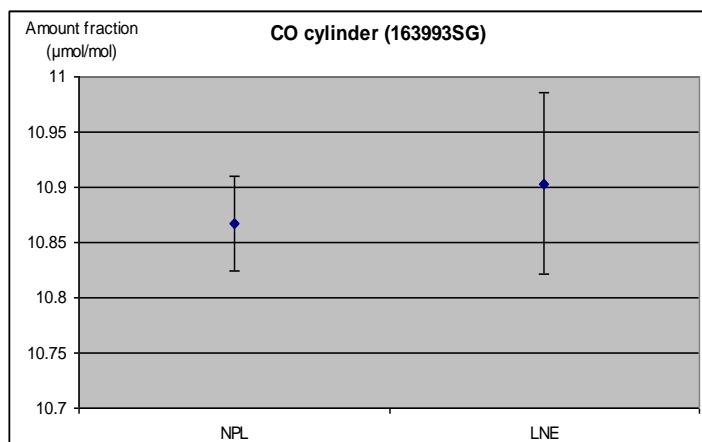
Figure 2: Representation of the amount fractions for CO
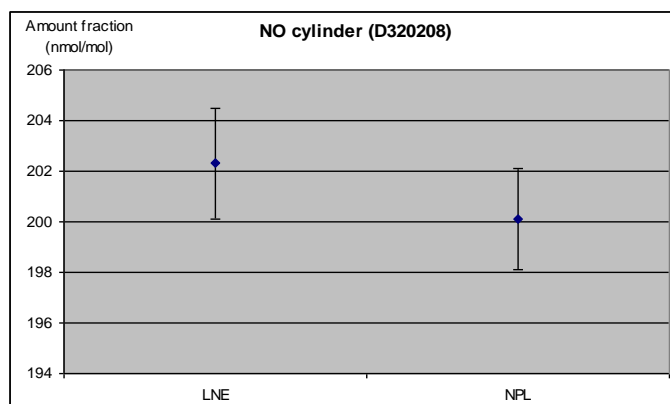
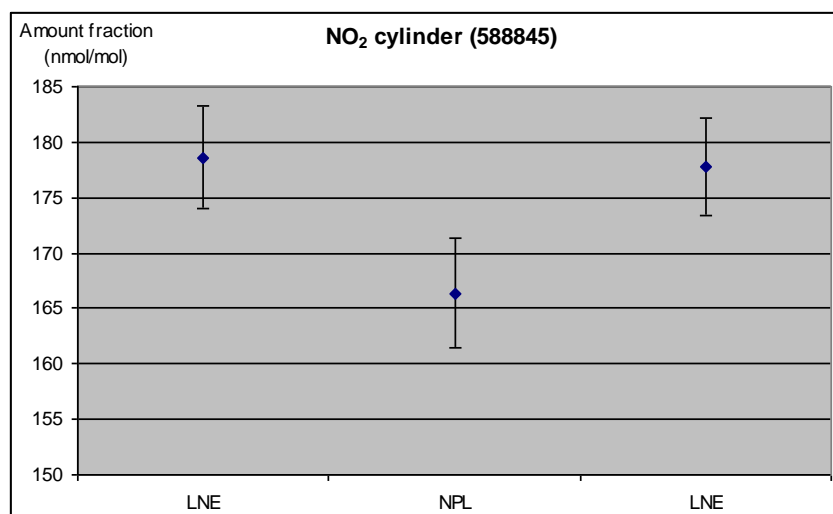**Figure 3:** Representation of the amount fractions for NO

The SO_2 and CO analytical results for LNE do not deviate from the NPL reference values by more than the expanded uncertainty. The NO analytical results for NPL do not deviate from the LNE reference value by more than the expanded uncertainty.

NO_2/air (Preliminary investigation)

A preliminary investigation was conducted. A commercial gas mixture of NO_2 in air at a nominal amount fraction of 200 nmol/mol from Messer was procured and certified by LNE. The mixture was then analysed by NPL. The results are shown in Table 7 and plotted in Figure 4.

