Results of the comparison exercise of NO, NO_2 and SO_2 at LVs

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Objective of the WP1 of MACPoll

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Objective

– To provide harmonized and validated dilution methods of air pollutant gases at the limit values of the european directive 2008/50/CE for calibration and quality control purposes

	Limit values (LV)
SO_2	One hour: 132 nmol/mol* One day: 47 nmol/mol* Calendar year: 8 nmol/mol#
NO_2	One hour: 105 nmol/mol* Calendar year: 21 nmol/mol*

SO_2: 40 - 150 nmol/mol

NO-NO_2: 20 - 100 nmol/mol

** air quality directive (2008/50/EC) Annex XI and art. 13*

 # air quality directive (2008/50/EC) Annex XIII and art. 14

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Organization of the comparison exercice -1

Objective

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– To organize a comparison exercice for testing the comparability between 3 different dilution methods and validating them

Static dilution : SO_2 and NO →

← Permeation : NO_2 and SO_2

Dynamic dilution of gas mixtures : →

NO, NO_2 and SO_2

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Organization of the comparison exercice -2

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- Description of the implementation program
  - Determination of the comparison protocol
  - Choice and characterization of the transfer standards
  - Planning of the comparison exercice
  - Measurements in the participant laboratories
  - Treatment of the results and conclusion
- 5 Participants
  - LNE, METAS, FMI, UBA, SMU

Comparison protocol

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- Generation of dynamic gas mixtures with 2 stable low concentrations in matrix ''air''
  - SO_2: 40 nmol/mol and 150 nmol/mol
  - NO: 20 nmol/mol and 100 nmol/mol
  - NO_2: 20 nmol/mol and 80 nmol/mol
- Determination of the analytical concentrations by the participants with their analysers, calibrated with their standards generating by the dilution methods
- Comparison of the results with the following targets
  - Comparability of results with relative degrees of equivalence
    - For NO and SO_2: D_i (rel) < 2%
    - For NO_2: D_i (rel) < 3%

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Choice of the travelling standard for NO and SO_2 -1

– Dynamic dilution of gas mixtures based on the use of very accurate laminar flowmeters (Molbloc/Molbox) developed by LNE

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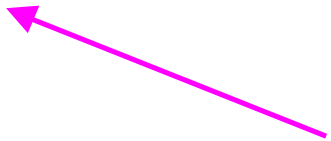
Pressure regulators



Molbox / Molbloc

MFC

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Choice of the travelling standard for NO_2

– Traceable Mobile Permeation standard gas mixture Generator (TMPG) developed by METAS based on:
  - Gravimetrically calibrated permeation devices
  - CMOSense MFC's and mass flow meter for sum of carrier and dilution gas flows
  - Temperature sensor at permeation device

