Standards for greenhouse gas monitoring

Paul Brewer

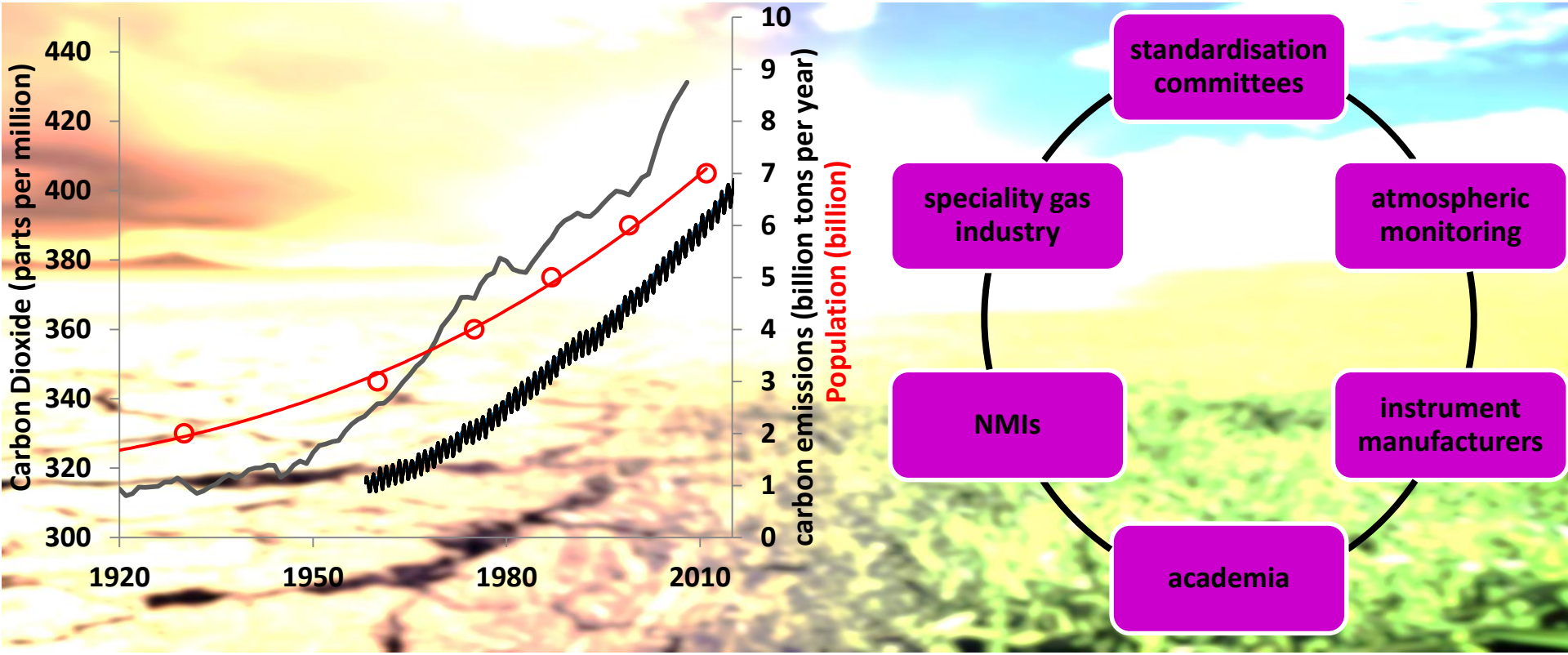
Workshop on Standards and Measurements for Clean Air