Table 7: Results of a preliminary investigation of 200 nmol/mol NO_2/air mixture

Component	Cylinder number	LNE (Beginning)		NPL		LNE (Return)	
		Reference value (nmol/mol)	Expanded uncertainty (k=2) (nmol/mol)	Analytical value (nmol/mol)	Expanded uncertainty (k=2) (nmol/mol)	Reference value (nmol/mol)	Expanded uncertainty (k=2) (nmol/mol)
NO_2	588845 (Messer)	178.6	4.6	166.4	5.0	177.8	4.4

Figure 4: Preliminary investigation of 200 nmol/mol NO_2/air mixture

Figure 4 shows a significant deviation between the amount fractions reported by each institute. An investigation was conducted to identify the cause of the discrepancy and produced the following information.

Both institutes used an analyser with the same principle based on chemiluminescence. However the laboratories calibrate their analyser in different ways:

✓ LNE calibrates it with a reference gas mixture of NO_2 in air at about 200 nmol/mol generated by the permeation method,

✓ NPL calibrates it with a reference gas mixture of NO in nitrogen at about 200 nmol/mol by dynamic dilution from a stable primary reference standard.

LNE has analysed gas mixture n°588845 by calibrating its NO/NOx analyser with a reference mixture of NO in air with nominal amount fraction of 200 nmol/mol. This was prepared by dynamic dilution with air from a gravimetric gas mixture of NO in nitrogen at about 10 µmol/mol. The analysed amount fraction was 175.6±5.5 nmol/mol: this amount fraction was not significantly different from the first set of amount fractions (178.6±4.6 nmol/mol and 177.8±4.4 nmol/mol) taking account the expanded uncertainties. The possibility that some NO_2 impurities can be present in the NO stable primary reference standard at 10 µmol/mol prepared by NPL has been raised. The impurities have been analysed in the NO primary reference standard with FTIR by

LNE: no impurity has been found which can interfere on the measurement made by a chemiluminescence analyser (cf. figure 5).
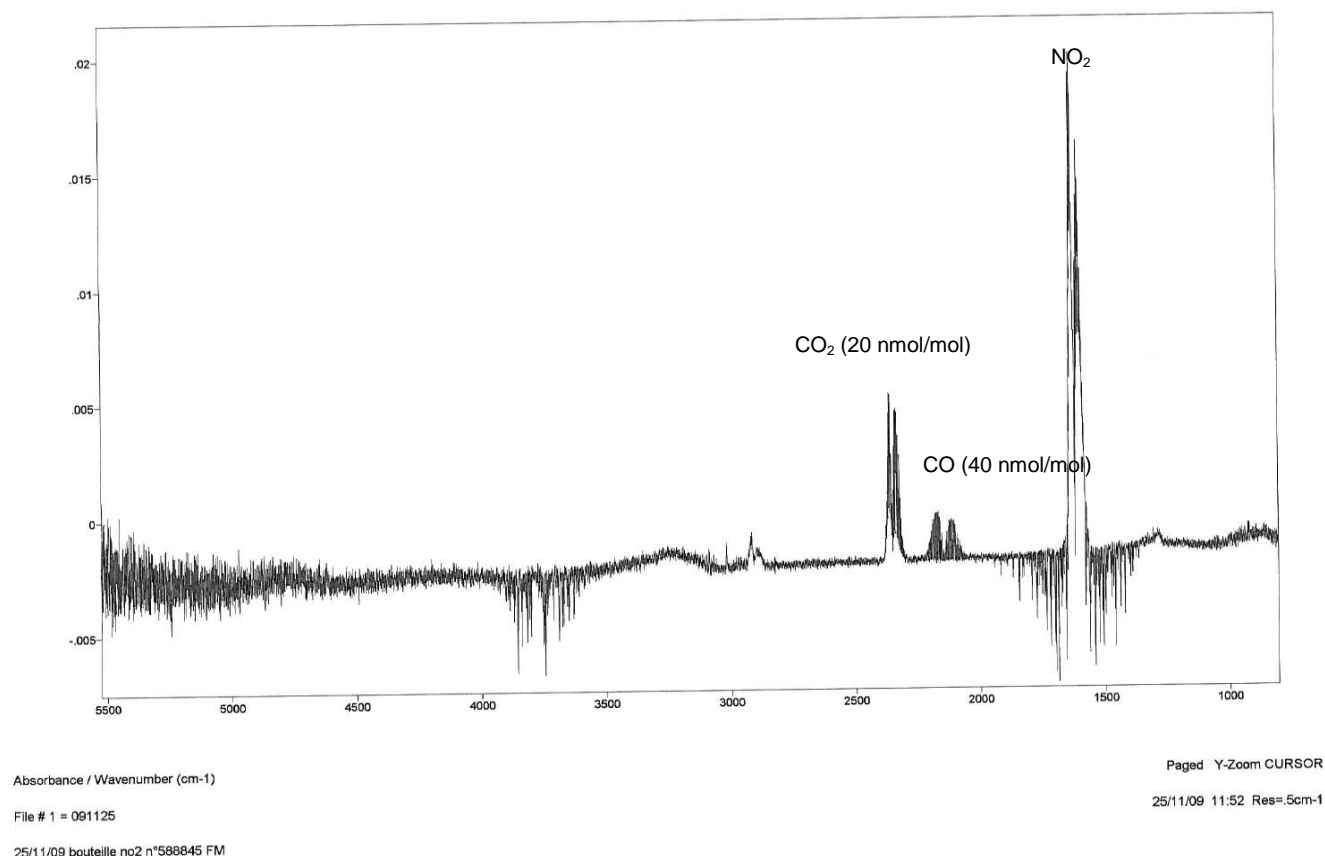
Figure 5: FTIR spectrum of the NO primary reference standard at about 10 µmol/mol prepared by NPL