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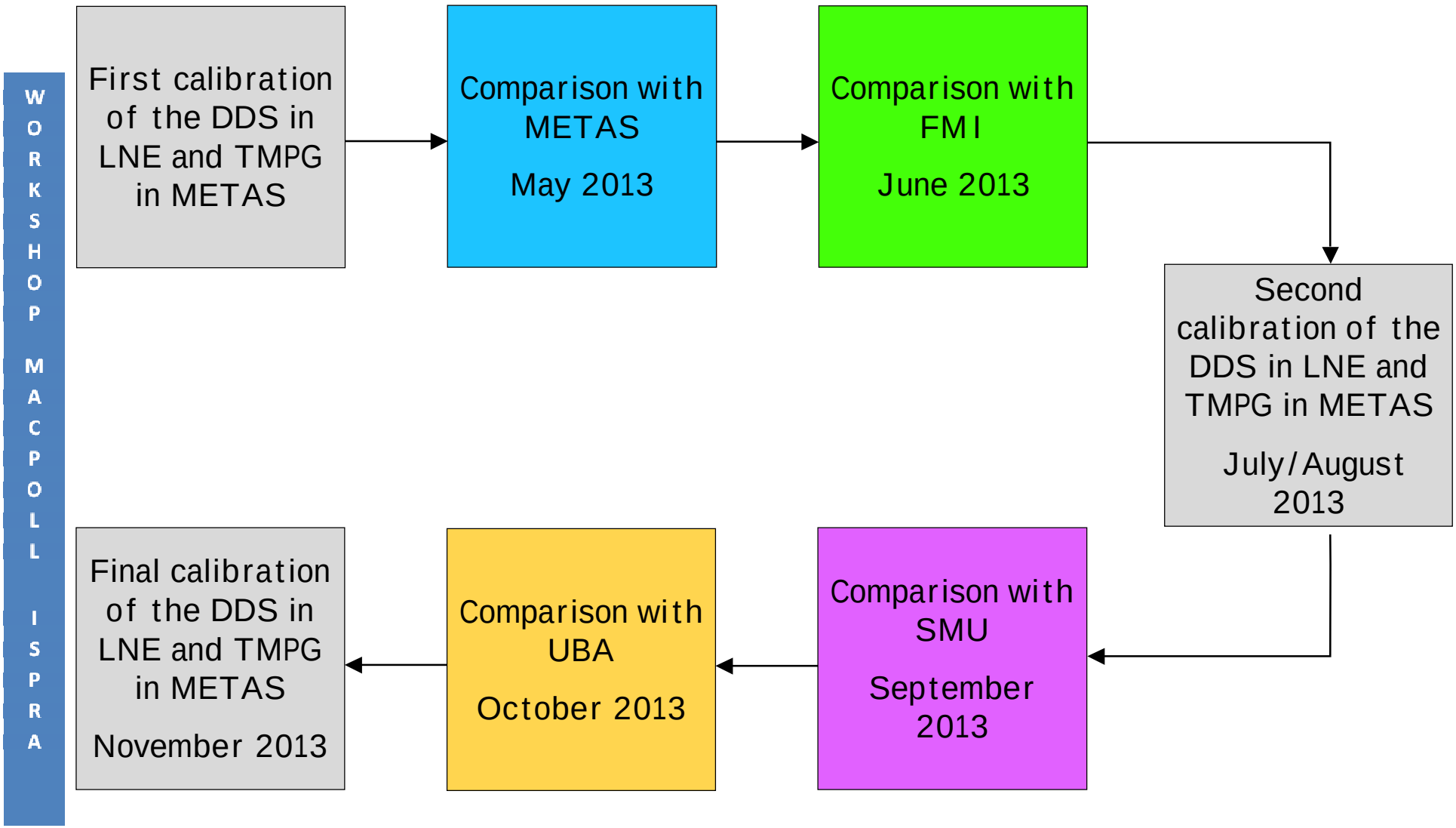
Planning of the comparison



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Results obtained for NO at 20 and 100 nmol/mol -1

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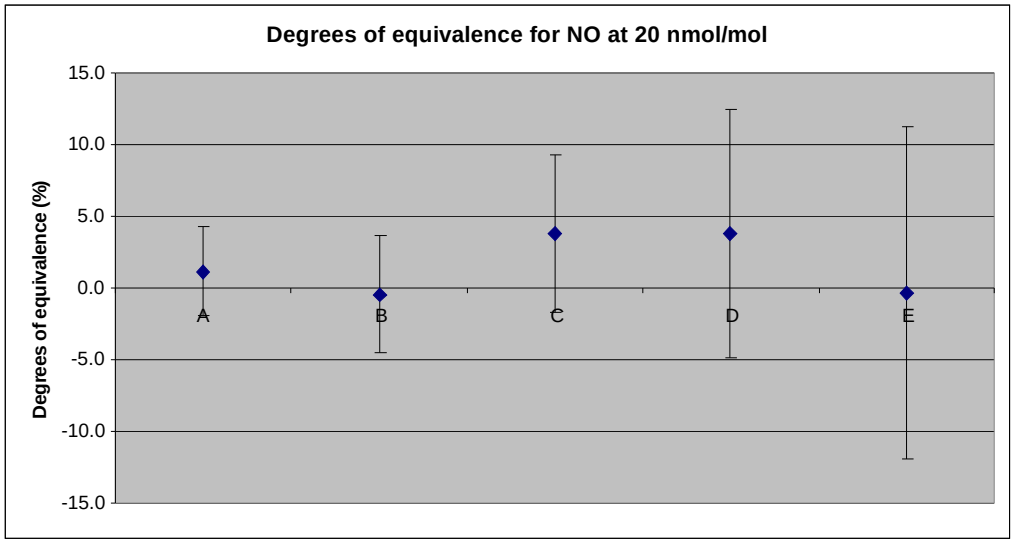
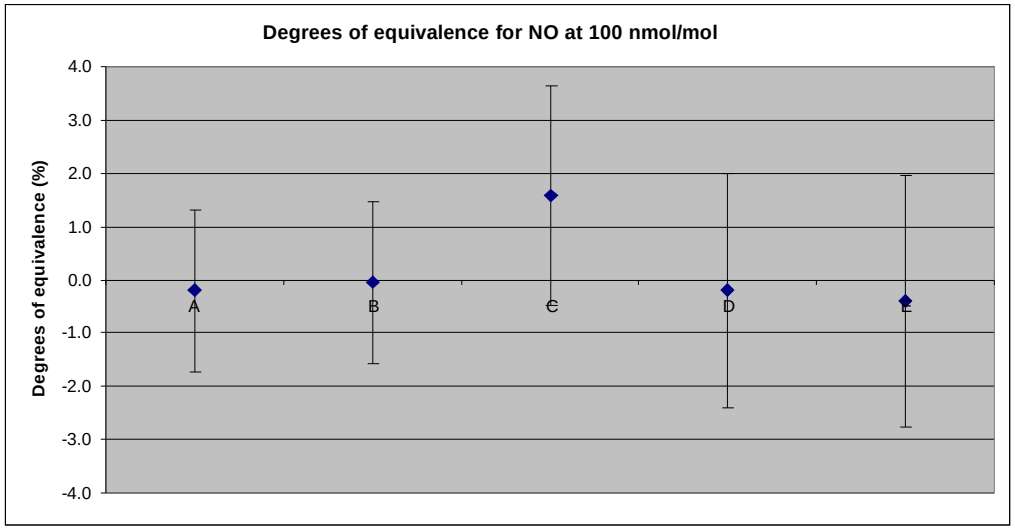