IPQ, Caparica

14th October 2016

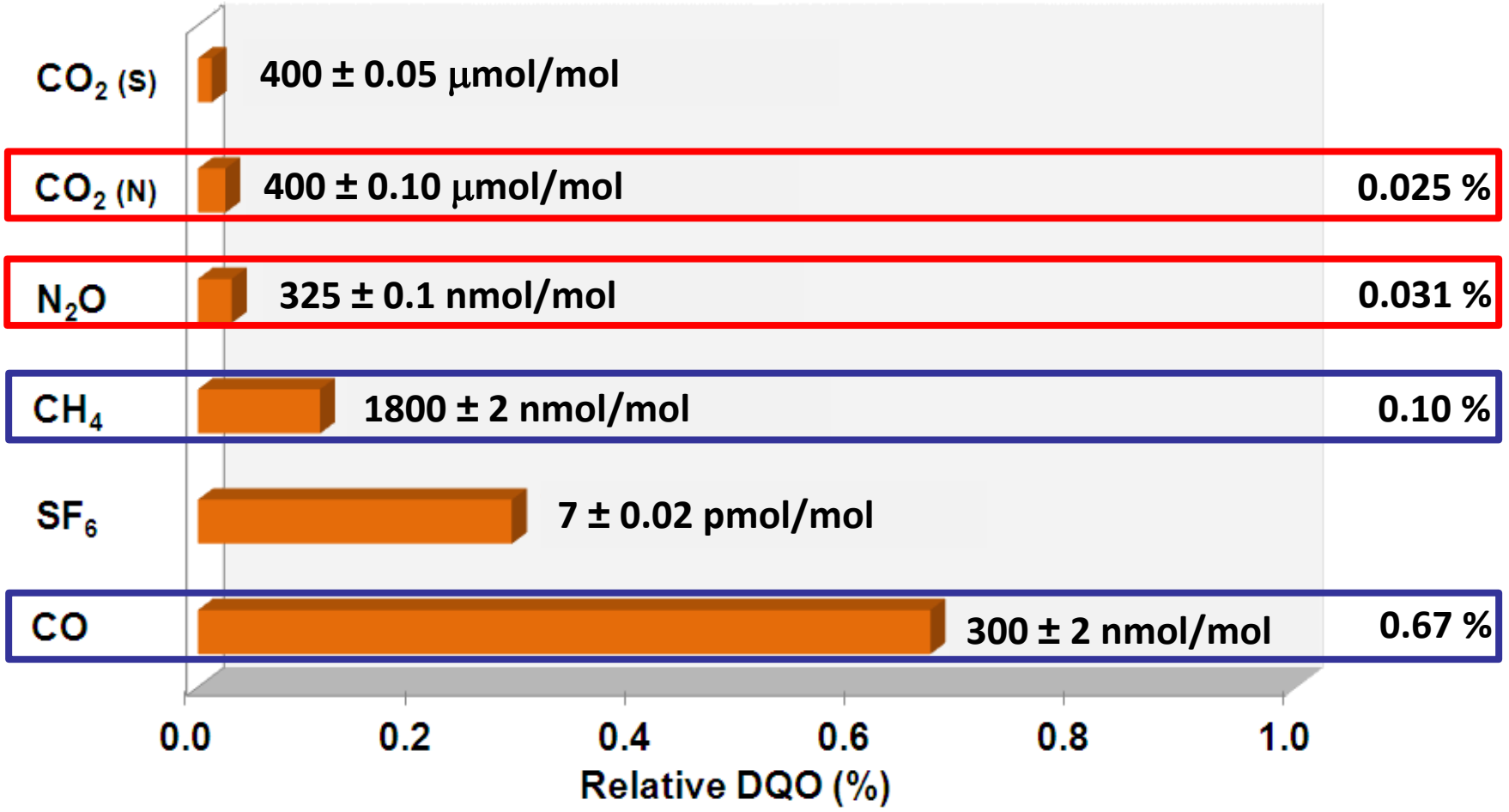
Rationale

- Requirement for traceability from the primary realisation of the mole
- Collaboration - WMO MRA signatory (quality assurance)

