Workshop – Aims

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Convenor EUROMET Gas Sub-committee

EC-JRC-IES

14 and 15 March 2007

Air Quality Reference Laboratories

Objectives of the Workshop

- Scope
  - NO
  - NO_2
  - SO_2
  - Not specifically O_3, CO or VOCs
  - Benzene, 1,3-butadiene ?

- Registered as a EUROMET project (No 888)

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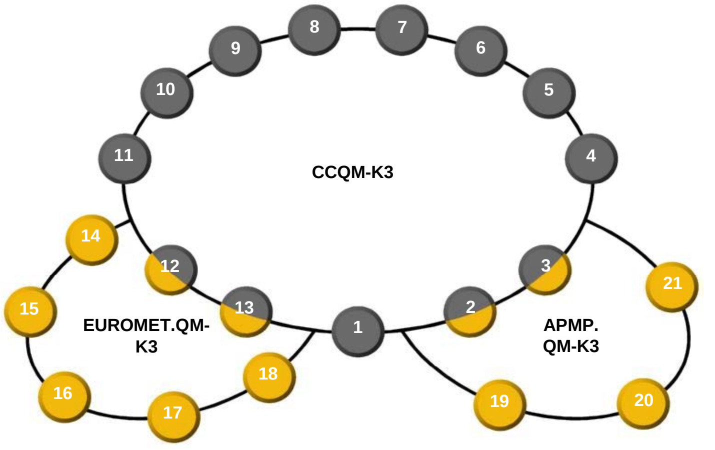
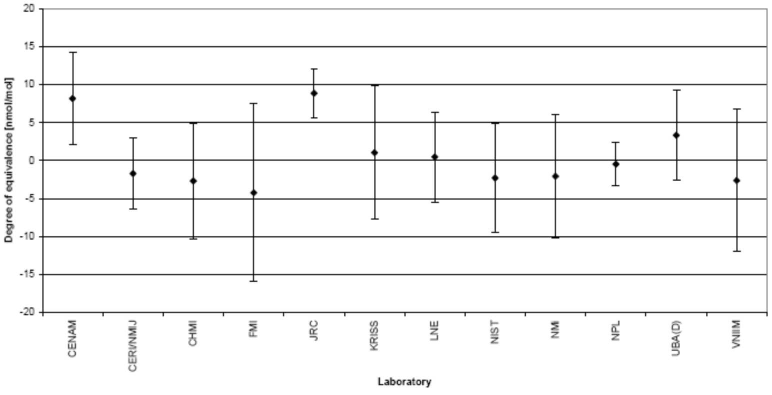
The CIPM MRA

Appendix B

- Information on CIPM (Comité International des Poids et Mesures) and RMO (Regional Metrology Organization) key and supplementary comparisons, together with results interpreted in terms of equivalence.





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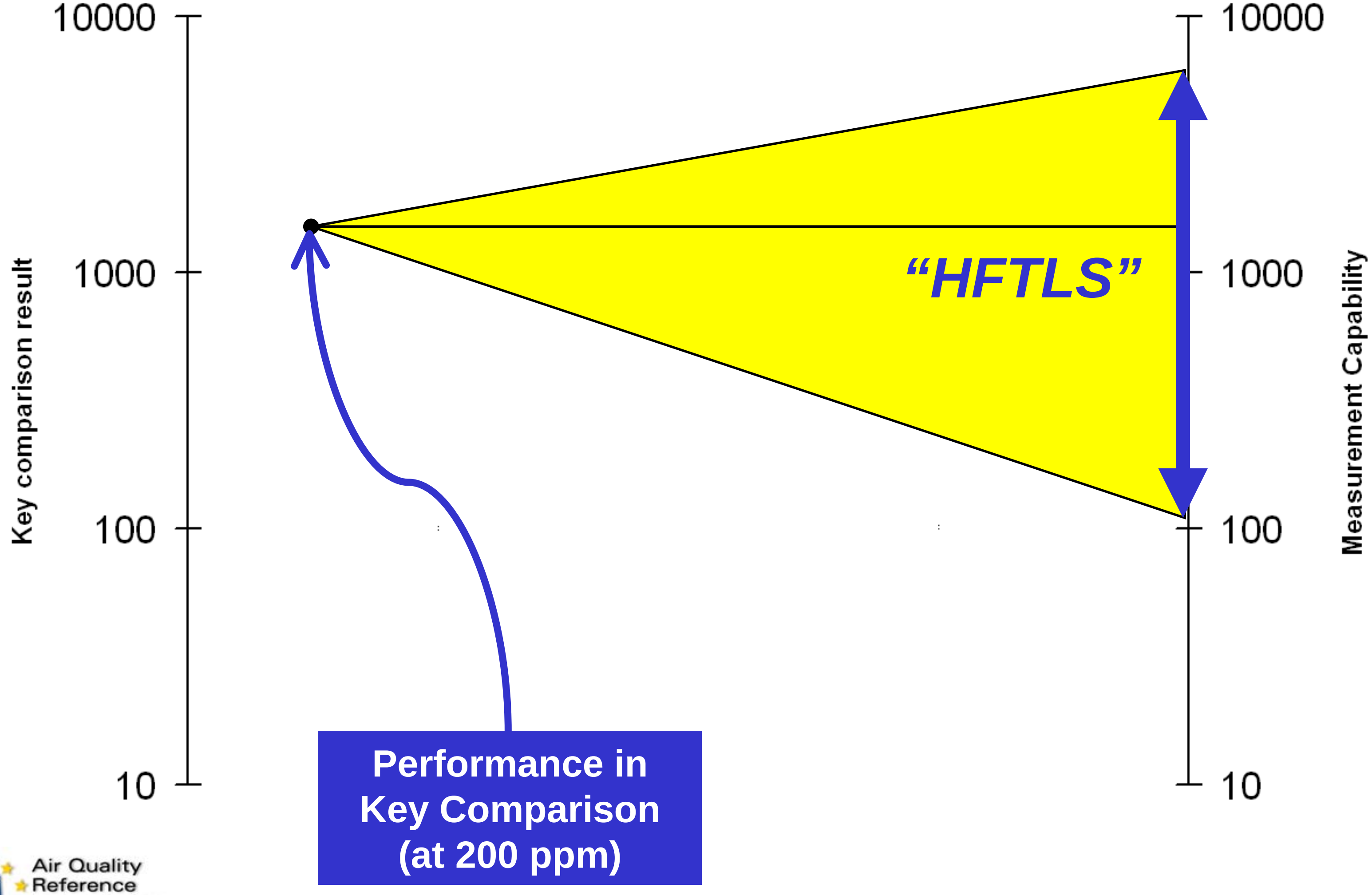
Appendix C

- Quantities for which calibration and measurements certificates are recognized by institutes participating in the Arrangement.

- Measurement capabilities are treated separately from the capability to prepare, certify and disseminate CRMs.