– NO at 20 nmol/mol
  - D_i (rel) = -0.4 to 3.8 %

– NO at 100 nmol/mol
  - D_i (rel) = -0.4 to 1.6 %



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Results obtained for NO at 20 and 100 nmol/mol -2

Component	Target concentration	Comparison results	Target agreement
NO	20 nmol/mol	-0.4 to 3.8 %	> 2 %
	100 nmol/mol	-0.4 to 1.6 %	< 2 %

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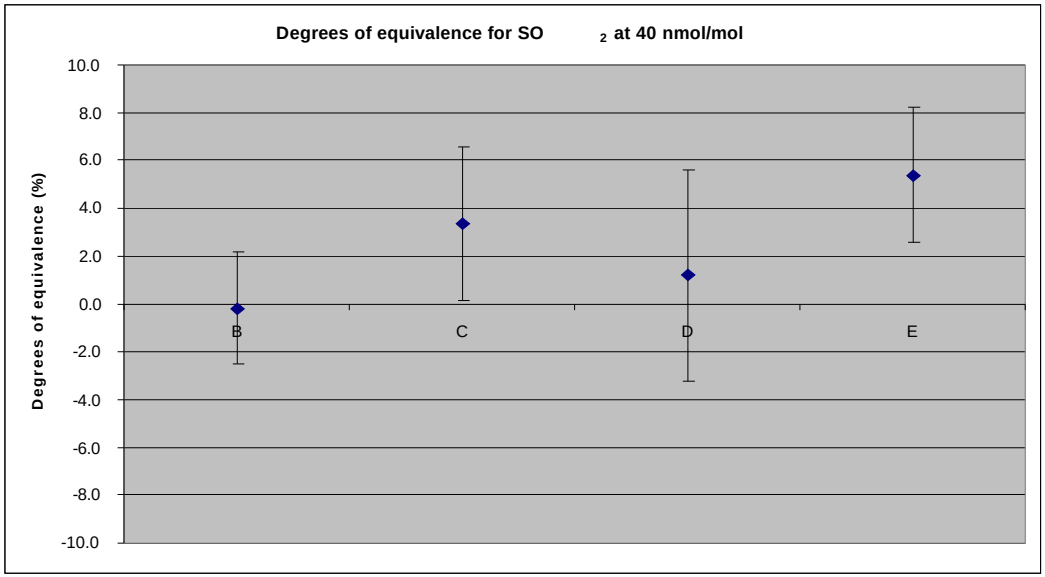
Concerning NO results at 20 nmol/mol