The converter efficiency of the catalyst in NPL's analyser was determined using a gas phase titration at three different amount fractions. The results were 98.7% at 200 nmol/mol, 97.7% at 500 nmol/mol and 97.9% at 800 nmol/mol. The change in the converter efficiency is negligible across the amount fraction range tested given an uncertainty of 1% (k=1) was employed in the uncertainty budget. Due to the discrepancy between NPL and LNE results a reference value could not be allocated.

NO$_2$/air

VSL was added as independent third party for the NO$_2$ measurements because the difference between the NPL and LNE values was unexpectedly large in the preliminary investigation and could not be explained in spite of several complementary experiments. A new commercial NO$_2$ gas mixture (D721882) from Air Liquide was used for the comparison because the original cylinder (588845) was almost empty. The results submitted by the participants are shown in Table 8. All of the uncertainties represent 95% confidence intervals (expanded using a coverage factor k of 2).

Table 8: NO$_2$ results (August 2011)
All the results are expressed in nmol/mol

Compo-nent	Cylinder number	LNE		VSL		LNE		NPL		LNE	
		Reference value	U (k=2)	Analytical value	U (k=2)	Reference value	U (k=2)	Analytical value	U (k=2)	Reference value	U (k=2)
NO$_2$	D721882 (Air Liquide)	199.6	4.4	205	5	192.7	4.9	196.3	5.9	193.4	4.3

In figure 6 the results are plotted in terms of amount fractions submitted by the participating laboratories.
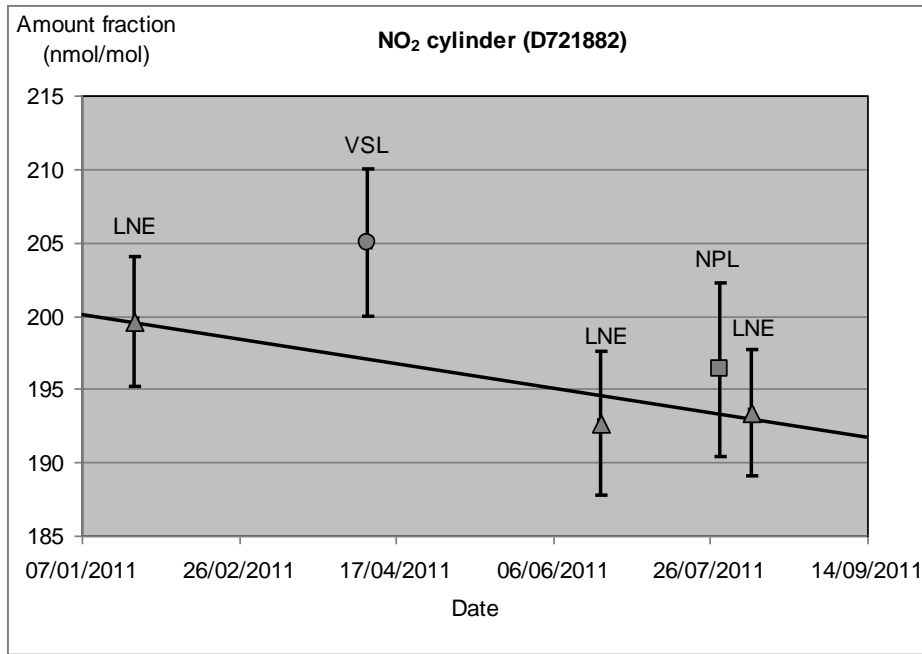
Figure 6: Reported NO$_2$ amount fractions plotted against measurement date. A first order curve was fitted using a generalised least squares method