How far the light shines (HFTLS)



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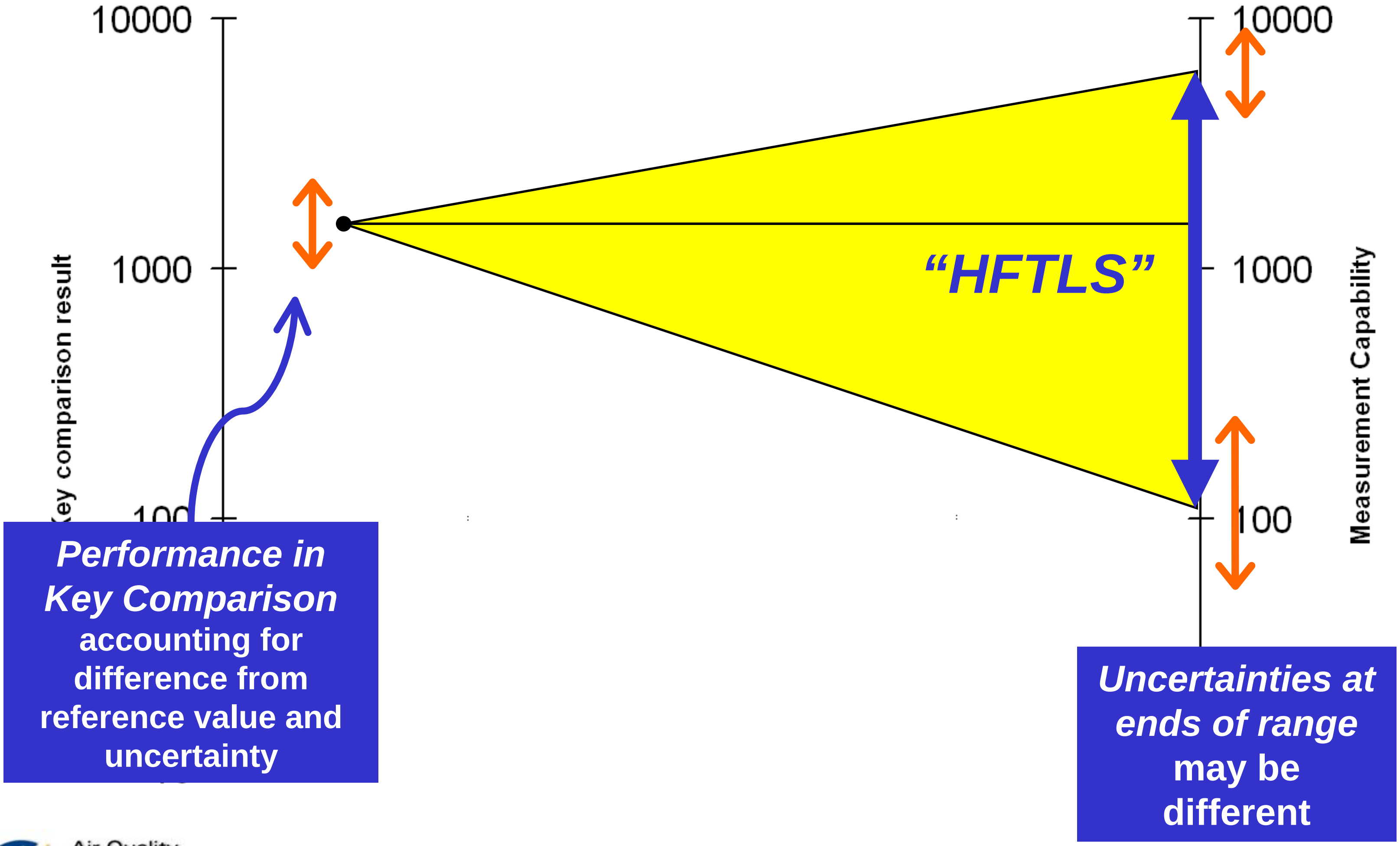
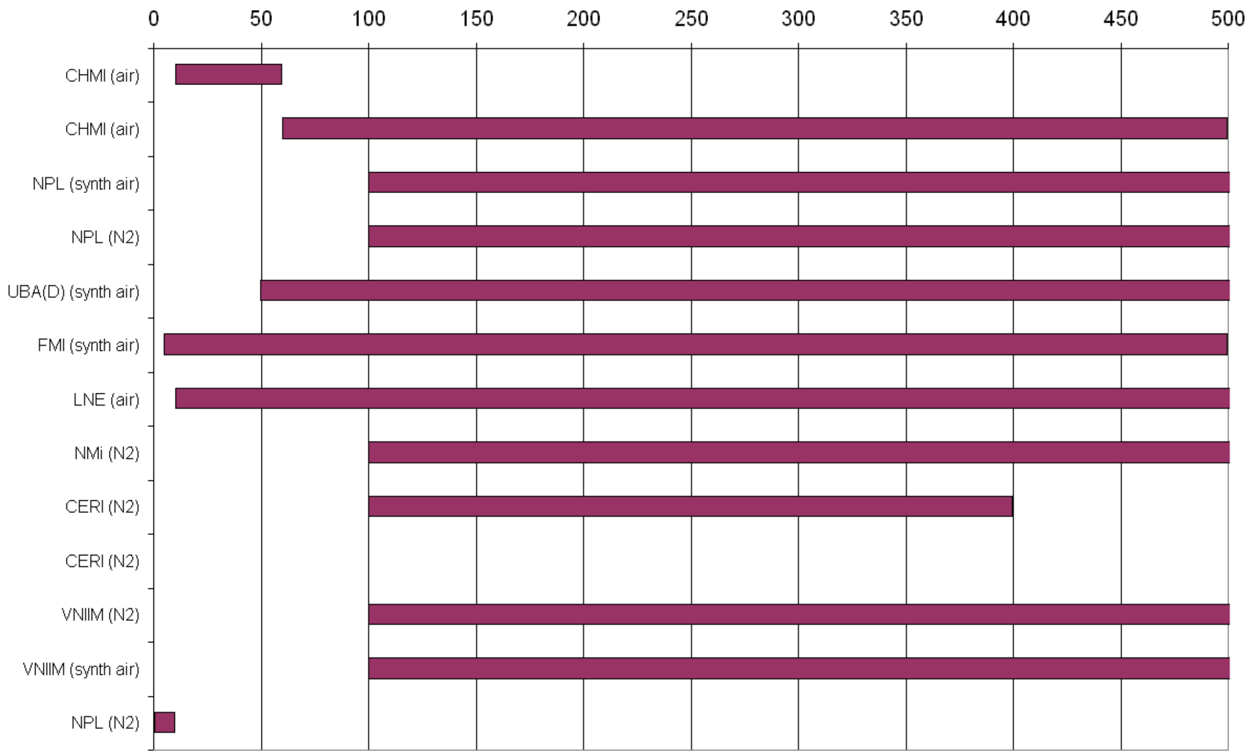
How far the light shines (HFTLS)



Sulphur dioxide



"The comparison is aimed at at typical calibration requirements for ambient SO2 analysers, which monitor concentrations using ultraviolet fluorescence. The techniques used for the comparison should be applicable to concentrations of SO2 between around 100 nmol/mol and 1 mmol/mol."

