Dynamic reference standards for CO and N$_2$O

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HIGHGAS

LNE
Le progrès, une passion à partager

MESURES
& RÉFÉRENCES
Clés de la COMPÉTITIVITÉ
et d'un MONDE PLUS SÛR

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Context

- **Results of international comparisons on greenhouse gases**

  - Dynamic generation methods do not have the necessary accuracy to meet the uncertainty requirements for global monitoring

- **Need of significant research to lead to accurate methods for providing these dynamic standards**

- **Key challenges for developing dynamic devices to provide high accuracy reference standards**

  - Lower concentrations

  - Lower uncertainties

  - Capability to provide stable measurements in long-term to be used in field monitoring

Objectives

- Development of ***dynamic generation methods and devices*** for

  - On-site preparation of reference standards with uncertainties that meet WMO targets for atmospheric CO and N_2O

    - CO

      - Measurement range: between 50 and 500 nmol/mol

      - Target expanded uncertainty: 2 nmol/mol

    - N_2O

      - Measurement range: between 50 and 500 nmol/mol

      - Target expanded uncertainty: 0.1 nmol/mol

Different steps of the project

- Involved laboratories : LNE, TUBITAK and FMI

- First step: development of high accuracy dynamic facilities for atmospheric CO and N_2O

  - Design of different dynamic systems from static reference standards using

    - Laminar flow meters (2 dynamic facilities)

    - Sonic nozzles (1 dynamic facility)
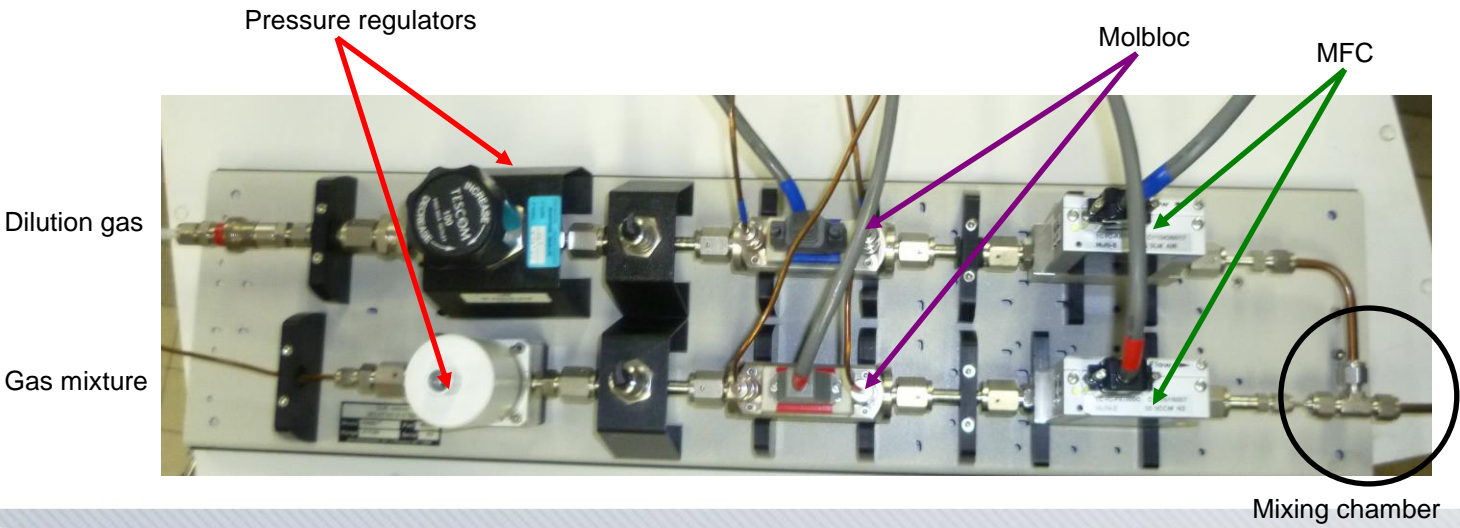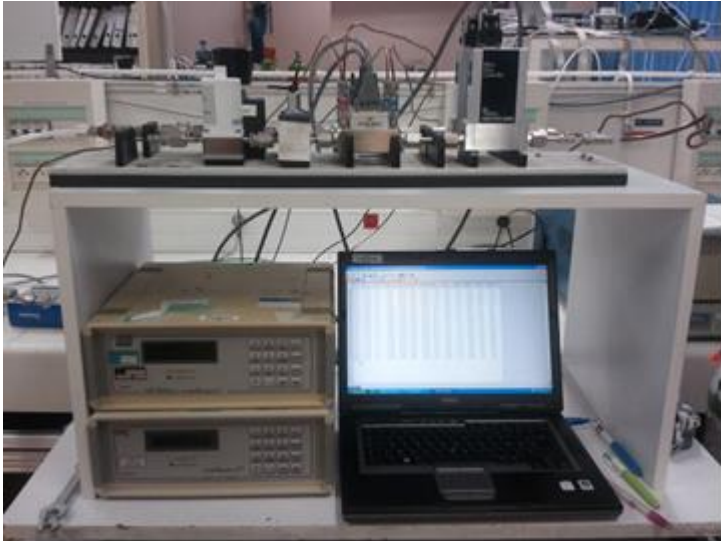
  - Development of the different dynamic devices

