WORKSHOP MACPOLL JRC

Validation of zero air generators & gas purifiers

Stefan Persijn (spersijn@vsl.nl)

JRC, Ispra, 19 November 2013, Italy

Claire Kaiser
Christophe Sutour
Tatiana Macé

Marta Doval Miñarro
Paul Brewer

Gerard Nieuwenkamp
Janneke van Wijk

Tanil Tarhan
(RMG)

Nikola Škundrić
(ESRMG)

EMRP
European Metrology Research Programme
Programme of EURAMET

The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union

Content presentation

WORKSHOP MACPOLL JRC

1) **Need for zero gas standards**

2) **Validation of gas purifiers**
   Measurement approach & Results

3) **Validation of zero air generators**
   Measurement approach & Results

4) **Certification protocol zero gas**

EMRP
European Metrology Research Programme
Programme of EURAMET
The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union

What is zero gas?

WORKSHOP MACPOLL JRC

Clean N_2 or air that is used in air quality measurements for:

– Zeroing analyzers

– Preparing and/or diluting calibration gas mixtures

Source of zero gas:

— N_2 or air of suitable grade is stored in cylinders

— Compressed and properly purified ambient air

EMRP
European Metrology Research Programme
Programme of EURAMET
The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union

Need for zero gas standards

WORKSHOP MACPOLL JRC

Driving factor is <u>regulation</u>:

- ❑ EU Air Quality Directive (2008/50/EC) regulates air chemical pollutants CO, SO_2, NO, NO_2, O_3, benzene
  - Limit Values
  - Data Quality Objectives (including traceability and uncertainty)
- ❑ US EPA and other regulatory bodies in other countries have similar approach

EMRP
European Metrology Research Programme
Programme of EURAMET
The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union

Example: NO_2

Calendar year Limit Value (2008/50/EC)	Uncertainty:
21 nmol/mol	15 % fixed measurements

→ Max zero gas contribution: 3 nmol/mol

NO: 1 ppb = 1.25 µg/m^3 1 µg/m^3 = 0.8 ppb
NO_2: 1 ppb = 1.91 µg/m^3 1 µg/m^3 = 0.523 ppb
SO_2: 1 ppb = 2.66 µg/m^3 1 µg/m^3 = 0.38 ppb
CO: 1 ppm = 1.16 mg/m^3 1 mg/m^3 = 0.86 ppm

EMRP
European Metrology Research Programme
Programme of EURAMET
The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union

The zero gas problem

WORKSHOP MACPOLL JRC

- Both zeroing and diluting rely on accurate quantification of NO/NO_2 in zero gas as this could give an offset and misreading ("chicken & egg problem").

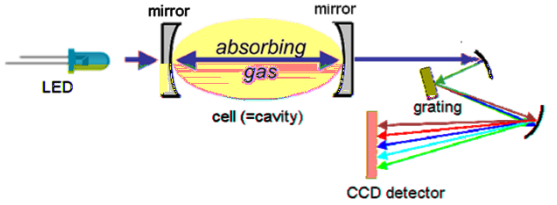
- At present no zero gas standards in EU exist and therefore comparability of measurement results is difficult (in Japan a zero gas standard exists mainly aimed at the automotive industry).

EMRP
European Metrology Research Programme
Programme of EURAMET
The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union

Work carried out in MACPoll on zero gas

WORKSHOP MACPOLL JRC

- Develop and validate sensitive methods for zero gas analysis
- Comparison classical & novel optical methods
- Study of NH_3 adsorption in sampling lines
- **Test gas purifiers & zero air generators**
- Workshop 'Zero gases' with participation of gas producers, instrument manufacturers, air quality laboratories, standardisation & NMI's (4 June 2013)
- Develop certification protocol zero gas standards (in progress)



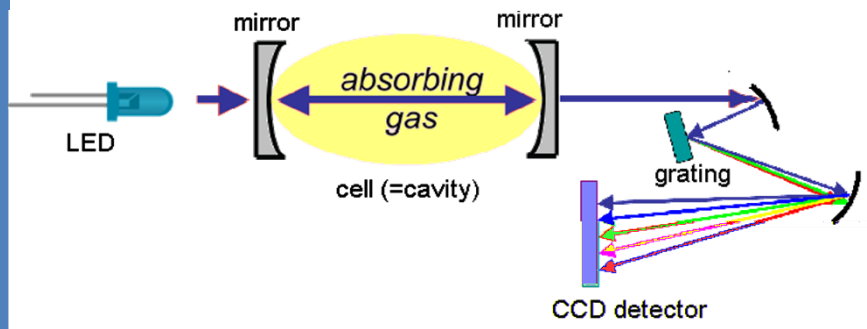

Appl. Phys. B
DOI 10.1007/s00340-013-5590-3
Applied Physics B
Lasers and Optics

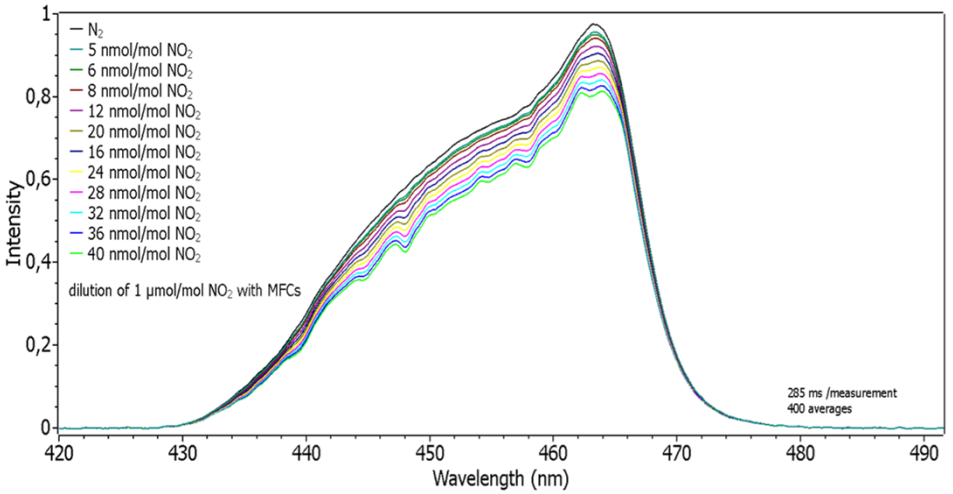
Adsorption of ammonia on treated stainless steel and polymer surfaces