	SO_2		to	
	CHMI (air)	2% at 10ppb		1.7% at 60 ppb
	CHMI (air)	3.3% at 60ppb		1.8% at 500 ppb
	NPL (synth air)	1% at 100 ppb		1% at 1000 ppb
	UBA(D) (synth air)	2% at 50 (***100***)ppb		1% at 1000 ppb
	FMI (synth air)	8% at 5 ppb		1% at 500 ppb
	LNE (air)	2% at 10ppb		1% at 1000 ppb
	NMi (N2)	2% at 100 ppb		2% at 2000 ppb
	CERI (N2)	6% at 100 ppb		2.5% at 400 ppb
	VNIIM (N2)	5% at 100 ppb		1% at 1000 ppb
	VNIIM (synth air)	5% at 100 ppb		1.5% at 2000 ppb
	NPL (N2)	***2% at 100 ppb***		***1.5% at 1000 ppb***

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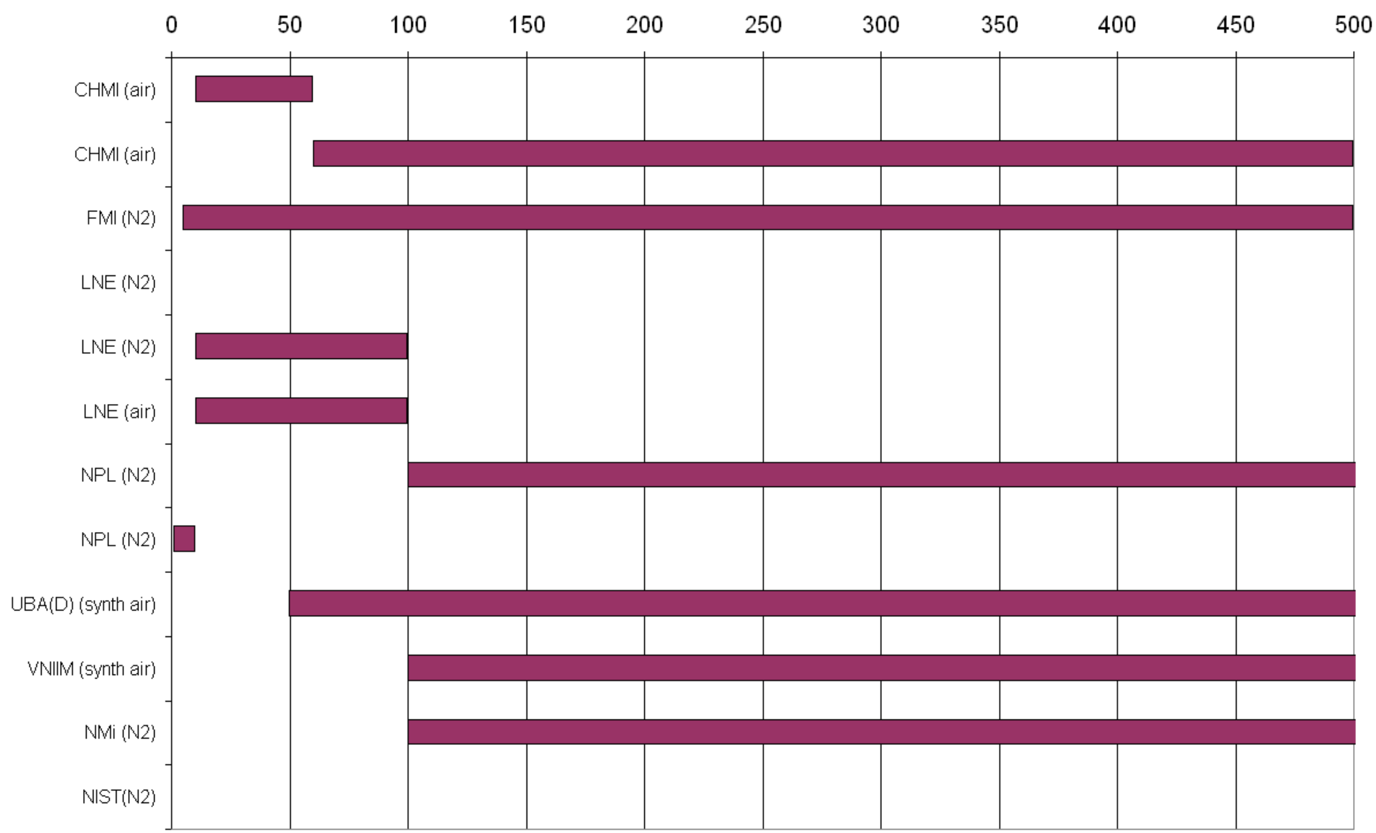
Nitrogen monoxide

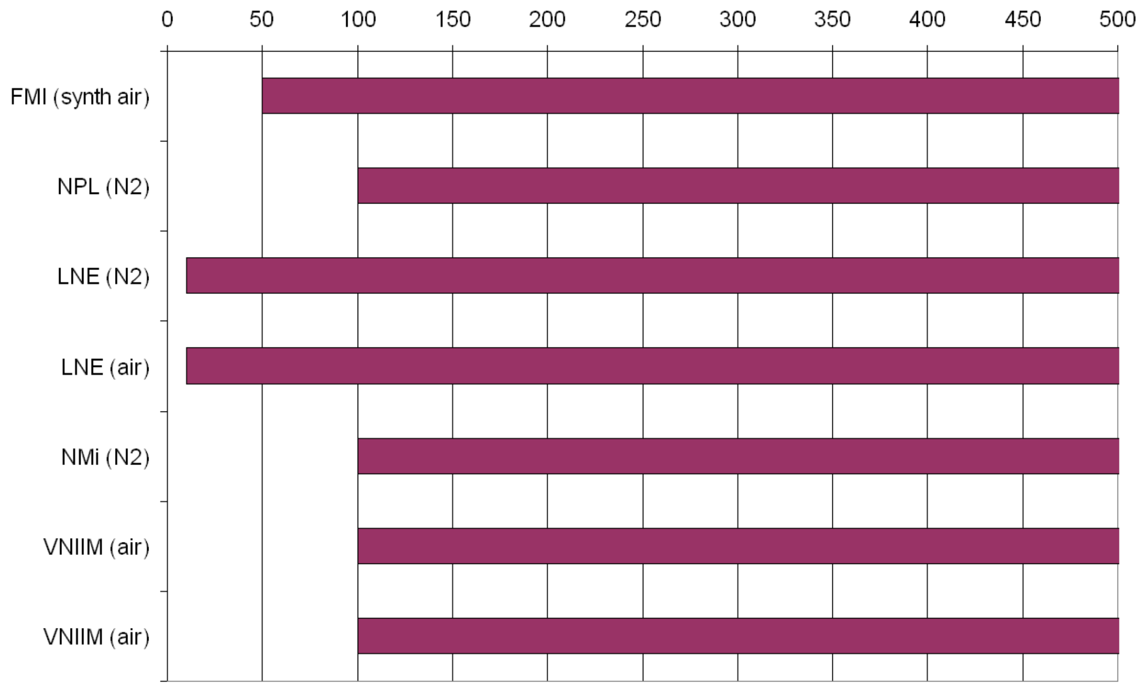


"The comparison is aimed at typical calibration requirements for ambient NOx analysers, which monitor nitrogen dioxide concentrations using catalytic conversion to nitrogen monoxide and chemiluminescent detection. The techniques used for the comparison should be applicable to concentrations of nitrogen monoxide between around 100 nmol/mol and 10 mmol/mol.

Where primary measurements of nitrogen dioxide are made by conversion to nitrogen monoxide using a well-characterised converter, the results will also be relevant to similar concentrations of nitrogen dioxide."