Figure 6 shows the data plotted against the measurement date. The results reported by LNE (triangles) indicate a decay in the amount fraction of NO$_2$ during the comparison. A first order curve was fitted using a generalized least-squares method which takes into account the uncertainties of each reference value. The solid line shows the results and the dotted lines indicate the expanded uncertainty of the analysis. After correcting for this decay rate, the reported results demonstrate good agreement between LNE and NPL within the uncertainties stated. The amount fraction reported by VSL exhibits a bias to the reference value.

8   CALCULATION OF DEGREES OF EQUIVALENCE

The degree of equivalence of the participating laboratory in the comparison is defined as

$$D_i = x_{lab} - x_{ref}$$

Where x_{ref} denotes the reference value and x_{lab} the result of each participating laboratory.

The standard uncertainty of D_i can be expressed as

$$u^2(D_i) = u^2_{lab} + u^2_{ref}$$

Where u_{ref} and u_{lab} are standard combined uncertainties of reference value and participating laboratory, respectively, assuming that the error terms associated with the laboratory result and the reference value are uncorrelated.

The expanded uncertainty of D_i, at 95% level of confidence, is given by

$$U(D_i) = 2 \times u(D_i)$$

The degrees of equivalence are listed in Table 9 and shown in Figure 7.
The LNE reference values were recalculated using the first order curve: 192.9 nmol/mol for VSL and 196.7 nmol/mol for NPL respectively.
An uncertainty due to the stability of the NO_2 amount fraction over the time has been calculated using the first order curve: this leads to a stability standard uncertainty equal to 1.61 nmol/mol. This stability standard uncertainty has been added to the mean of the 3 expanded uncertainties of 4.4, 4.9 and 4.3 nmol/mol which is equal to 4.5 nmol/mol. After correcting for the decay rate, the reported results demonstrate good agreement between LNE and NPL within the uncertainties stated but show that the bias between LNE and VSL remains (see figure 7).

Table 9: Calculation of the degrees of equivalence

Reference laboratory	Participant laboratory	Component	x_{ref} (nmol/mol)	U_{ref} (nmol/mol)	x_{lab} (nmol/mol)	U_{lab} (nmol/mol)	D_i (nmol/mol)	$U(D_i)$ (nmol/mol)
NPL	LNE	SO_2	275.6	5.5	269.6	3.0	-6.00	6.26
LNE	NPL	NO	202.3	2.2	200.1	2.0	-2.20	2.97
LNE	NPL	NO_2	192.9	5.6	196.3	5.9	3.40	8.13
LNE	VSL	NO_2	196.7	5.6	205	5	8.30	7.51