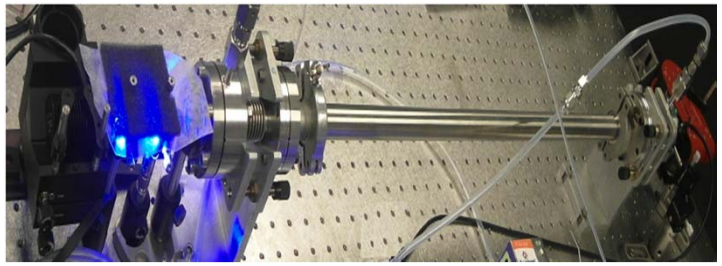
EMRP
European Metrology Research Programme
Programme of EURAMET
The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union

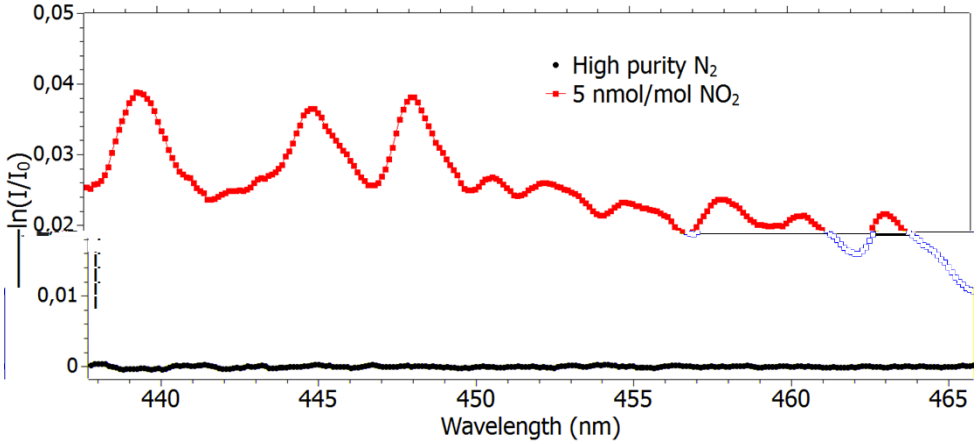
Cavity-enhanced absorption spectroscopy

WORKSHOP MACPOLL JRC







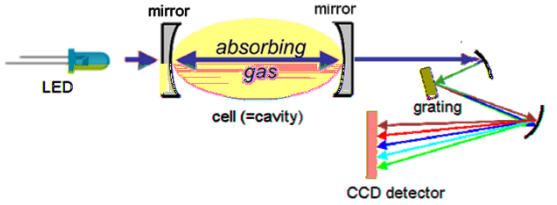


EMRP
European Metrology Research Programme
Programme of EURAMET
The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union

Work carried out in MACPoll on zero gas

WORKSHOP MACPOLL JRC

- Develop and validate sensitive methods for zero gas analysis
- Comparison classical & novel optical methods
- Study of NH_3 adsorption in sampling lines
- **Test gas purifiers & zero air generators**
- Workshop 'Zero gases' with participation of gas producers, instrument manufacturers, air quality laboratories, standardisation & NMI's (4 June 2013)
- Develop certification protocol zero gas standards (in progress)




Appl. Phys. B
DOI 10.1007/s00340-013-5590-3
Applied Physics B
Lasers and Optics

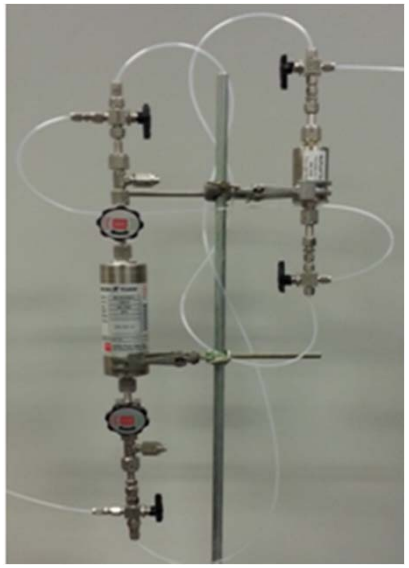
Adsorption of ammonia on treated stainless steel and polymer surfaces

EMRP
European Metrology Research Programme
Programme of EURAMET
The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union

Validation of purifiers

WORKSHOP MACPOLL JRC

- Review of gas purifiers (10 brands)
- A selection was made and 2 manufacturers provided a purifier for testing
- Tested analytes: NO, NO_2, SO_2 & CO
- Challenges of 1, 3 and 10 nmol/mol



EMRP
European Metrology Research Programme
Programme of EURAMET
The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union

Specifications gas purifiers

WORKSHOP MACPOLL JRC

	Company	Filter Model	Gases Purified	Impurities Re-moved	Outlet Perf.	Max Pressure	Max Flowrate	Regenerability
Purifier 1	SAES Pure Gas, Inc.	MICRO TORR® MC190-906FV	CDA[1] N_2 O_2	H_2O CO, CO_2 NMHCs[3]	< 1 ppb	250 psig[4]	50 slpm	factory regenerable
Purifier 2	NuPure	Optics™ OA 00200	CDA[1] N_2 O_2 He	SO_2/SO_X, H_2S Toluene, CO/CO_2 NH_3, H_2O NMHCs[2]	< 0.5 ppb	250 psig[4]	25 slpm	factory or field regenerable

[1] *Compressed Dry Air*
[2] *Acid gases, alcohols, amines, ammonia, CO/CO_2, hydrocarbons, H_2O, H_2S, NOx, SO_2, SO_x, siloxanes and toluene*
[3] *Organics (C>4); Volatile Acids including SO_2, NOx, HCl, H_2S, etc.; Volatile Bases including NH_3 and amines; Refractories: hydrocarbons with etheratoms such as Si, Halogens, P, B, S, or metals*
[4] *250 psi is equal to 17.2 bar*

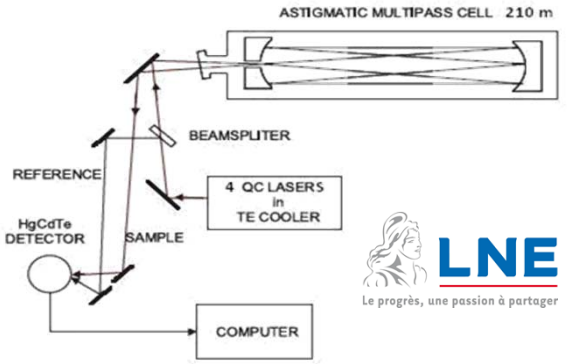
EMRP
European Metrology Research Programme
Programme of EURAMET
The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union