NO		*to*	
CHMI (air)	1.8% at 10ppb		1.7% at 60 ppb
CHMI (air)	3% at 60ppb		1.4% at 500 ppb
FMI (N2)	8% at 5 ppb		1% at 500 ppb
LNE (N2)	2% at 500ppb		1% at 20000 ppb
LNE (N2)	2% at 10ppb		1% at 100 ppb
LNE (air)	2% at 10ppb		1% at 100 ppb
NPL (N2)	3% at 100 ppb		2% at 1000 ppb
NPL (N2)	10% at 1 ppb		10% at 10 ppb
UBA(D) (synth air)	2% at 50 ppb		1% at 1000 ppb
VNIIM (synth air)	5% at 100 ppb		1.6% at 1000 ppb
NMi (N2)	3% at 100 ppb		2% at 1000 ppb

Nitrogen dioxide



“The comparison is aimed at typical calibration requirements for ambient NOx analysers, which monitor nitrogen dioxide concentrations using catalytic conversion to nitrogen monoxide and chemiluminescent detection. The techniques used for the comparison should be applicable to concentrations of nitrogen monoxide between around 100 nmol/mol and 10 mmol/mol.

Where primary measurements of nitrogen dioxide are made by conversion to nitrogen monoxide using a well-characterised converter, the results will also be relevant to similar concentrations of nitrogen dioxide.”

NO_2		to	
FMI (synth air)	2 at 50 ppb		17 at 600 ppb
NPL (N2)	3% at 100 ppb		3% at 1000 ppb
LNE (N2)	2% at 10ppb		1% at 1000 ppb
LNE (air)	2% at 10ppb		1% at 1000 ppb
NMi (N2)	3% at 100 ppb		2% at 2000 ppb
VNIIM (air)	5% at 100 ppb		1.5% at 2000 ppb
VNIIM (N2)	5% at 100 ppb		1.5% at 2000 ppb

Ozone

CMCs for ozone

		Range nmol/mol	Absolute uncertainty nmol/mol	Range nmol/mol	Relative uncertainty %(rel)
Exisiting claims					
	CHMI	10 to 100	2.3 to 2.4	100 to 1000	2.4 to 2.1
	FMI	5 to 100	2.7		
		100 to 500	2.7 to 12		
	INRIM	0 to 100	2	100 to 1000	2
	LNE	0 to 100	2	100 to 1000	2
	UBA(D)			20 to 200	3 to 2
	METAS	0 to 100	2	100 to 1000	2
	NPL	20 to 100	2	100 to 1000	2 to 1.5
	NIST	1 to 100	1	100 to 1000	1
New claims (Cycle VII)					
	Nmi	20 to 100	0.8 to 0.95		
		100 to 400	0.95 to 2.0		
	UBA(D)	3 to 100	1	100 to 1000	1 to 0.1
	METAS			0 to 1000	Q[1.1, 0.017x(O3)], x(O3) in nmol/mol

Summary

We will return to this subject

in the final session.

What have we learned about dynamic methods from Key Comparisons?

K26a NO methods

Laboratory	Analyser	Method
Key comparison		
CENAM	HORIBA Model APNA-360CE (Chemiluminescence)	The concentration was calculated by interpolation of a calibration curve using three concentration levels of CENAM primary gas mixtures
CERI/NMIJ	Thermo Environmental Instruments Inc. Model 42C Trace Level	High/Low bracketing using two PSMs.
CHMI	Thermo Environmental Instruments Model 42C and 42 (Chemiluminescence)	Diluted PRM by manometric static injection. Direct from manometric static injection system to analysers. Cylinder with reduction valve MG FE62 to analysers.
FMI	TEI Model 42C (Chemiluminescence)	Dynamic dilution method (ISO 6145-6). The measurements of the samples took place according to a sequence of instrument calibration, sample analysis, injection of zero gas into the analyser, and calibration of the analyser (against NPL secondary standard (number QE11/N03/050)
JRC	TEC 42C (Chemiluminescence)	Calibration gases produced by permeation method and static dilution method. A TE 42 C is calibrated with zero gas, span gas 1 and span gas 2. After the calibration the sample is measured.
KRISS	Thermo Environmental Instruments Inc, Model 42 (Chemiluminescence)	Four standard gases were used as reference gases. A-B-A ratio method used
LNE	TEC 42C (Chemiluminescence)	Zero/span calibration using dilution method (Molbloc) to generate span value.

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K26a NO methods

NIST	TEC Model 42C (Chemiluminescence)	Ratio of travelling standard against 8 NIST standards
Nmi	Thermo Environmental Instruments Inc. Model 17C Ammonia Analyzer (Chemiluminescence)	Calibration has been performed using Primary Standard Gas Mixtures (PSMs). A suite of four PSMs ranging in amount-of-substance fraction level from 400 to 1000 nmol/mol NO (nominal) were used.
NPL	Eco-physics Model CLD 700 AL (Chemiluminescence)	Bracketing method using single gravimetrically prepared standards, in an ABABA sequence.
UBA(D)	(Chemiluminescence)	Calibration by a 2 point bracketing procedure. Preparation of the calibration standards by static volumetric injection method according to ISO 6144 and VDI 3490 (p14).
VNIIM	Environment S.A. ModelAC-30M (Chemiluminescence)	The method of absolute calibration (comparison method) was used. Two approx. 700 ppb standards used.
Pilot study		
IPQ		
METAS	(Chemiluminescence)	The calibration standards used were produced by dilution of two METAS NO-standards (with an amount of substance fraction of NO in N_2 of about $60 \cdot 10^{-6}$ mol/mol) with nitrogen of a quality of 99.999 %.
UBA(A)	(Chemiluminescence)	NMi MS 7356, 90,2±0,5 μmol/mol NO