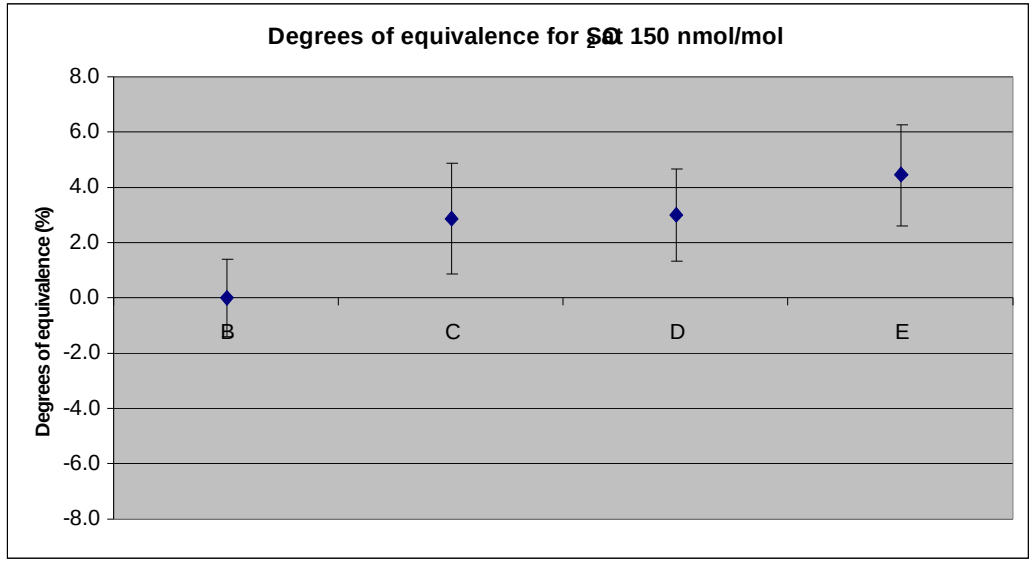
- Laboratory C
  - Set up of the calibration equipment (Sonimix Dilutor)
    - Dilution of a standard gas mixture at 50 µmol/mol ⇒ very low flow of this gas mixture to generate dynamic gas mixture at 20 nmol/mol (several ml/min)
    - Determination of the different dilution factors with a CO gas mixture
- Laboratory D
  - Drift of the analyser at zero and scale points

Results obtained for SO_2 at 40 and 150 nmol/mol -1



- SO_2 at 40 nmol/mol
  - D_i (rel) = -0.2 to 5.4 %

- SO_2 at 150 nmol/mol
  - D_i (rel) = 0 to 4.5 %



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Results obtained for SO_2 at 40 and 150 nmol/mol -2

Component	Target concentration	Comparison results	Target agreement
SO_2	40 nmol/mol	-0.2 to 5.4 %	> 2 %
	150 nmol/mol	0 to 4.5 %	> 2 %

Concerning SO_2 results at 40 (C and E) and 150 nmol/mol (C, D and E)

- Laboratories C and D
  - Same assumptions as those for NO
    - Set up of the calibration equipment (Sonimix Dilutor) (Laboratory C)
    - Drift of the analyser at zero and scale points (Laboratory D)
- Laboratory E
  - Static dilution
    - Adsorption/desorption in the mixing chamber
    - High uncertainty on the volume of the syringe

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Results obtained for SO_2 at 40 and 150 nmol/mol -3

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Concerning SO_2 results at 40 (C and E) and 150 nmol/mol (C, D and E)

- Positive deviations between the reference concentrations (LNE) and the concentrations given by the participants
  - Reference concentrations

	Cylinder concentration + flowrates		Permeation method	
	May 2013	November 2013	May 2013	November 2013
SO_2 40 nmol/mol	42.62 ± 0.75 nmol/mol	42.69 ± 0.70 nmol/mol	42.7 ± 0.7 nmol/mol	42.4 ± 0.7 nmol/mol
SO_2 150 nmol/mol	149.8 ± 1.7 nmol/mol	150.1 ± 1.5 nmol/mol	150.1 ± 1.2 nmol/mol	149.2 ± 1.2 nmol/mol

  - Other explanations
    - Nature of the materials in contact with the SO_2 gas mixture
    - Calibration : Time between the injection of the standards and the ajustment of the analyser too short
    - Use of pressure regulator with high dead volumes for very low flow

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Results obtained for NO_2 at 20 and 80 nmol/mol