Analytical methods

WORKSHOP MACPOLL JRC

Analyte	Instrument	Detection limit nmol/mol	Instrument	Detection limit nmol/mol	Instrument	Detection limit nmol/mol
NO	Thermo Scientific 42i TL (CLD)	0.075	CLD 66 analyser	0.5	QC-TILDAS[1] using 4 QC-lasers	0.5
NO_2		0.075	CRDS (Los Gatos Research)	0.15		0.5
SO_2	—		Thermo Scientific 43i-TLE	0.05		0.5
CO	—		—			0.5

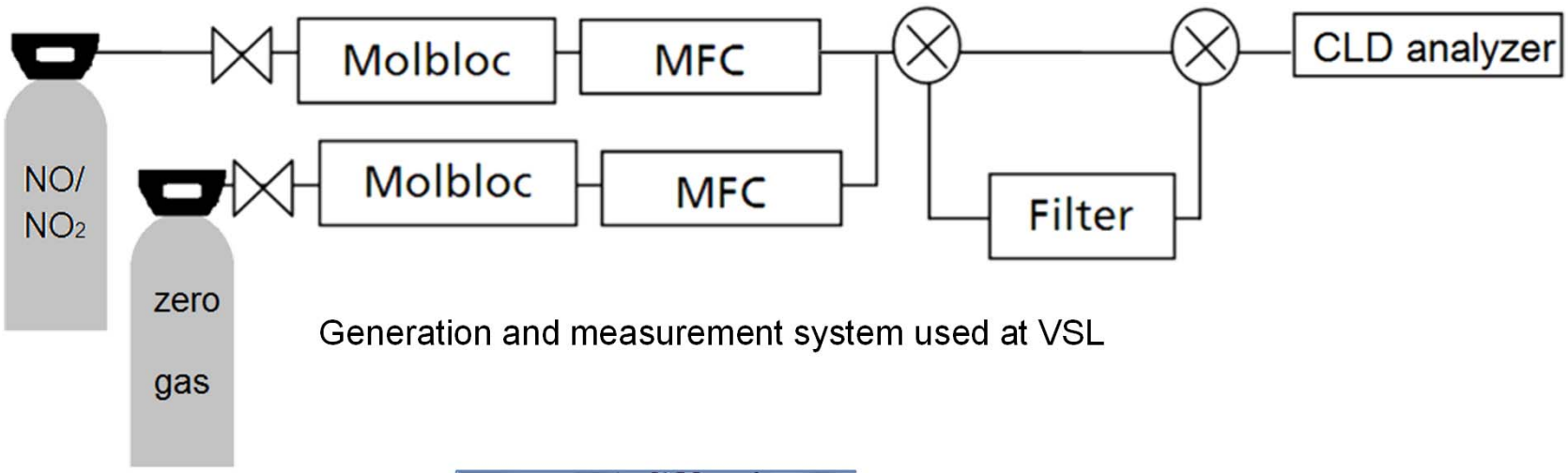
[1]QC-TILDAS Quantum Cascade Tunable Infrared Laser Differential Absorption Spectrometer operated at LNE



EMRP
European Metrology Research Programme
Programme of EURAMET
The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union

Set-up for purifier validation (VSL)

WORKSHOP MACPOLL JRC



Generation and measurement system used at VSL

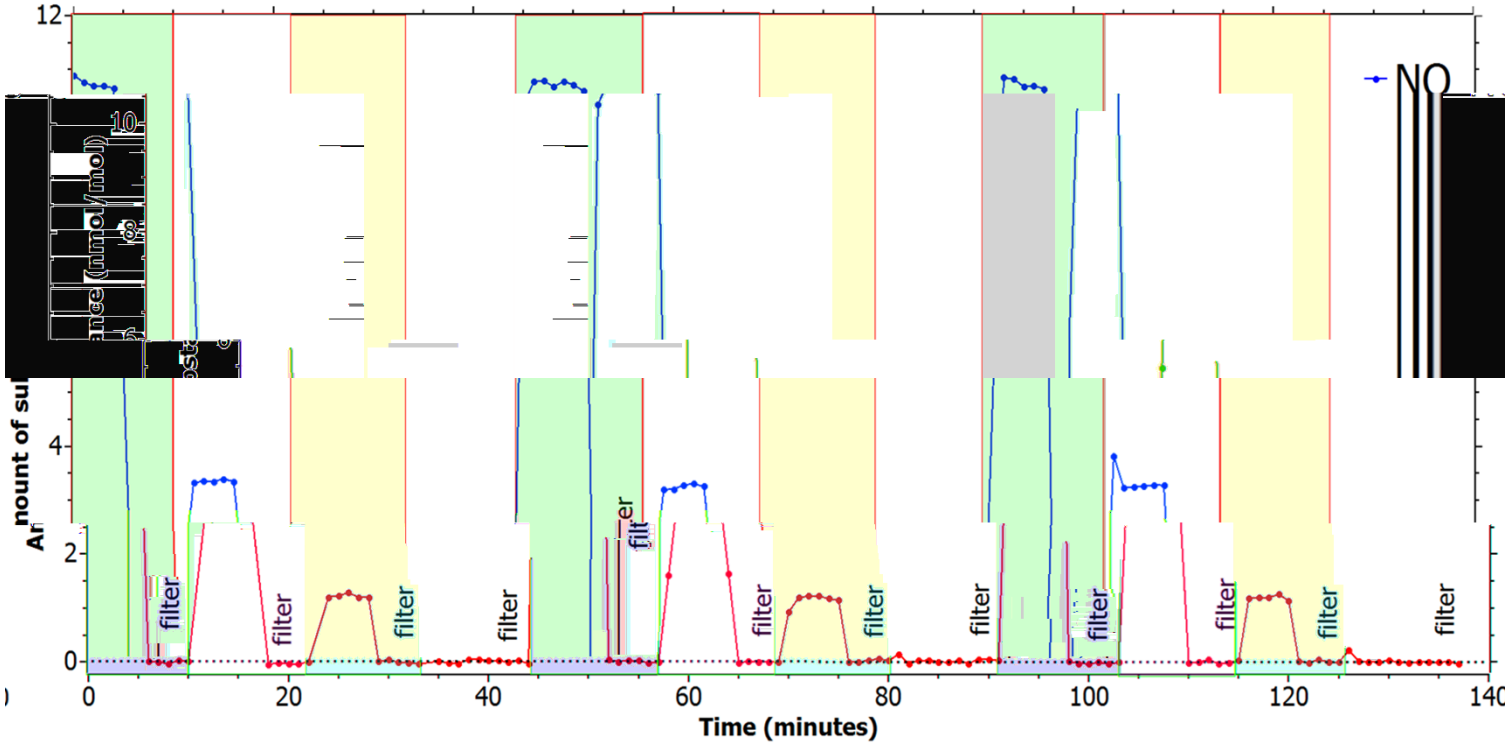
Molbloc/molbox systems connected to mass flow controllers