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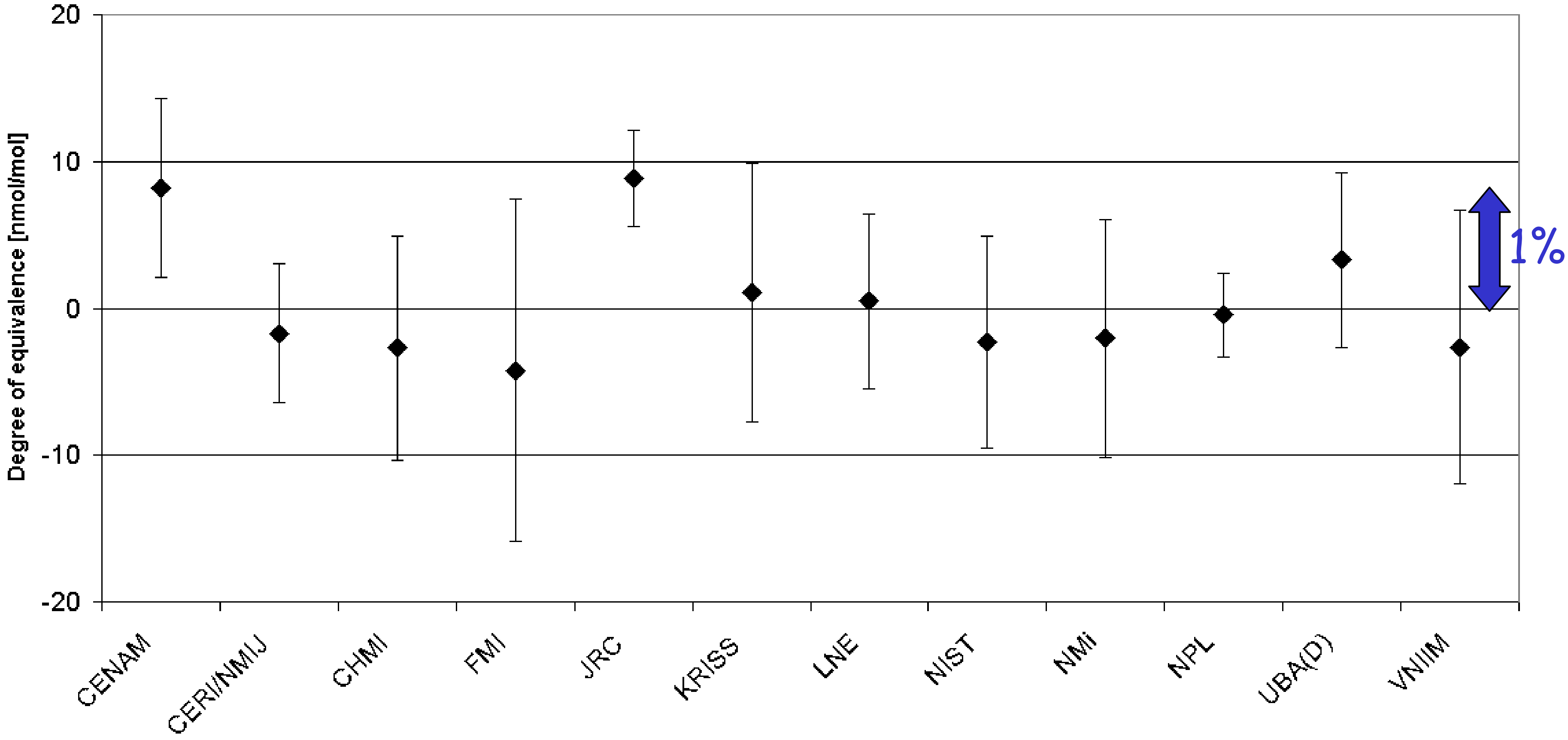
K26a NO results



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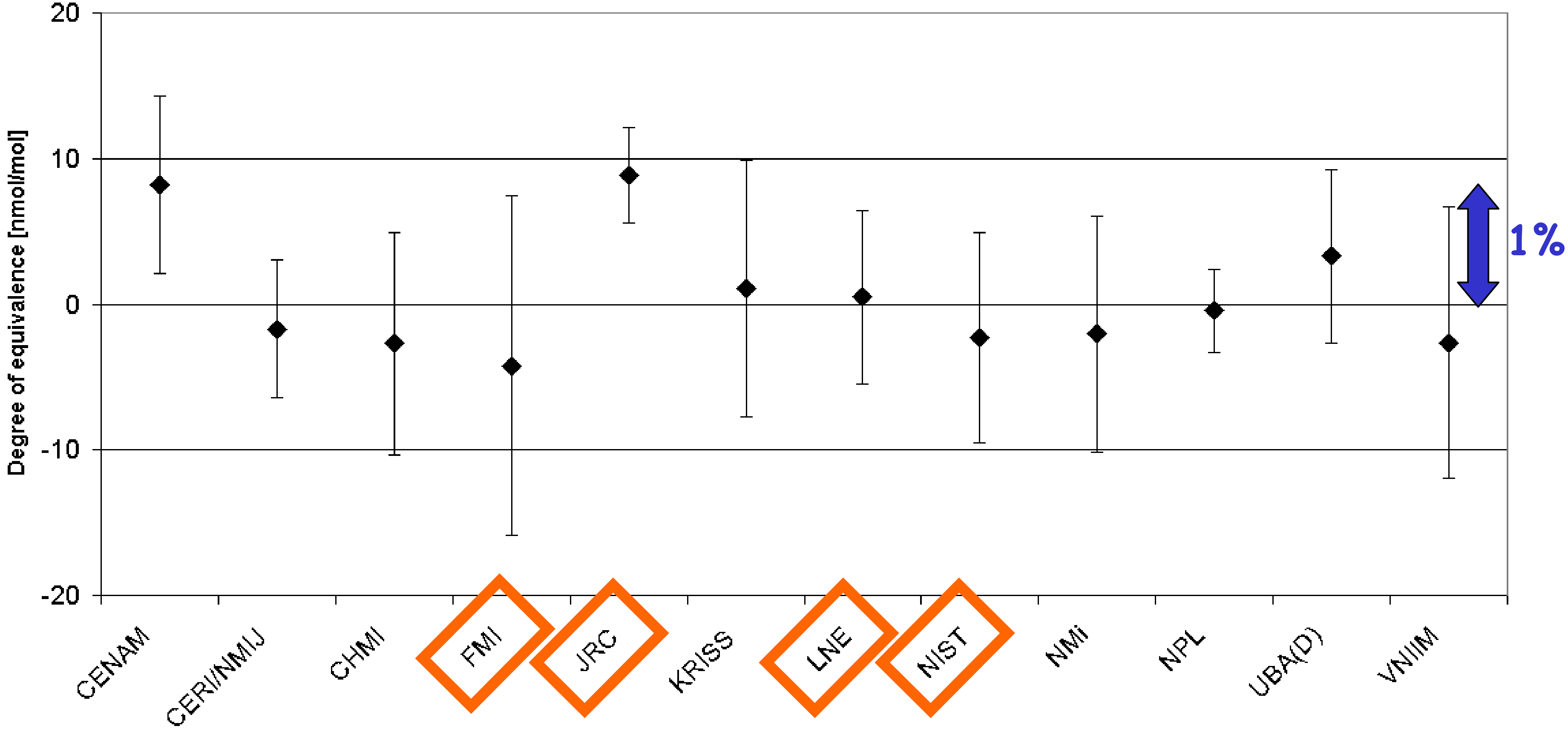
K26a NO results