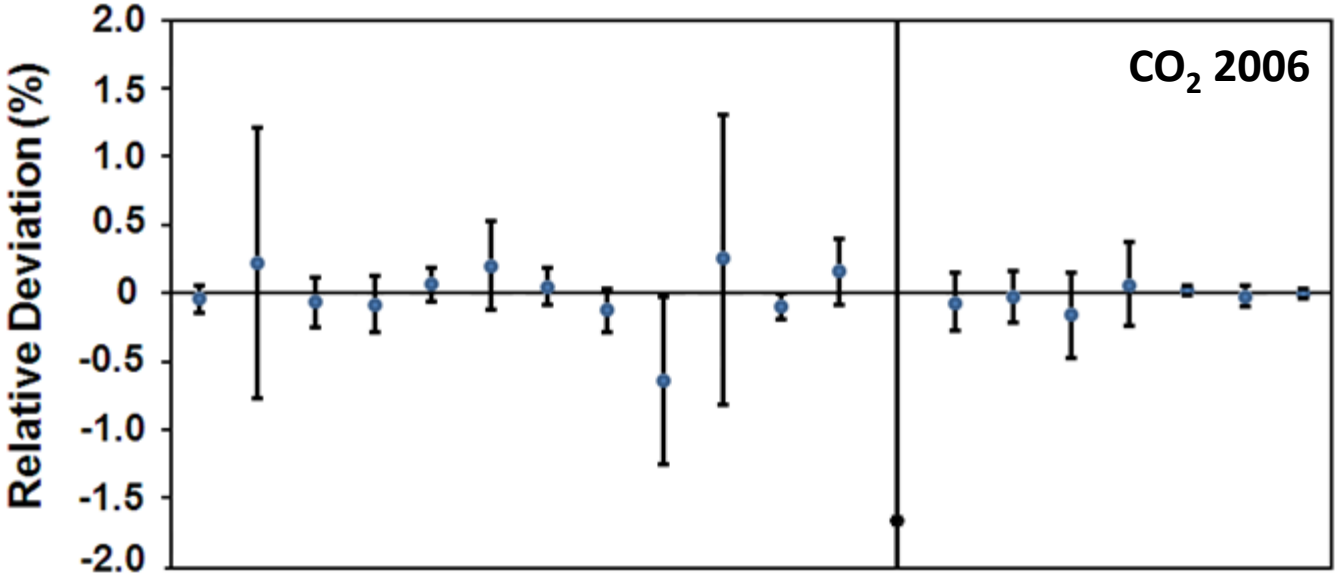


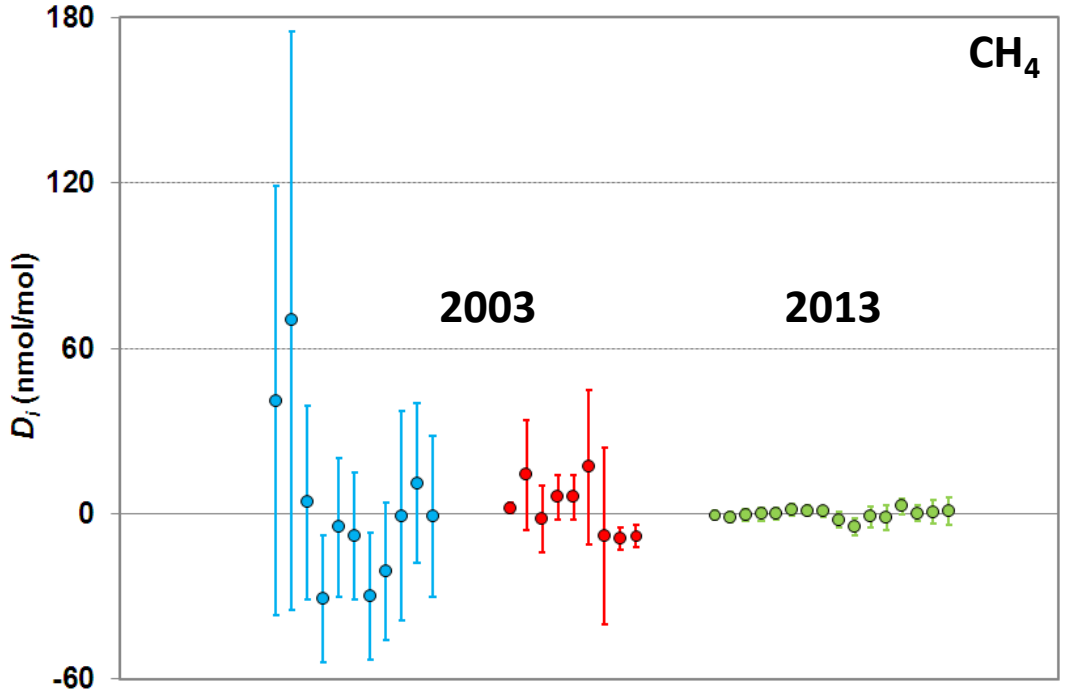
- Legislation aimed at reducing emissions and their measurement
- Long-term observations based on accurate and stable standards
- SI traceability to provide coherence and confidence