Thermo Scientific 42i TL chemiluminescence based analyzer For NO, NO_2 & NO_x measurement

EMRP
European Metrology Research Programme
Programme of EURAMET
The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union

Result for NO in N_2 (purifier 1)

WORKSHOP MACPOLL JRC



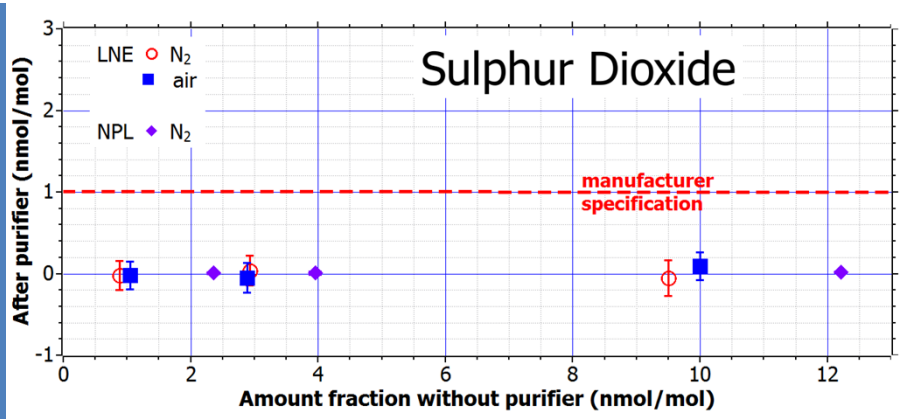
1) 10.74 nmol/mol NO without & with purifier
2) 3.29 nmol/mol NO without & with purifier.
3) 1.21 nmol/mol NO without & with purifier.
4) high purity N_2 without & with purifier.

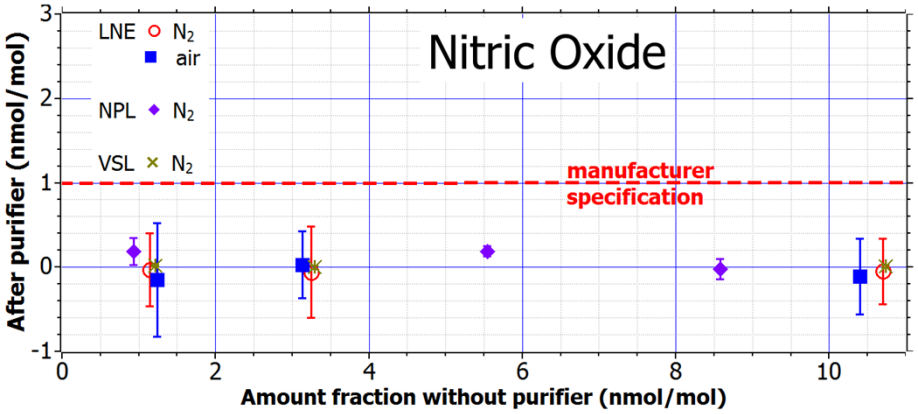
} Repeated 3 times

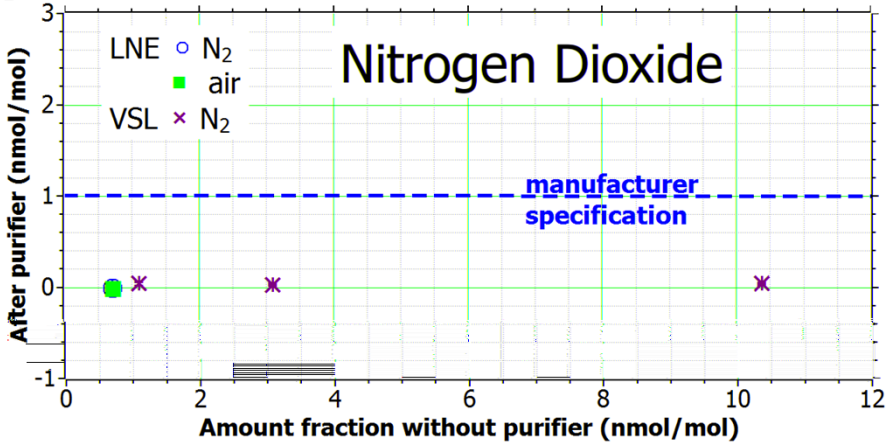
EMRP
European Metrology Research Programme
Programme of EURAMET
The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union