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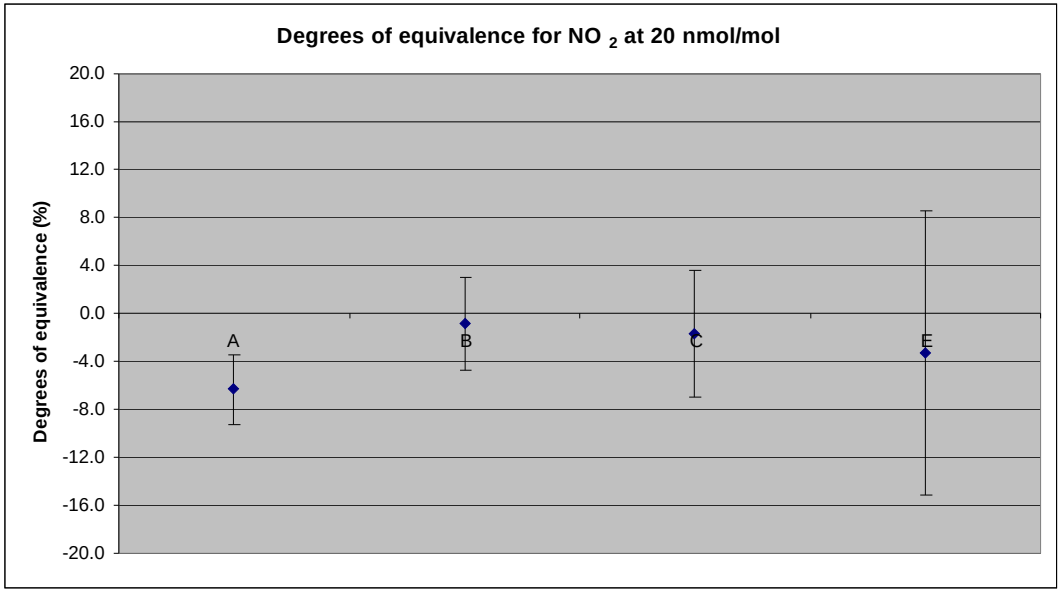
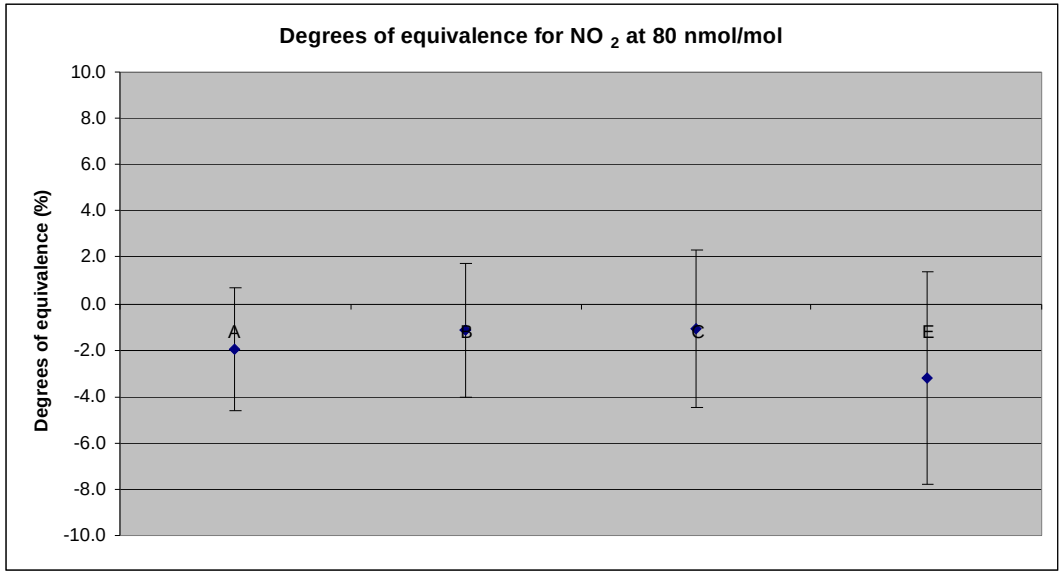


– NO_2 at 20 nmol/mol
  - D_i (rel) = -0.8 to -6.4 %

– NO_2 at 80 nmol/mol
  - D_i (rel) = -1.1 to -3.2 %



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Conclusion -1

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- Preliminary results of the comparison exercice

NO 20 nmol/mol	$D_i(rel) \approx 2$ % except 2 labs at 20 nmol/mol
NO 100 nmol/mol	
SO_2 40 nmol/mol	$D_i(rel) < 5$ %
SO_2 150 nmol/mol	
NO_2 20 nmol/mol	$D_i(rel) \approx 3$ % except 1 lab at 20 nmol/mol
NO_2 80 nmol/mol	

$\Rightarrow$ Results not so bad for very low concentrations

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Conclusion -2

- This European project MACPoll aimes the participants
  - To improve the dilution methods for ambient air pollutants (NO, NO_2 and SO_2) for low concentrations
  - To develop stable and accurate travelling standards based on
    - Permeation for NO_2
    - Dynamic dilution of high concentration gas mixtures for NO and SO_2

- Concerning the deliverables
  - Available report on the results of the comparison in January 2014
  - Provision of guides free accessible on MACPoll website (www.macpoll.eu) from January 2014
    - Guide on dynamic dilution for NO, NO_2 and SO_2 at limit values
    - Guide on permeation method for NO_2 and SO_2 at limit values
    - Guide on static dilution for NO and SO_2 at limit values

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