WMO compatibility goals

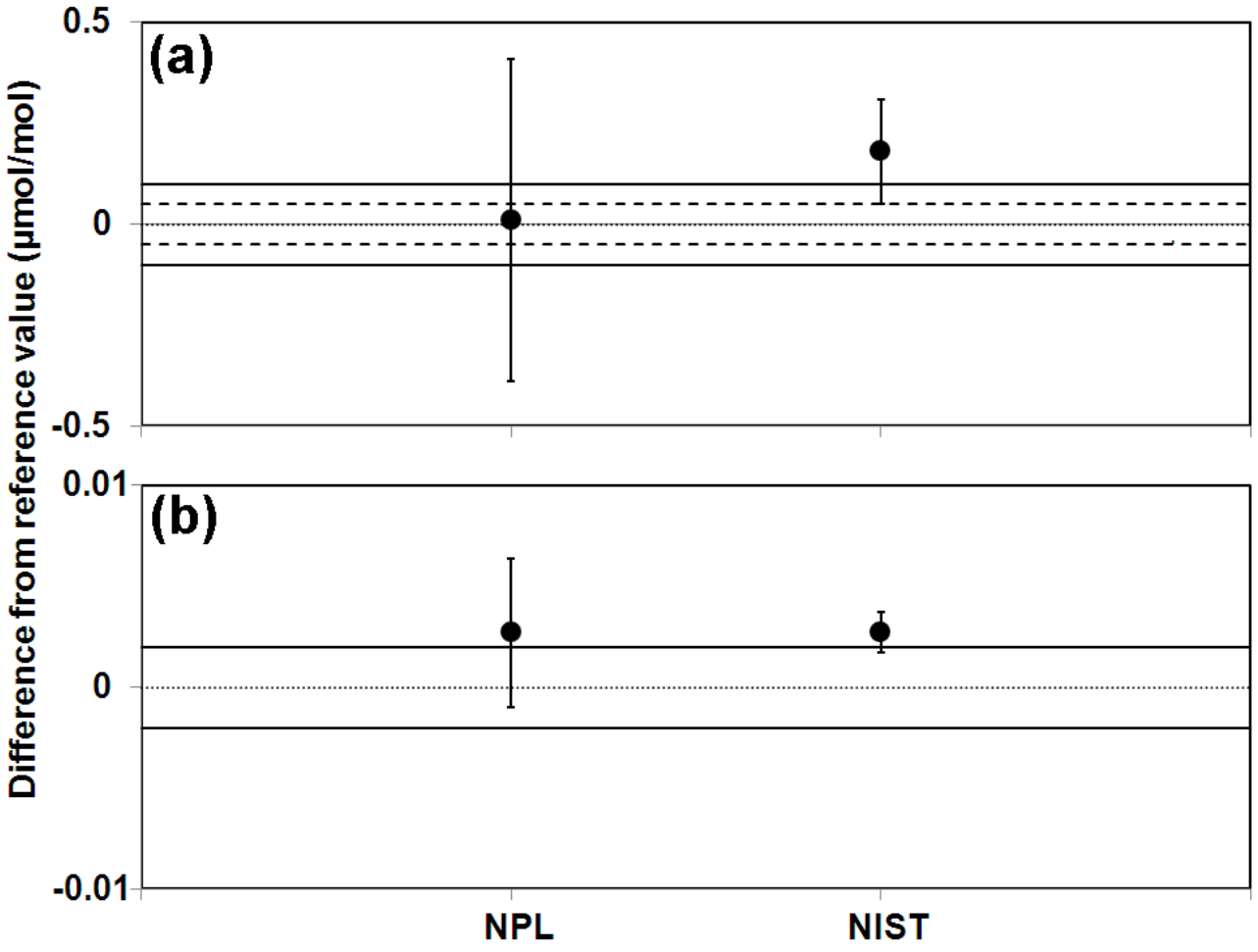


Comparability





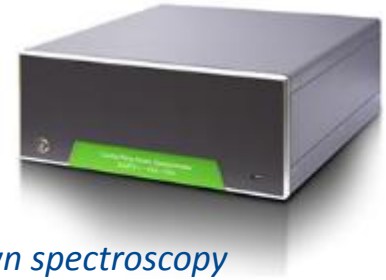
Comparability



- Isotopic composition of $^{12}CO_2$ - $^{13}CO_2$ matched to natural abundance
- Uncertainty < 0.05 % for CO_2 and < 0.1 % for CH_4 (k=1)