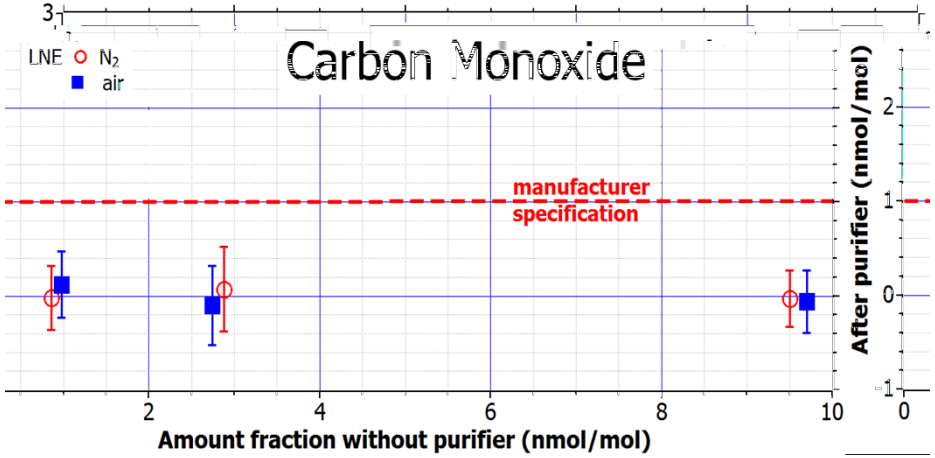
Results gas purifier 1

WORKSHOP MACPOLL JRC





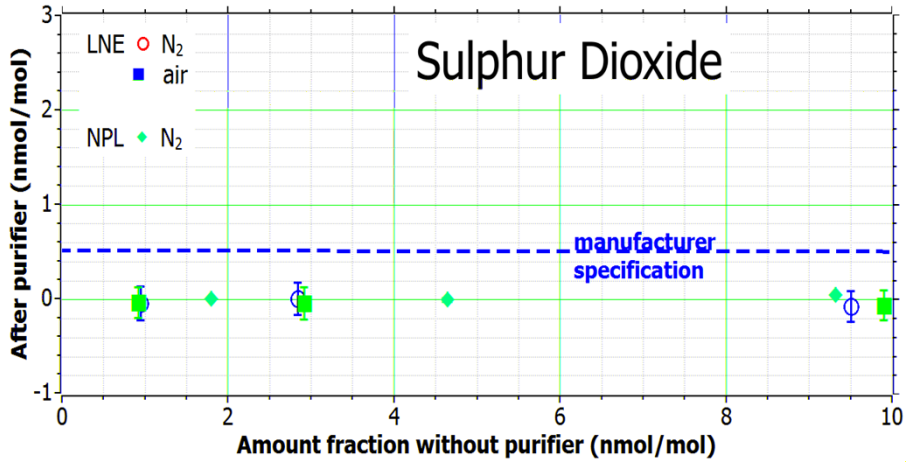


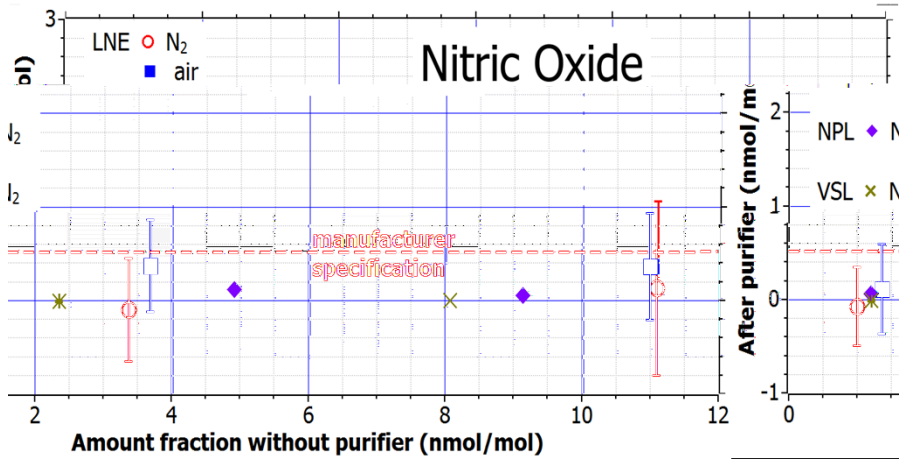


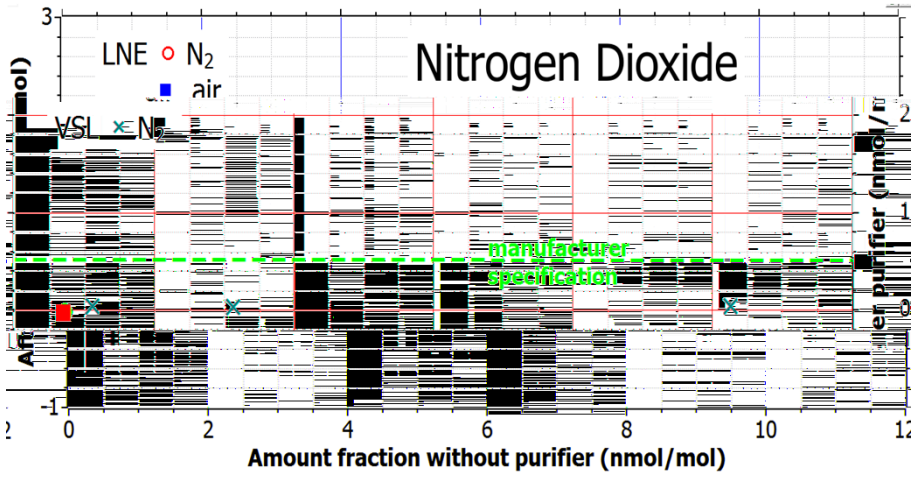
EMRP
European Metrology Research Programme
Programme of EURAMET
The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union

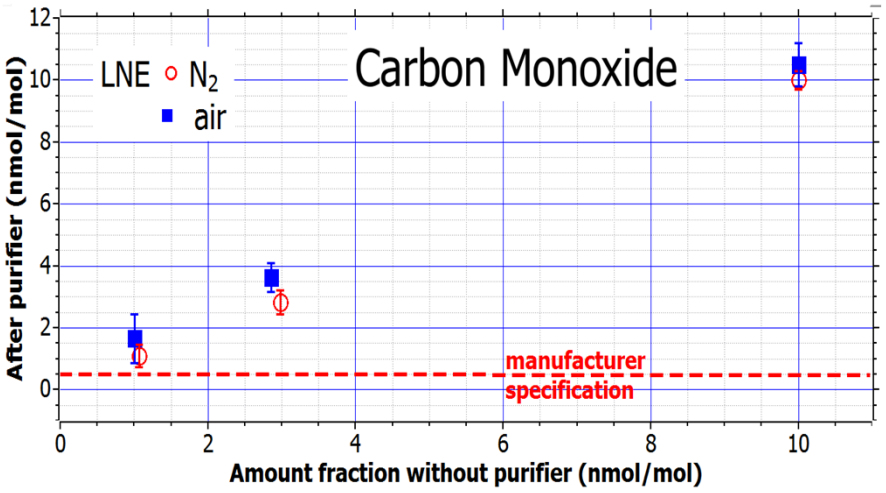
Results gas purifier 2

WORKSHOP MACPOLL JRC









EMRP
European Metrology Research Programme
Programme of EURAMET
The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union

Summary gas purifiers

WORKSHOP MACPOLL JRC

—Gas purifier 1 removes NO, NO_2, SO_2 and CO to levels below 0.5 nmol/mol, i.e., below EN standards specifications (and in line with manufacturer specification <1 nmol/mol).

—Gas purifier 2 removes NO, NO_2, SO_2 to levels below 0.5 nmol/mol i.e., below EN standards specifications. CO is not removed at all. The manufacturer agrees with our findings and will change the product specifications.