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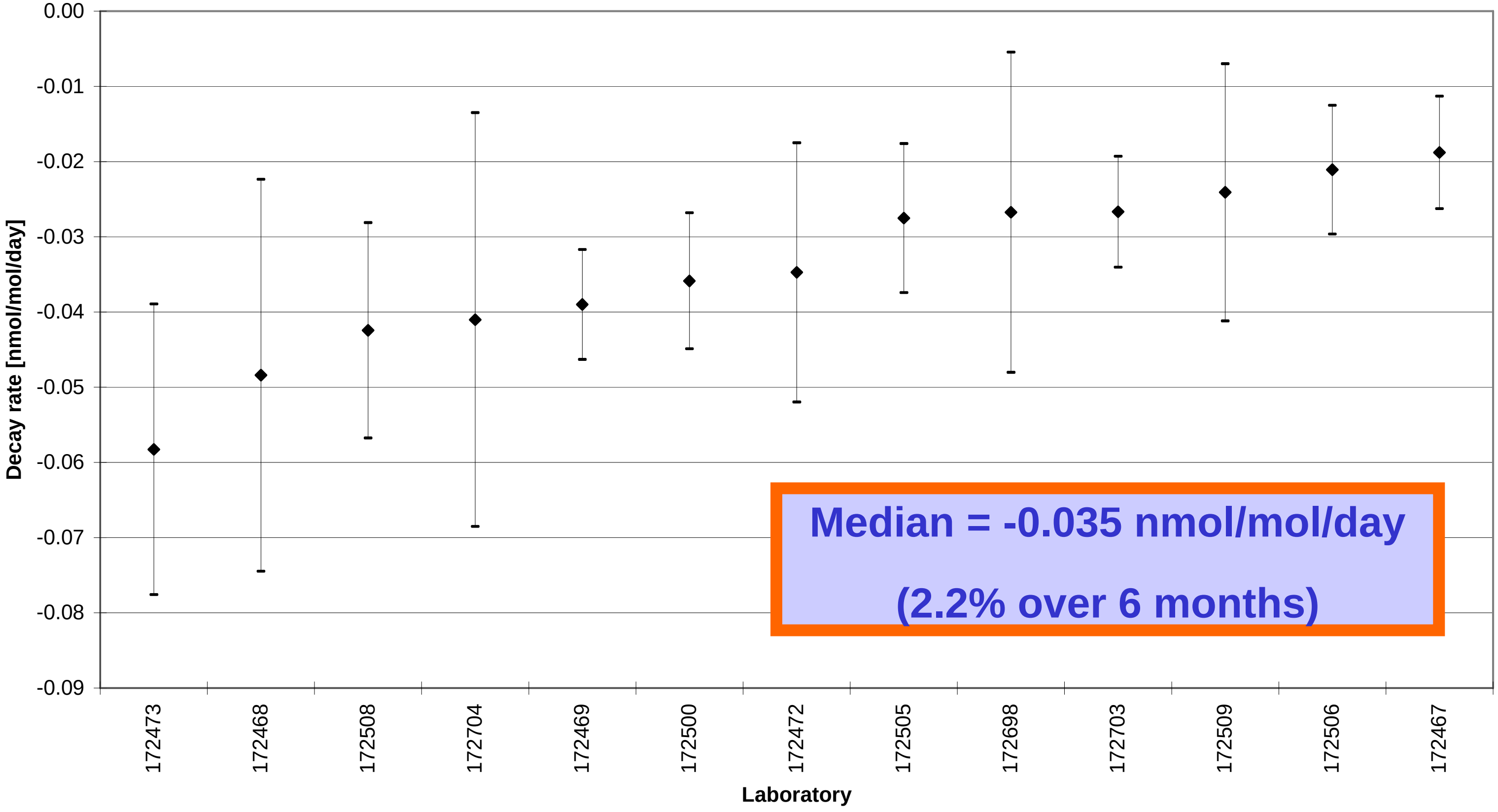
K26b – SO_2
Drift rate of all travelling standards



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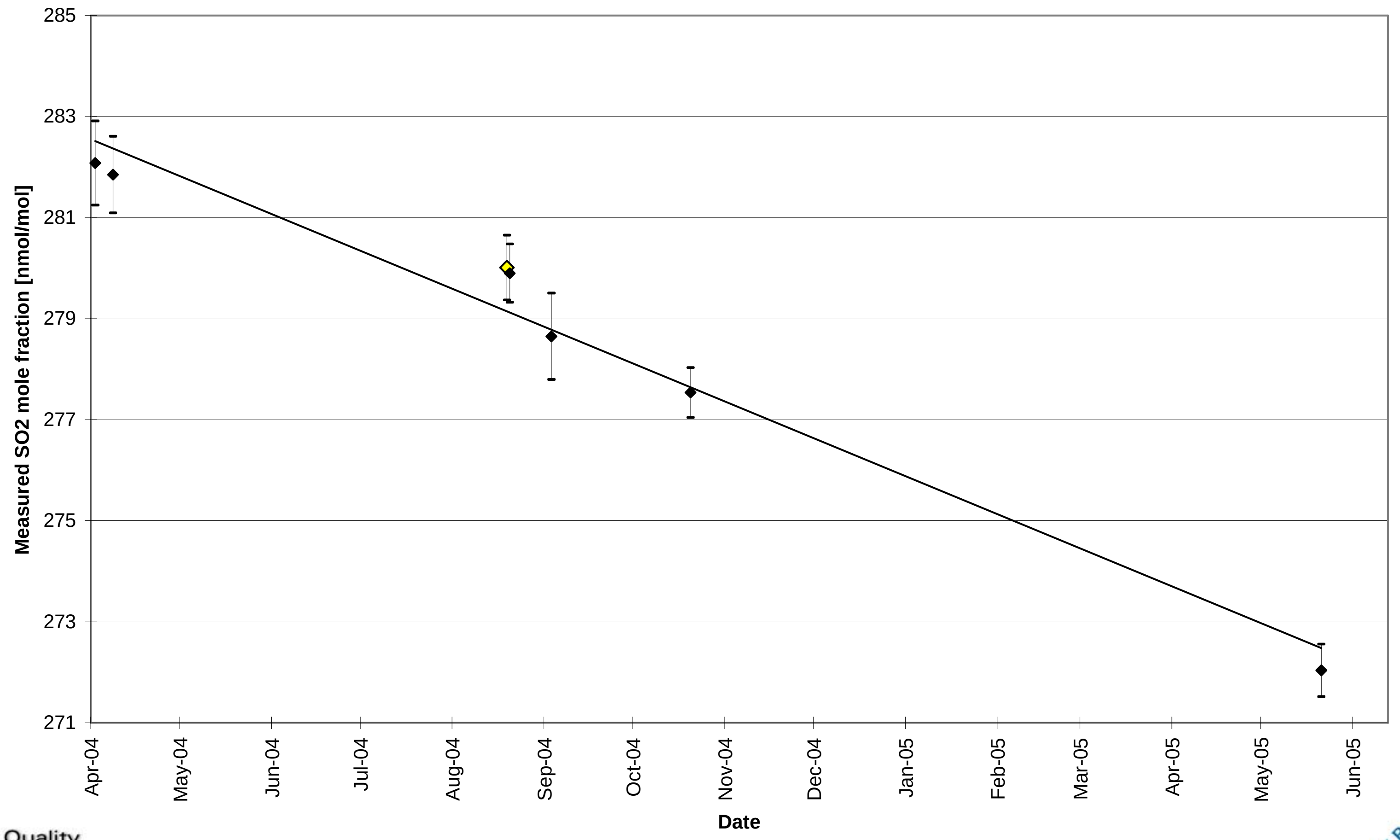
Long-term monitoring



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Methods

Participant	Method	Standard	Calibration Protocol	Static Vessel (if any)	Analyser
CERI/NMIJ	Static gravimetric	PRMs (prepared by CERI/NMIJ) at 250 ppb	2 point	10 litre e'polished Al cylinder (at 250 ppb)	UV fluorescence (Thermo)
CHMI	Static volumetric	Dilution of a PRM (prepared by NMi at 10 ppm)	Single point (ratio)	111 litre glass chamber(at 250 ppb)	UV fluorescence (Thermo)
FMI	Dynamic volumetric	Dilution of a PRM (prepared by NPL at 100 ppm) using a critical orifice dilution system (LNI)	5 point	10 litre cylinder (at 100 ppm)	UV fluorescence (Thermo)
IPQ	Dynamic gravimetric	Periodic weighing of a permeation device.	5 point	None	UV fluorescence (Thermo)
JRC-IES	Dynamic gravimetric	Periodic weighing of three permeation devices.	3 point	None	UV fluorescence (Env SA)
KRISS	Static gravimetric	PRMs (prepared by KRISS) at 250 ppb	4 point	10 litre e'polished Al cylinder (at 250 ppb)	UV fluorescence (Thermo)
LNE	Dynamic volumetric	Dilution of a PRM (prepared by LNE at 10 ppm) using high accuracy flow controllers (MolBloc)	Single point (ratio)	10 litre cylinder (at 10 ppm)	UV fluorescence (Env SA)
NMi	Dynamic gravimetric	Continuous weighing of a permeation device.	5 point	None	UV fluorescence (Thermo)
NPL	Dynamic gravimetric	Continuous weighing of a permeation device.	Single point (ratio)	None	UV fluorescence (Thermo)
UBA(A)	Dynamic volumetric	Dilution of a PRM (prepared by NMi) using a thermal mass flow controller system (Horiba)	2 point	5 litre cylinder (at 90 ppm)	UV fluorescence (Thermo)
UBA(D)	Static volumetric	Volumetric dilution from pure materials	2 point	14.7 litre (at 250 ppb)	UV fluorescence (Horiba)
VNIIM	Dynamic gravimetric	Continuous weighing of a permeation device.	Single point (ratio)	None	UV fluorescence (Env SA)