- Second step

  - Determination of the expanded uncertainties on the concentrations of the dynamic gas mixtures

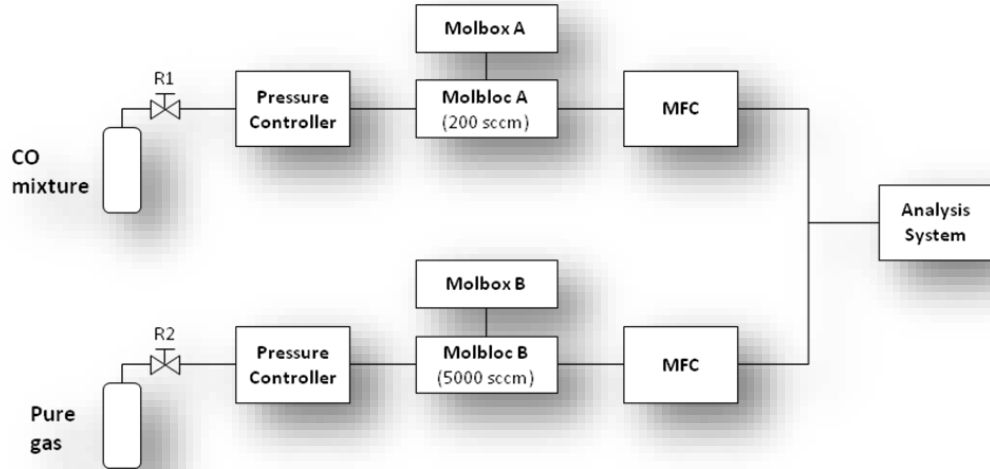 - Validation of dynamic facilities

LNE's dynamic facility based on Molbloc/Molbox flowmeters (CO and N_2O)