Synthetic Reference Standards

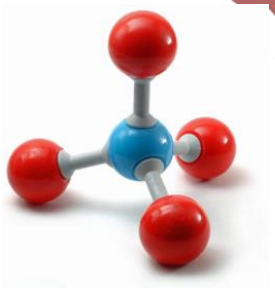
NPL
National Physical Laboratory

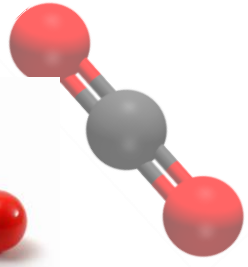


- **Gravimetric preparation**
- **Purity analysis**

Carbon dioxide

Methane





cavity ring down spectroscopy

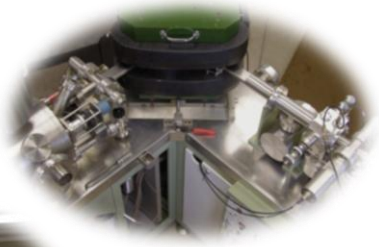
Oxygen

Nitrogen

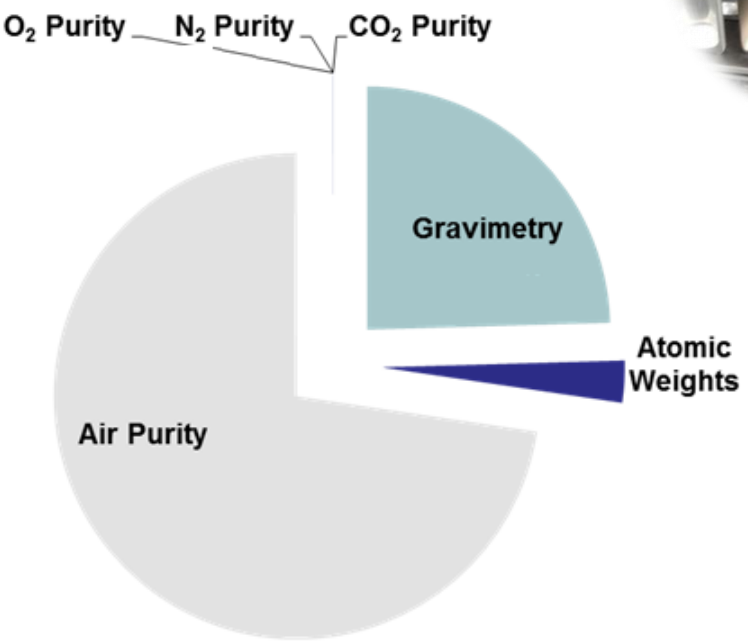
Argon

gas chromatography with helium discharge ionisation detector

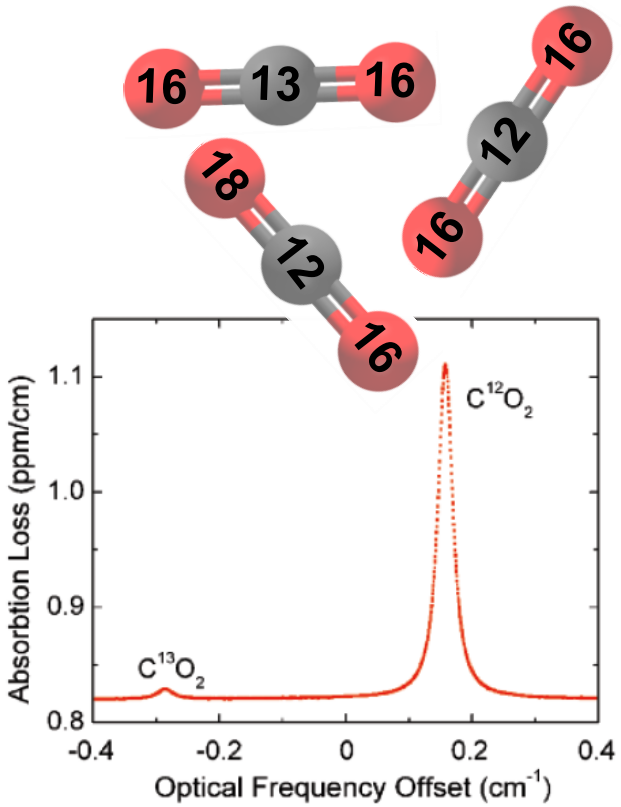
Challenges



- Purity and gravimetry
- Stability