Reference laboratory	Participant laboratory	Component	x_{ref} (µmol/mol)	U_{ref} (µmol/mol)	x_{lab} (µmol/mol)	U_{lab} (µmol/mol)	D_i (µmol/mol)	$U(D_i)$ (µmol/mol)
NPL	LNE	CO	10.867	0.043	10.903	0.082	0.04	0.09
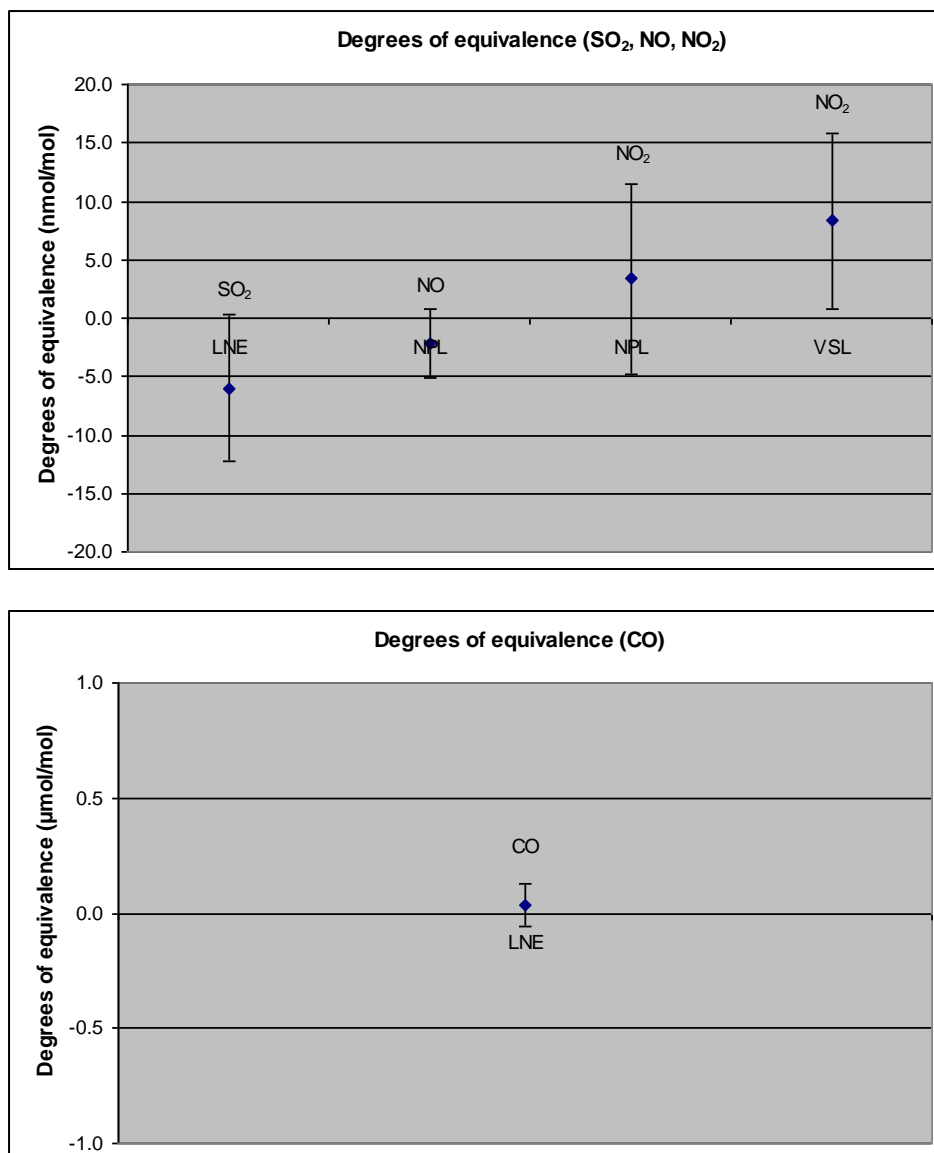
Figure 7: Representation of the degrees of equivalence

9   DISCUSSION OF RESULTS

The analytical amount fractions obtained by NPL and LNE for SO_2, CO and NO are in a good agreement. Results from a preliminary investigation showed significant deviation between the NO_2 amount fractions determined by LNE and NPL. Several complementary tests were carried out but no scientific explanations were found to explain the deviations. Consequently another national metrological institute (VSL) was invited to participate in the NO_2 comparison. Three results were reported by LNE, measured at regular intervals over the duration of the comparison. The results indicated decay in the amount fraction of the comparison mixture. A first order curve was fitted to the data using a generalised least squares approach in order to determine the decay rate of NO_2. After correcting for this decay rate, the reported results demonstrate good

agreement between LNE and NPL within the uncertainties stated but not between LNE and VSL. VSL may have slightly underestimated the uncertainty of the dynamic dilution to produce the calibration line used for determining the NO_2 concentration of the gas mixture.

10 CONCLUSIONS

After making some investigations the agreement of the results between LNE and NPL in this EURAMET Project 1084 is good for amount fractions of:

- ✓ CO at about 10 µmol/mol,
- ✓ SO_2 at about 270 nmol/mol,
- ✓ NO at about 200 nmol/mol,
- ✓ NO_2 at about 200 nmol/mol.