Pressure regulators

Molbloc
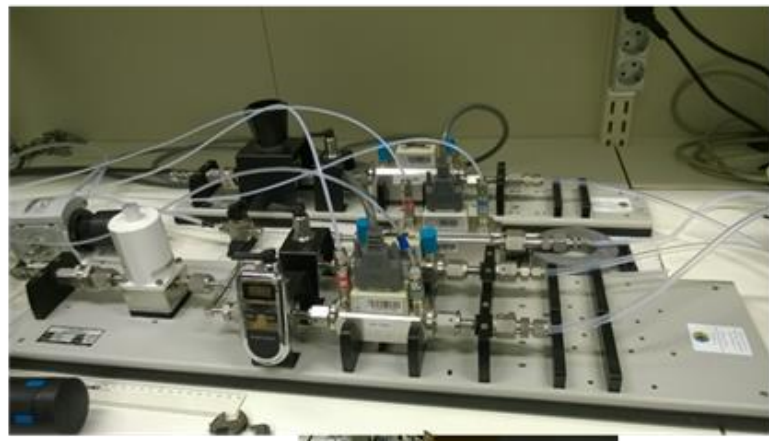
MFC

Dilution gas

Gas mixture

Mixing chamber

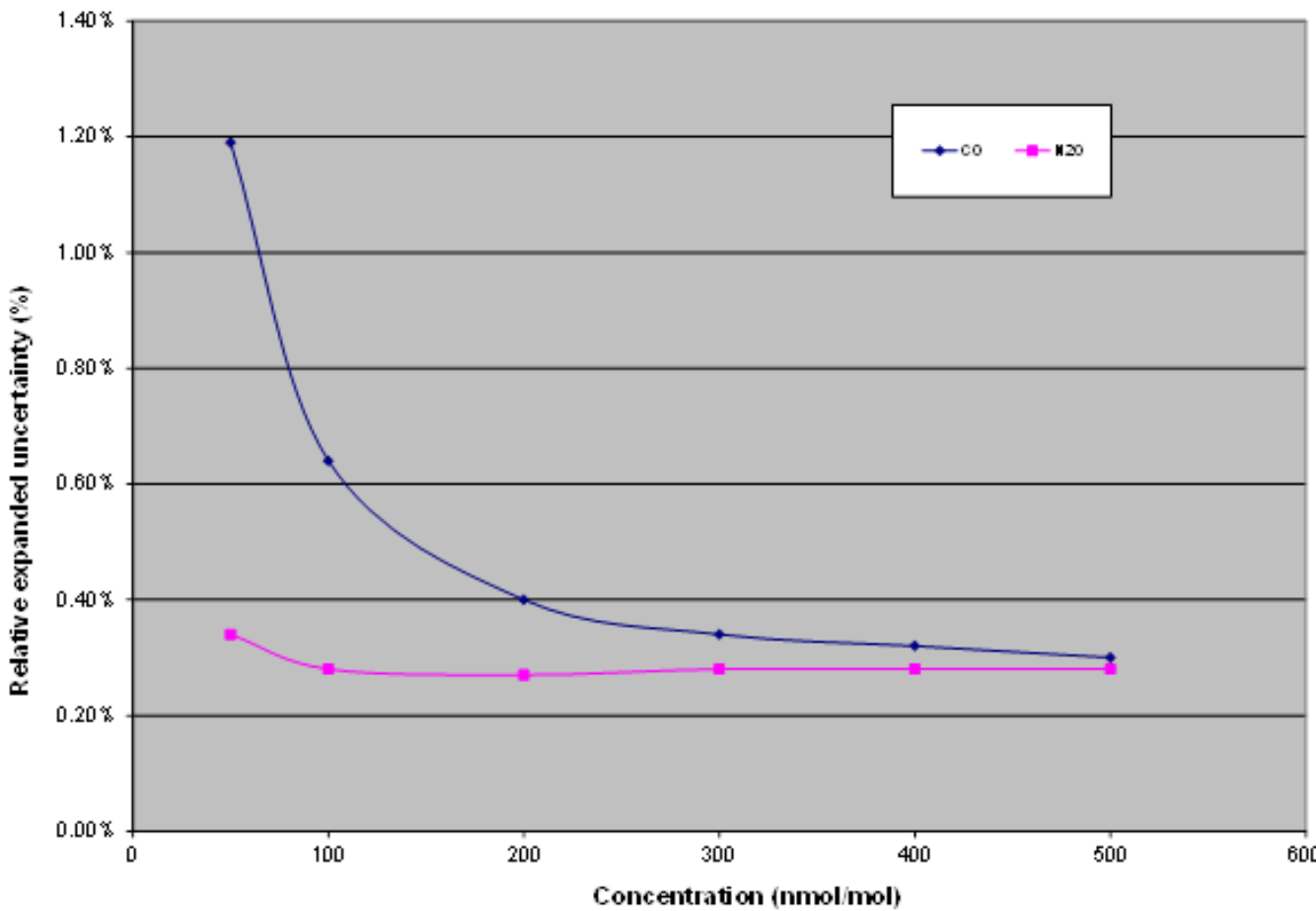TUBITAK's dynamic facility based on Molbloc/Molbox flowmeters (CO)