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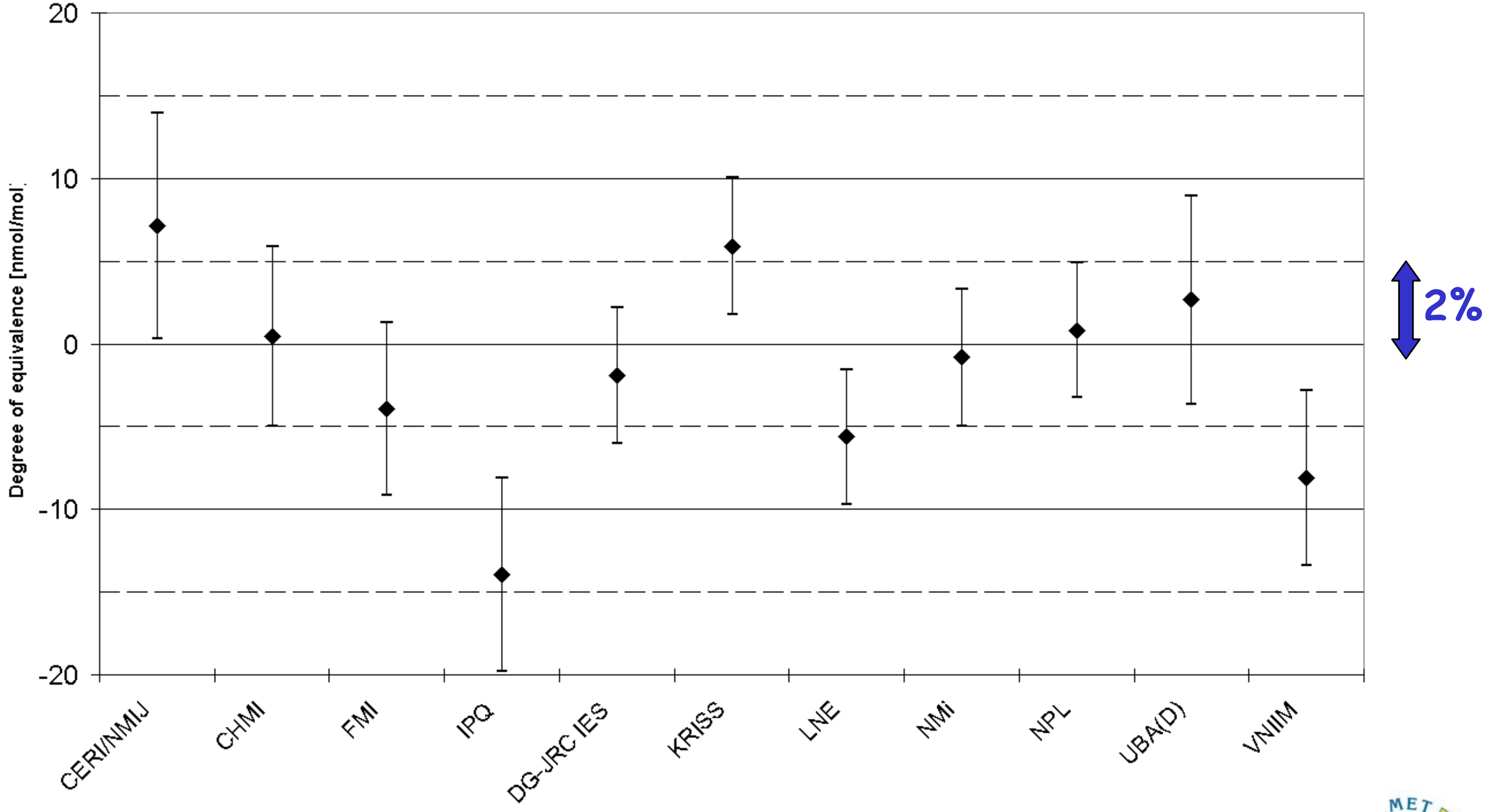
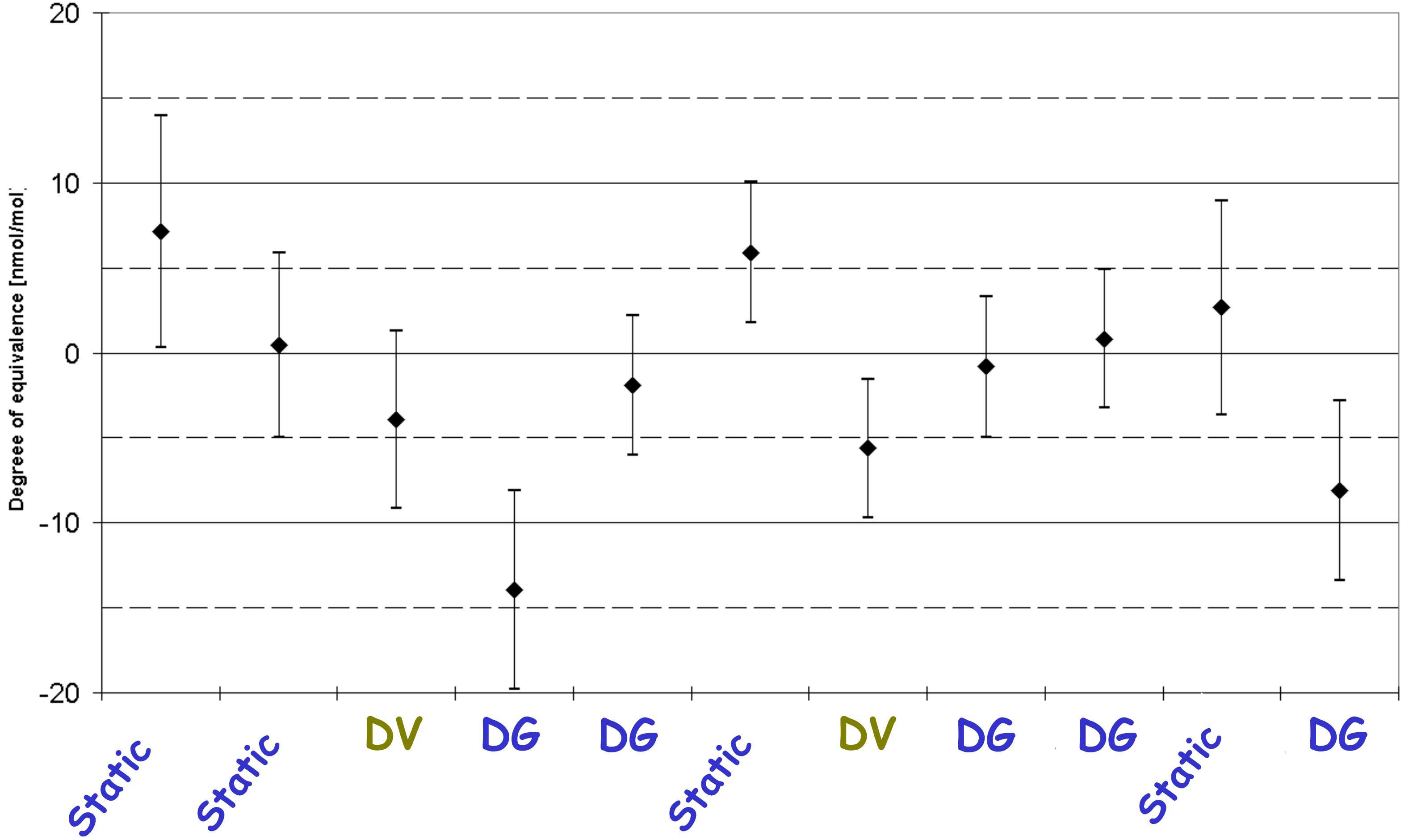
Degrees of equivalence