—Good agreement between results VSL, NPL and LNE

EMRP
European Metrology Research Programme
Programme of EURAMET
The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union

Validation of zero air generators

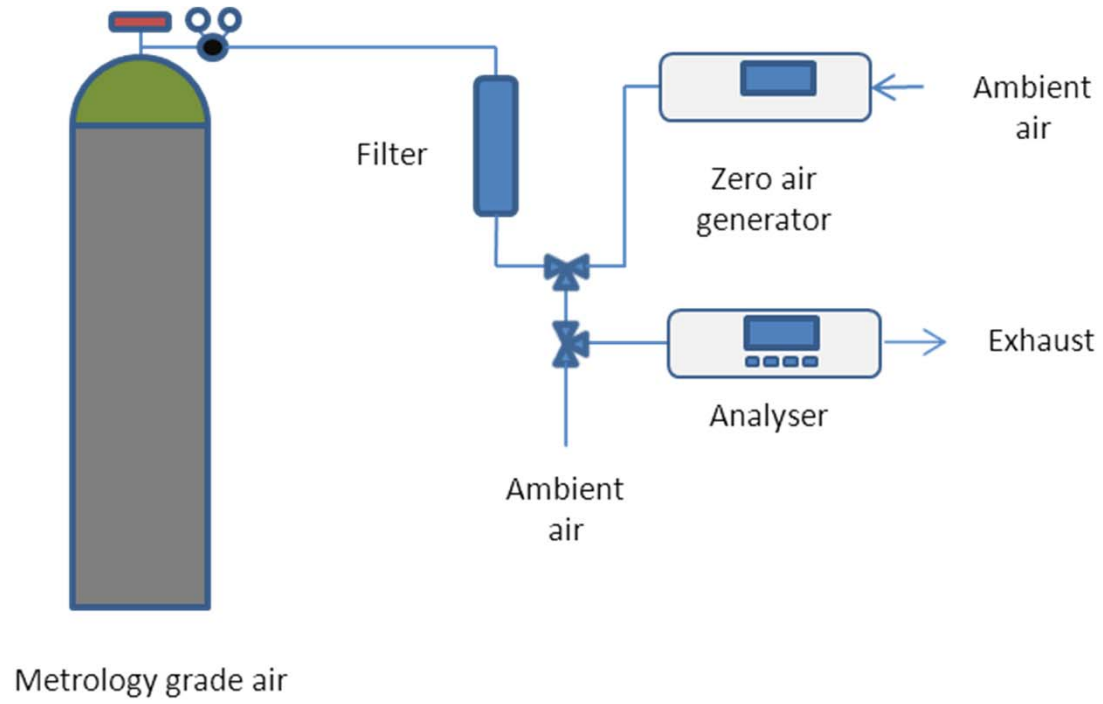
WORKSHOP MACPOLL JRC

- Review of gas purifiers (21 brands)
- A selection was made and 2 manufacturers & 1 air quality lab provided a generator for testing
- Tested analytes: NO, NO_2, SO_2 & CO

EMRP
European Metrology Research Programme
Programme of EURAMET
The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union

Set-up zero air generator validation

WORKSHOP MACPOLL JRC



Generation and measurement system used at NPL

EMRP
European Metrology Research Programme
Programme of EURAMET
The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union

Specifications zero air generators

WORKSHOP MACPOLL JRC

Summary of output concentrations zero gas generators as specified by the manufacturers.

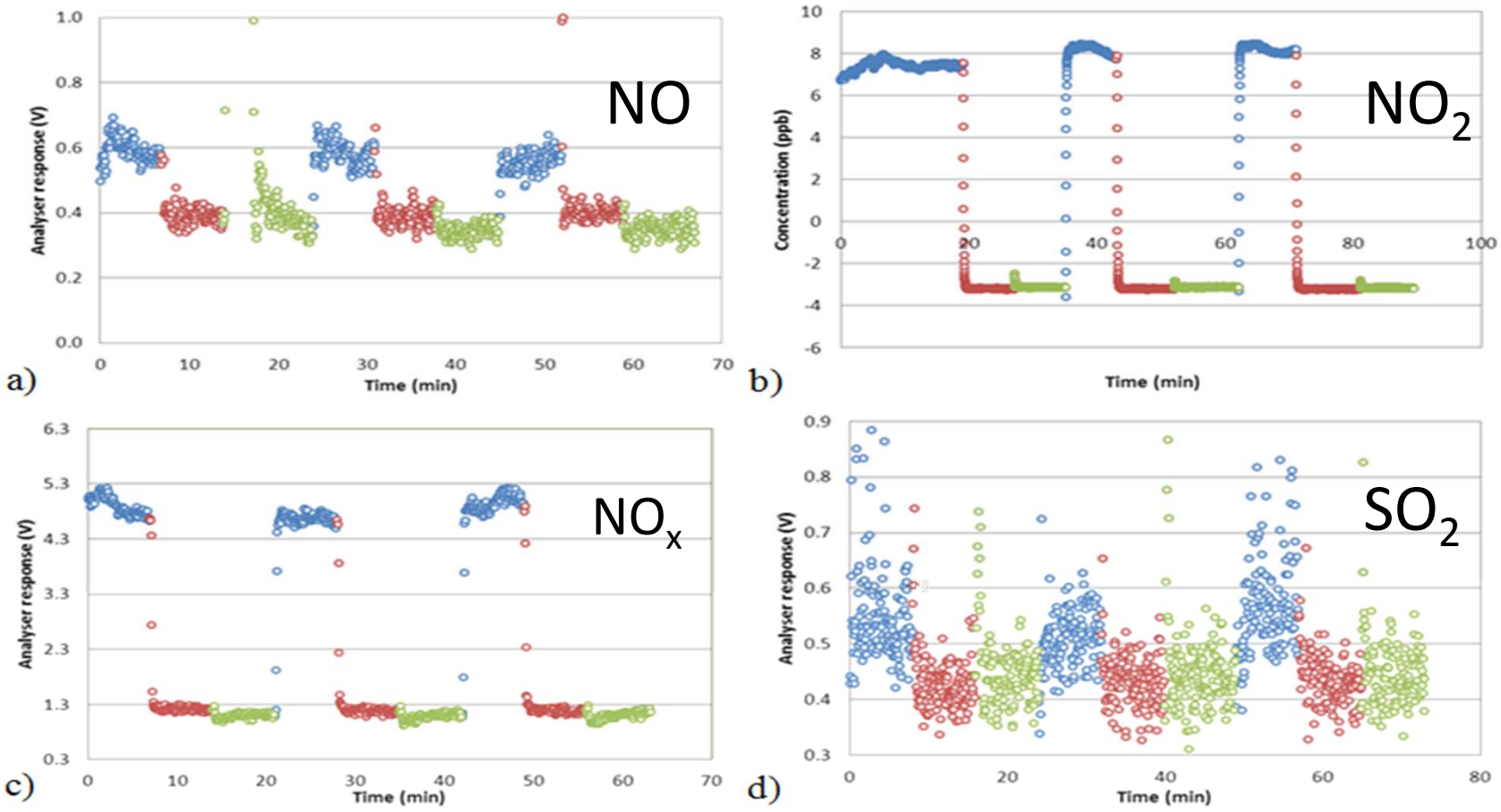
	NO (ppb)	NO_2 (ppb)	NO_x (ppb)	SO_2 (ppb)	CO (ppb)
Generator 1	<0.5	<0.5		<0.5	<50
Generator 2	<0.5	<0.5		<0.5	
Generator 3			<0.01	<0.01	