FMI's dynamic facility based on commercial dilution device Sonimix 6000 A1 from LN-Industries (sonic nozzles) for CO and N_2O

▶ Expanded uncertainties on CO and N$_2$O concentrations for LNE's dynamic facility based on Molbloc/Molbox flowmeters
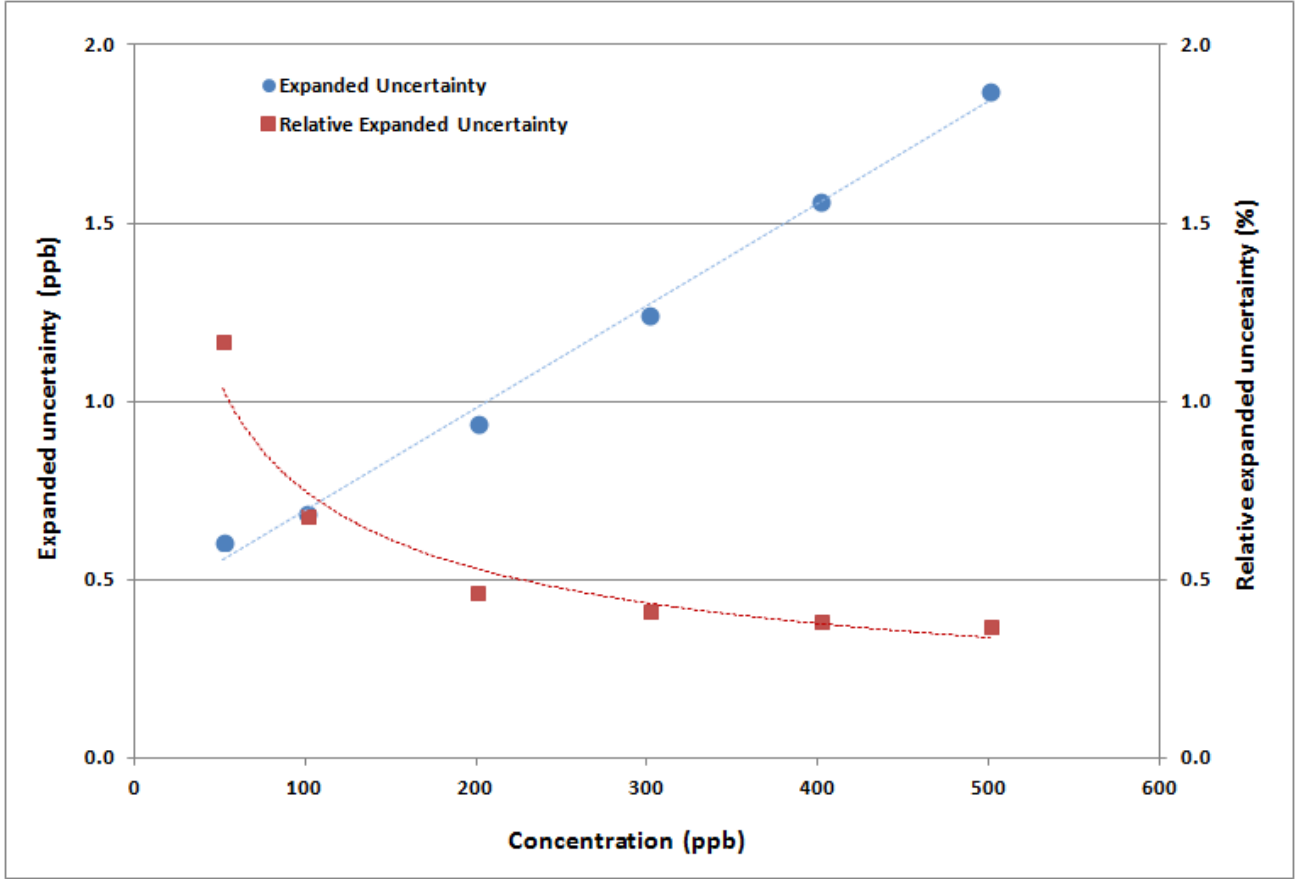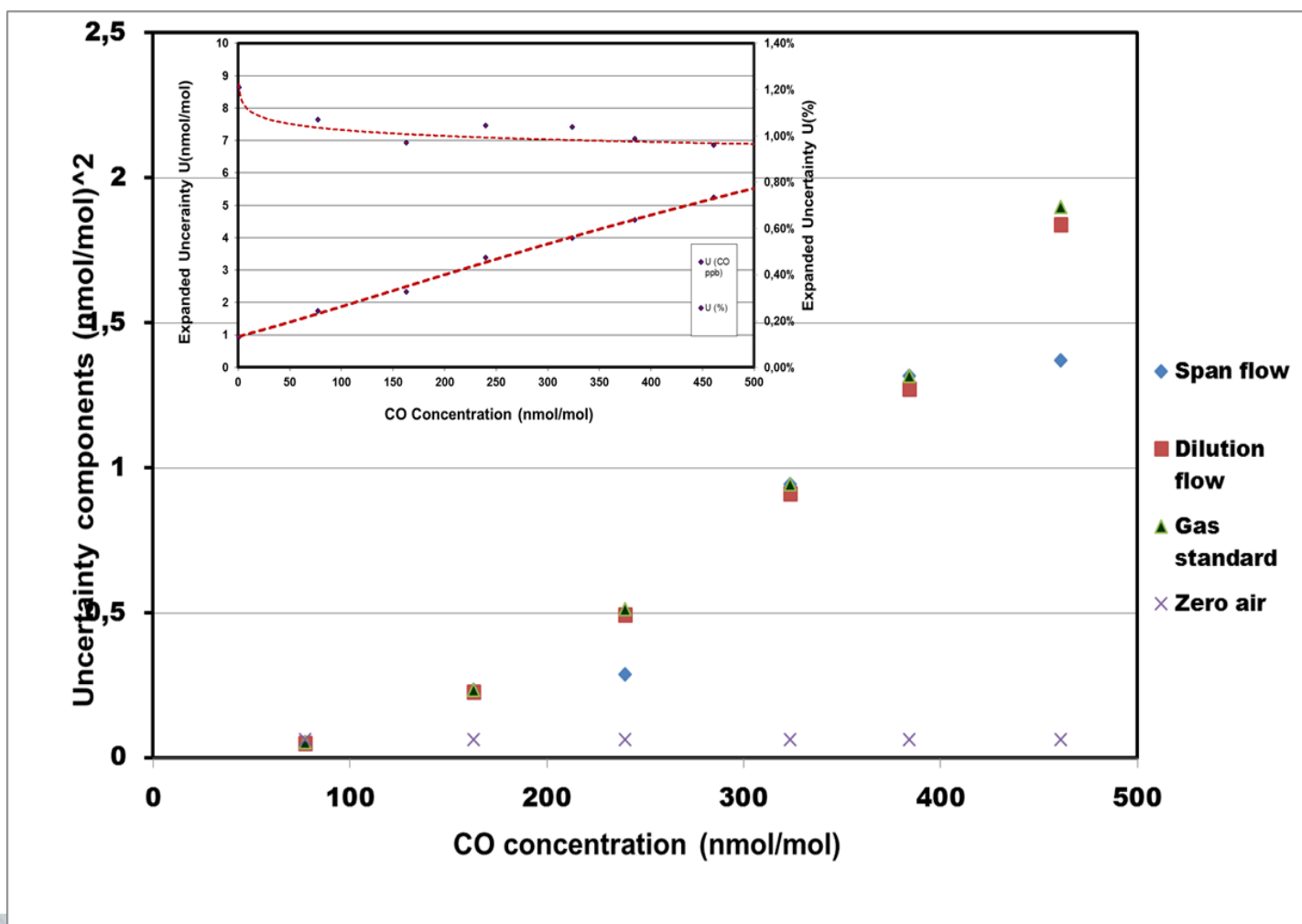
▶ Expanded uncertainties on CO concentrations for TUBITAK's