Reference Laboratories

Degrees of equivalence



Laboratories

886: Comparison of ozone precursors

- EU Directive 2002/3/EC mandates countries within the EU to make measurements of a specific set of 30 VOC ozone precursors involved in this comparison.
- Comparison organised as a cooperation between EUROMET and AQUILA.
- Coordinating laboratories: NPL and EC-JRC(IES).
- All standards to be prepared and analysed by NPL (before and after the comparison).

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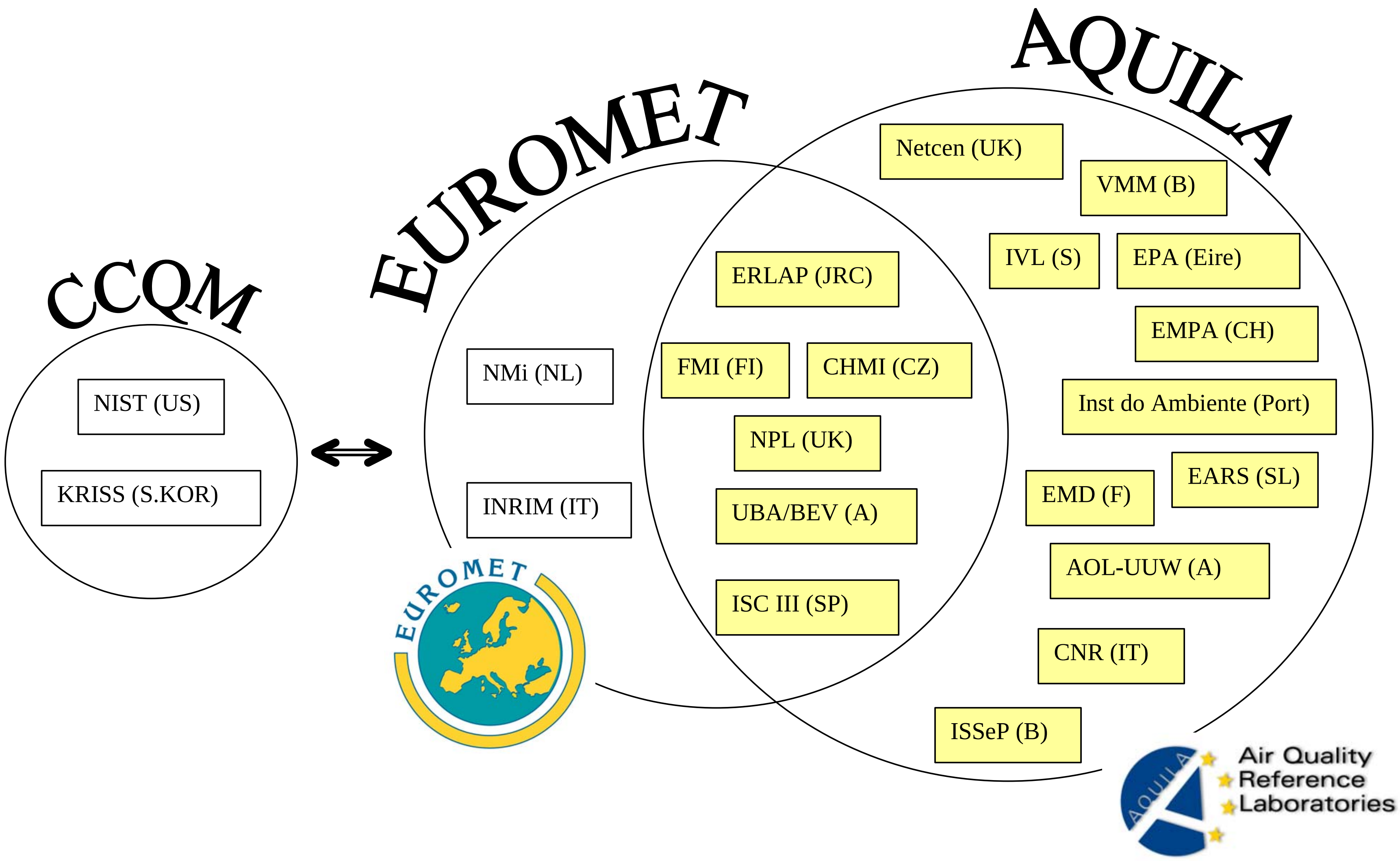
886: Comparison of ozone precursors

- ethane
- ethene (ethylene)
- ethyne (acetylene)
- propane
- propene
- n-butane
- i-butane (2 methyl propane)
- 1-butene
- trans-2-butene
- cis-2-butene
- 1,3-butadiene
- n-pentane
- i-pentane (2 methyl butane)
- 1-pentene
- (trans) 2-pentene
- isoprene (2 methyl 1,3-butadiene)
- n-hexane
- i-hexane (2 methyl pentane)
- n-heptane
- n-octane
- i-octane (2,2,4-trimethyl pentane)
- benzene
- toluene
- o-xylene
- m-xylene
- ethyl benzene
- 1,2,3-trimethyl benzene
- 1,2,4-trimethyl benzene
- 1,3,5-trimethyl benzene

886: Comparison of ozone precursors



886: Comparison of ozone precursors

- Coordinating laboratories: NPL and JRC (EI)
  - METCHEM participants
    - UBA(A), CHMI, NPL, JRC(EI), FMI , NMi, PTB (7)
  - expert laboratories from AQUILA
    - AEAT, EARS, ISSEP, EMD, IIA-CNR, IVL, EMPA, ISC III, EPA, IdA, AOL-UUW (11)
    - + NIST, KRISS
- Timetable
    - Nov 06 - Preparation of standards and start of cylinder stability trials
    - May 07 - Dispatch of standards to participants
    - July 07 - Return of results and standards to coordinating laboratory.
    - Oct 07 - Circulation of Draft A report
    - Feb 08 - Circulation of Draft B report
    - July 08 - Publication of Final Report

Summary

- Dynamic methods have been used in CCQM comparisons to generate ambient level NO and SO_2
- The data shows no significant difference from static methods.

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