EMRP
European Metrology Research Programme
Programme of EURAMET
The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union

Example: zero air generator 2

WORKSHOP MACPOLL JRC

o = ambient air o zero air generator o purified metrology grade air

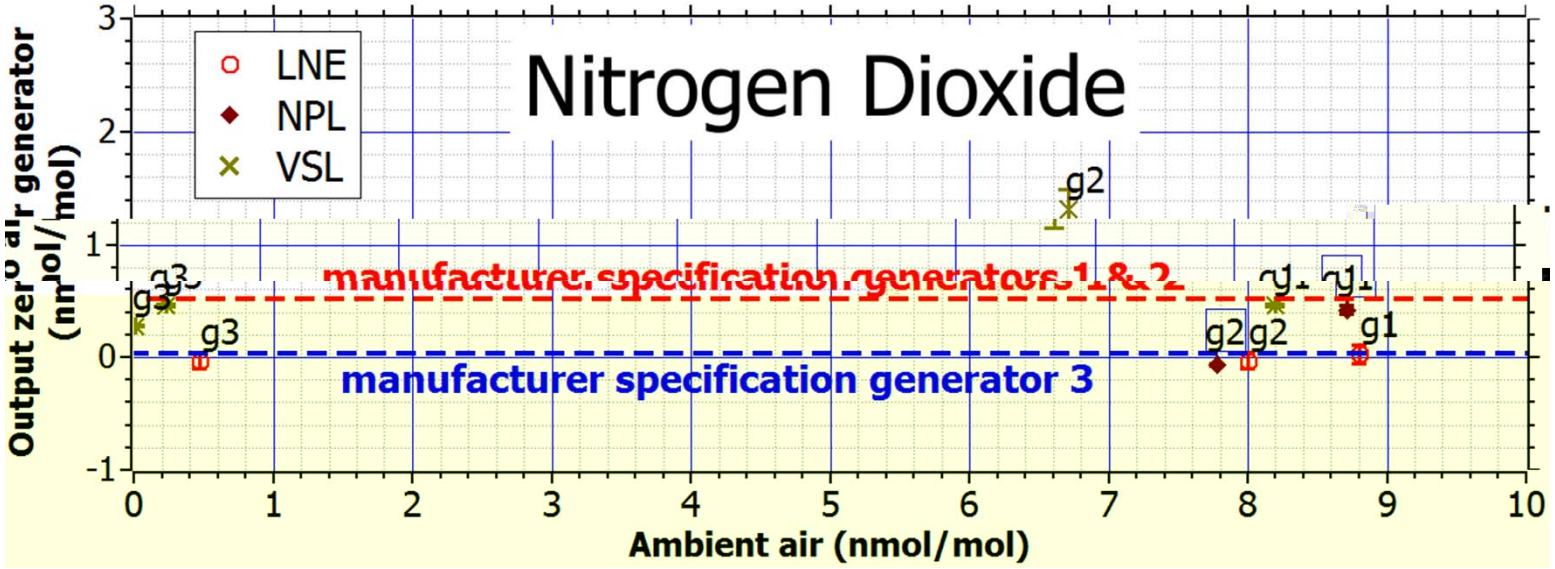


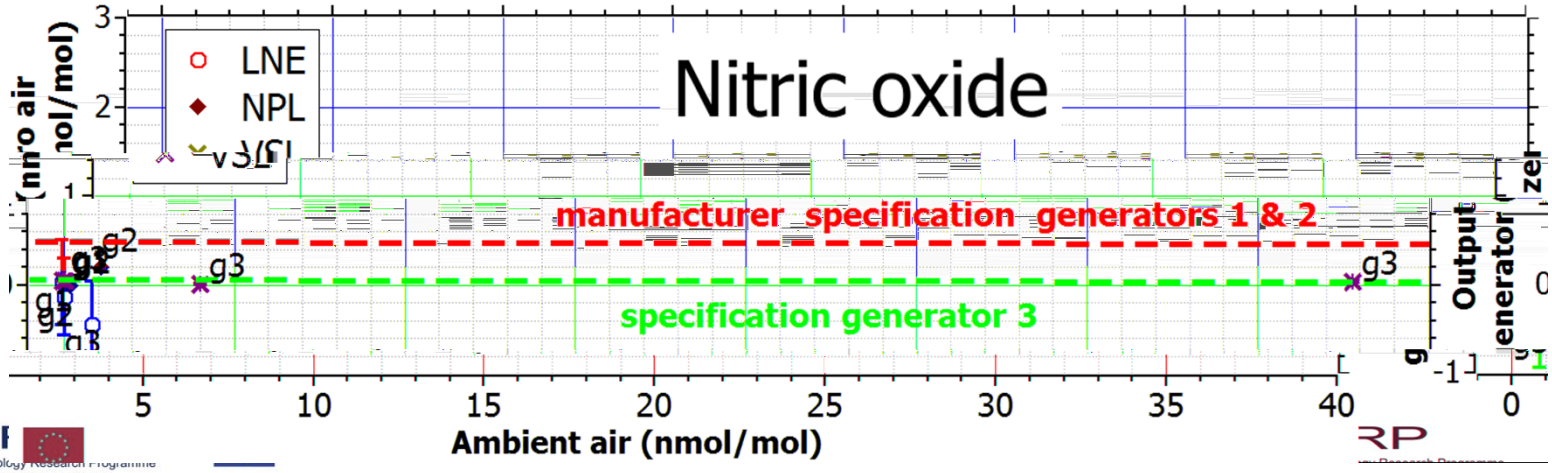
EMRP
European Metrology Research Programme
Programme of EURAMET