dynamic facility based on Molbloc/Molbox flowmeters
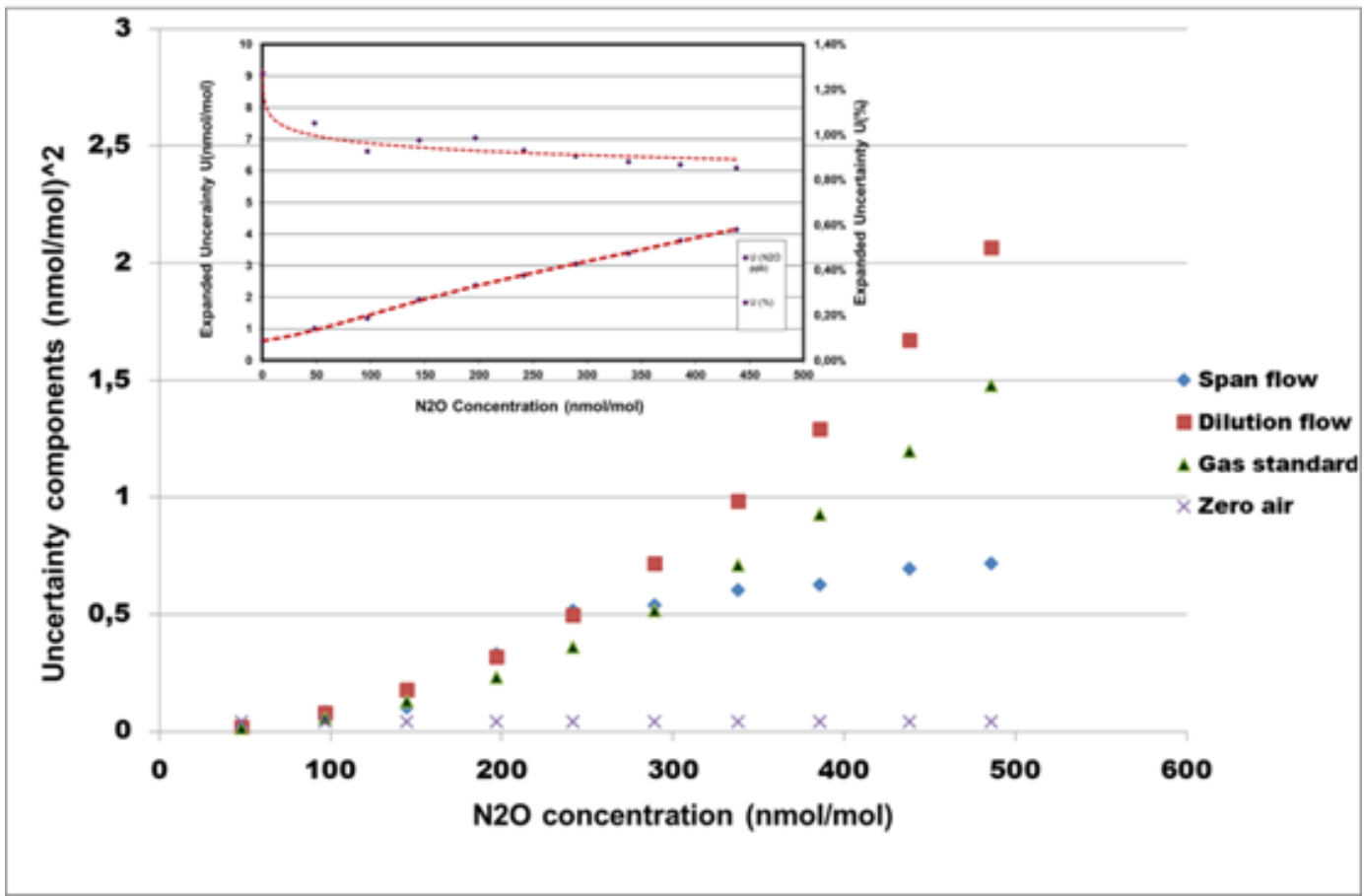
▶ Expanded uncertainties on CO concentrations for FMI's dynamic facility based on sonic nozzles

▶ Expanded uncertainties on N_2O concentrations for FMI's dynamic facility based on sonic nozzles

CO at 300 nmol/mol			N_2O at 325 nmol/mol	
Molbloc/Molbox		Sonic nozzles	Molbloc/Molbox	Sonic nozzles
U(k=2) for LNE's dynamic facility	U(k=2) for TUBITAK's dynamic facility	U(k=2) for FMI's dynamic facility	U(k=2) for the dynamic facility 1	U(k=2) for FMI's dynamic facility
1.03 nmol/mol	1.24 nmol/mol	1.98 nmol/mol	0.9 nmol/mol	2.0 nmol/mol

► Calculated expanded uncertainties on dynamic gas mixtures

- Fulfil with the uncertainty of 2 nmol/mol set by the WMO for CO at 300 nmol/mol

- But don't fulfil with the uncertainty of 0.1 nmol/mol set by the WMO for N_2O at 325 nmol/mol

► Expanded uncertainties set by WMO

- Repeatability uncertainties but not expanded uncertainties

Validation of dynamic facilities -1

▶ Validation of dynamic facilities with comparison made to in-house static reference standards

■ Calibration of the analyser with a standard gas mixture of CO or N_2O generated with the dilution facilities

■ Injection of a gravimetric gas mixture of CO or N_2O

■ Determination of its analytical concentration

■ Calculation of the E_n value

$$E_n = \frac{\left|x_{grav} - x_{anal}\right|}{\sqrt{U_{grav}^2 + U_{anal}^2}}$$

x_{grav}	: gravimetric concentration
x_{anal}	: analytical concentration
U_{grav}	: expanded uncertainty of gravimetric concentration
U_{anal}	: expanded uncertainty of analytical concentration

Validation of dynamic facilities -2

▶ LNE's dynamic facility

Mixture	x_{grav} (nmol/mol)	U_{grav} (nmol/mol)	x_{anal} (nmol/mol)	U_{anal} (nmol/mol)	E_n value
CO/Air_0012	301.22	1.2	301.77	1.03	0.22
CO/Air_0013	299.98	1.2	300.42	1.03	0.18

Mixture	x_{grav} (nmol/mol)	U_{grav} (nmol/mol)	x_{anal} (nmol/mol)	U_{anal} (nmol/mol)	E_n value
N2O/Air 0001	332.72	0.19	332.10	0.9	0.73
N2O/Air 0002	324.40	0.18	323.58	0.9	0.97

Validation of dynamic facilities -3

▶ TUBITAK's dynamic facility

Mixture	x_{grav} (nmol/mol)	U_{grav} (nmol/mol)	x_{anal} (nmol/mol)	U_{anal} (nmol/mol)	E_n value
D298355	299.95	2.24	299.11	1.14	0.33
D298343	301.90	2.24	300.21	1.06	0.68

▶ FMI's dynamic facility

N_2O

Reference standard	x_{ref} (nmol/mol)	U_{ref} (nmol/mol)	x_{meas} (nmol/mol)	Umeas (nmol/mol)	$\mid x_{ref} - x_{meas} \mid$ (nmol/mol)	E_n (nmol/mol)
D784491	323,53	0,65	323,22	1,93	0,3	0,15

CO

Reference standard	x_{ref} (nmol/mol)	U_{ref} (nmol/mol)	x_{meas} (nmol/mol)	Umeas (nmol/mol)	$\mid x_{ref} - x_{meas} \mid$ (nmol/mol)	E_n (nmol/mol)
D790817	130,3	0,8	129,78	1,01	0,52	0,40

Conclusion

- ▶ Development of dynamic facilities for CO and N_2O based on
  - ■ Molbloc/Molbox flowmeters
  - ■ Sonic nozzles

- ▶ Validation of the developed dynamic facilities against in-house CO and N_2O gravimetric gas mixtures

- ▶ Use of the dynamic facilities for preparation of accurate gas mixtures
  - ■ For calibration purposes
  - ■ For determination of the metrological performances of the devices (linearity, repeatability…)

- ▶ WMO's expanded uncertainties very challenging
  - ■ The developed dynamic facilities fulfil the uncertainty of 2 nmol/mol for CO, but not the uncertainty of 0.1 nmol/mol for N_2O
  - ■ But which sources of uncertainties are included in the WMO's expanded uncertainties ?

Thank you for your attention

Any questions ?