The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union

Results zero air generators

WORKSHOP MACPOLL JRC

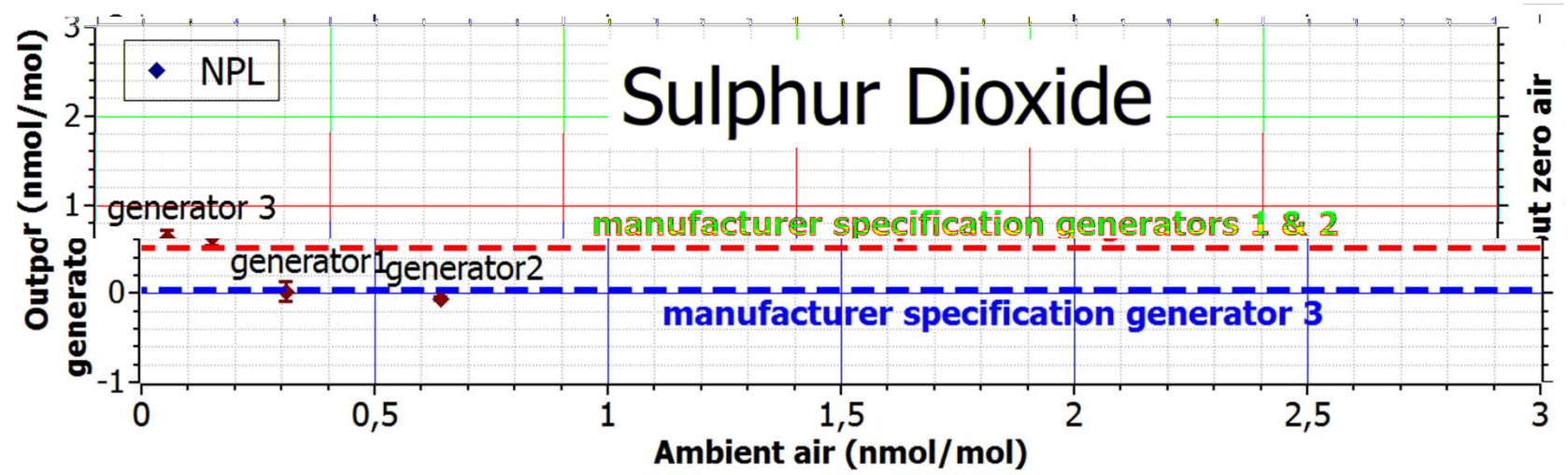


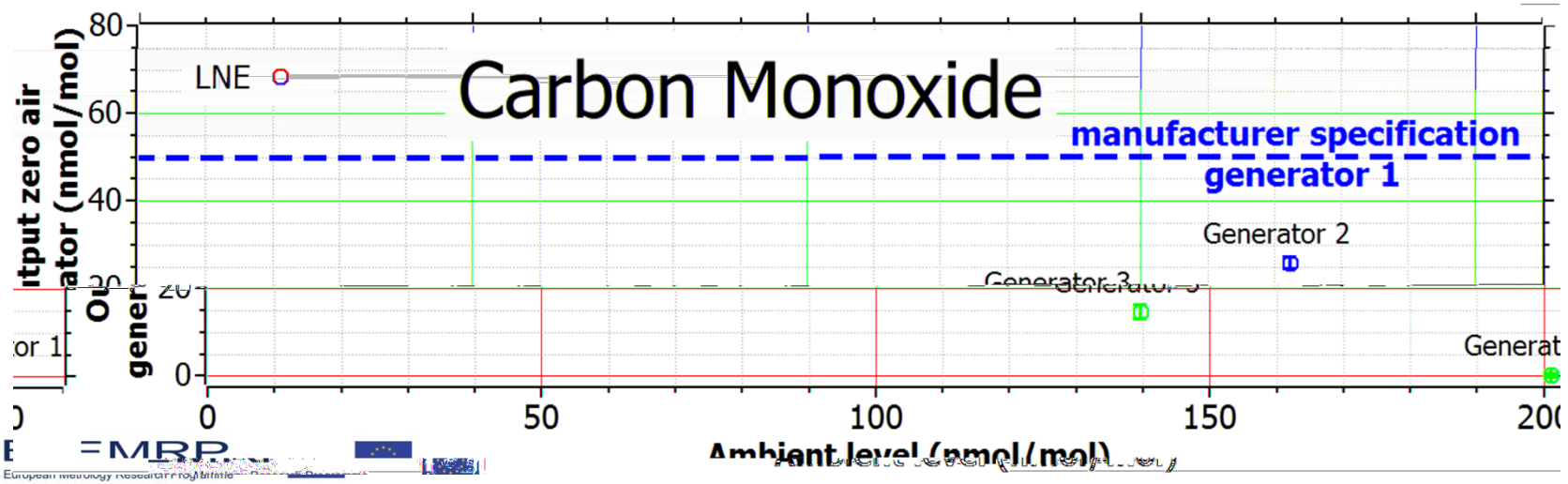


The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union

Results zero air generators

WORKSHOP MACPOLL JRC





EMRP
Programme of EURAMET
The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union

Results zero air generators

WORKSHOP MACPOLL JRC

— The NO_2 output levels meet the specification of EN14211, only VSL found generator 2 to be slightly high.

—SO_2 & NO levels in the air were low => hard to assess the performance of the generators for these analytes.

—CO output levels meet the specification in EN14626 .
Generator 1 provides the lowest output values (note: only for this generator the CO output level is specified by the manufacturer).

—Reasonable agreement between results VSL, NPL & LNE

EMRP
European Metrology Research Programme
Programme of EURAMET
The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union

Slide 25

PS(,M1

Generator 1
For NO2 the results agree. 3 different measurement techniques and all 3 show the removal of NO2

Wht happens to NO and NOx is still an open issue. Results ar not in line with each other yet.

Persijn, Stefan (S.T.) , Mr; 14/11/2013

Roadmap certification protocol zero gas

WORKSHOP MACPOLL JRC

ISO 6142 & 6145 will refer to a new working item which is under preparation (prEN19229) "**Gas analysis — Purity analysis and the treatment of purity data**"

Aim is to use the certification protocol (draft expected 1st half of 2014) as input for this new standard.

Your ideas for this protocol are welcome (spersijn@vsl.nl)

EMRP
European Metrology Research Programme
Programme of EURAMET
The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union