- Commutability

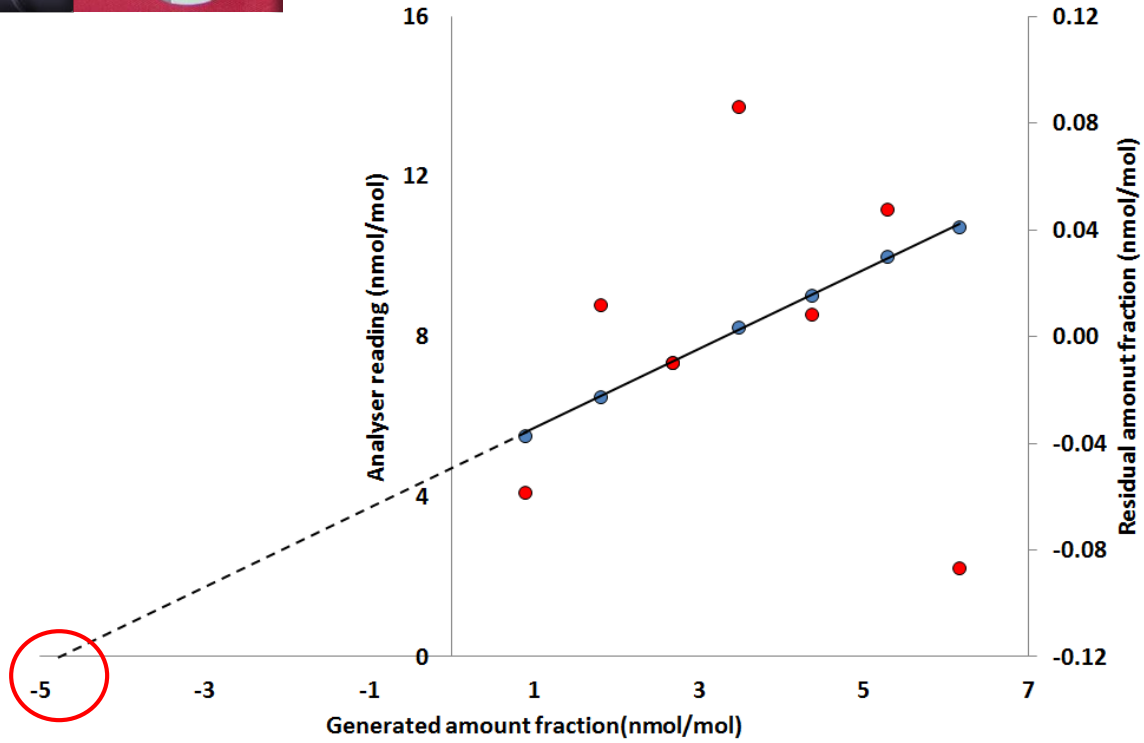


NPL
National Physical Laboratory

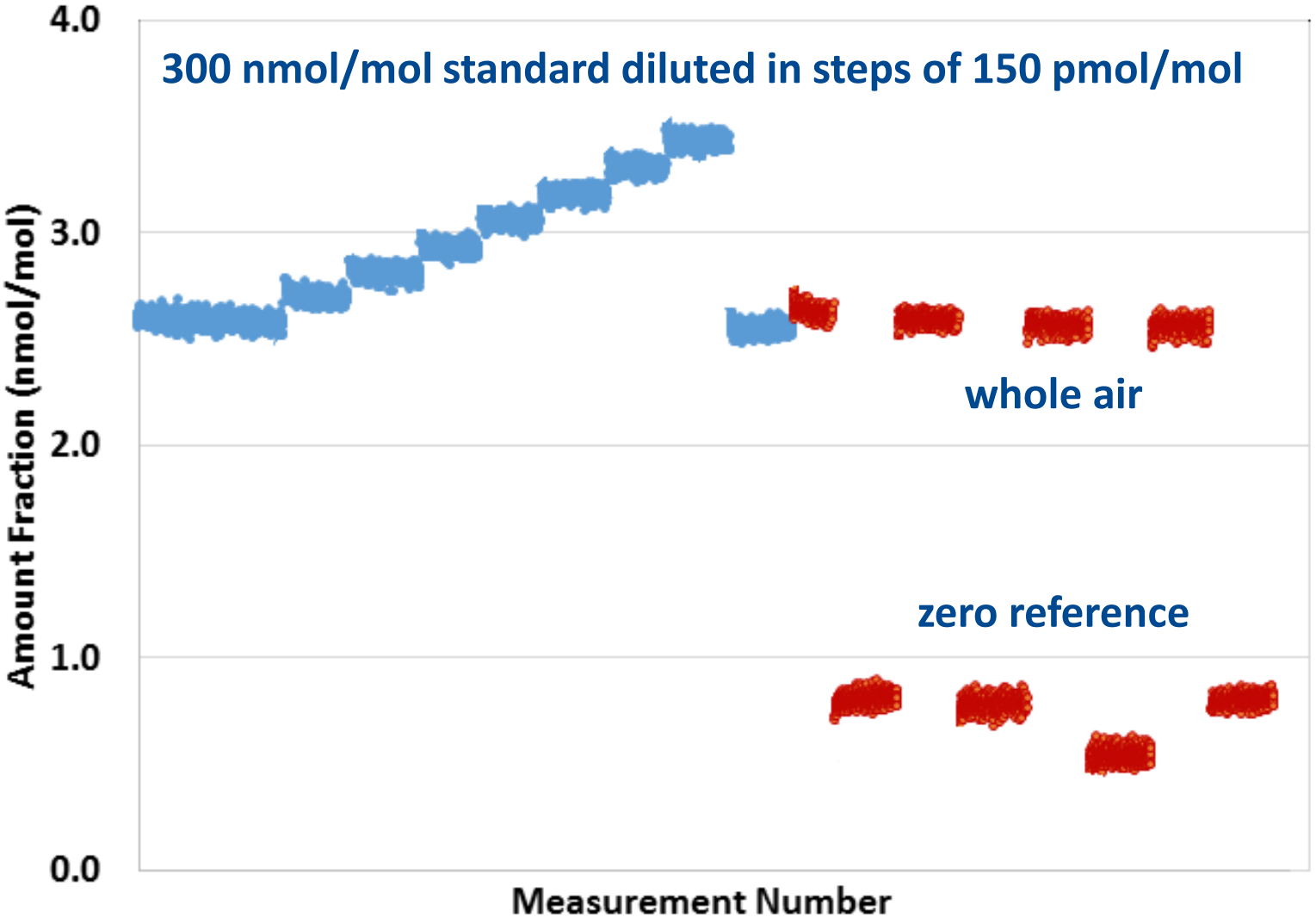


Purity

- New method with lower uncertainty
- NPL Adjustable Gas Standard (AGS)
- Quantification by standard addition



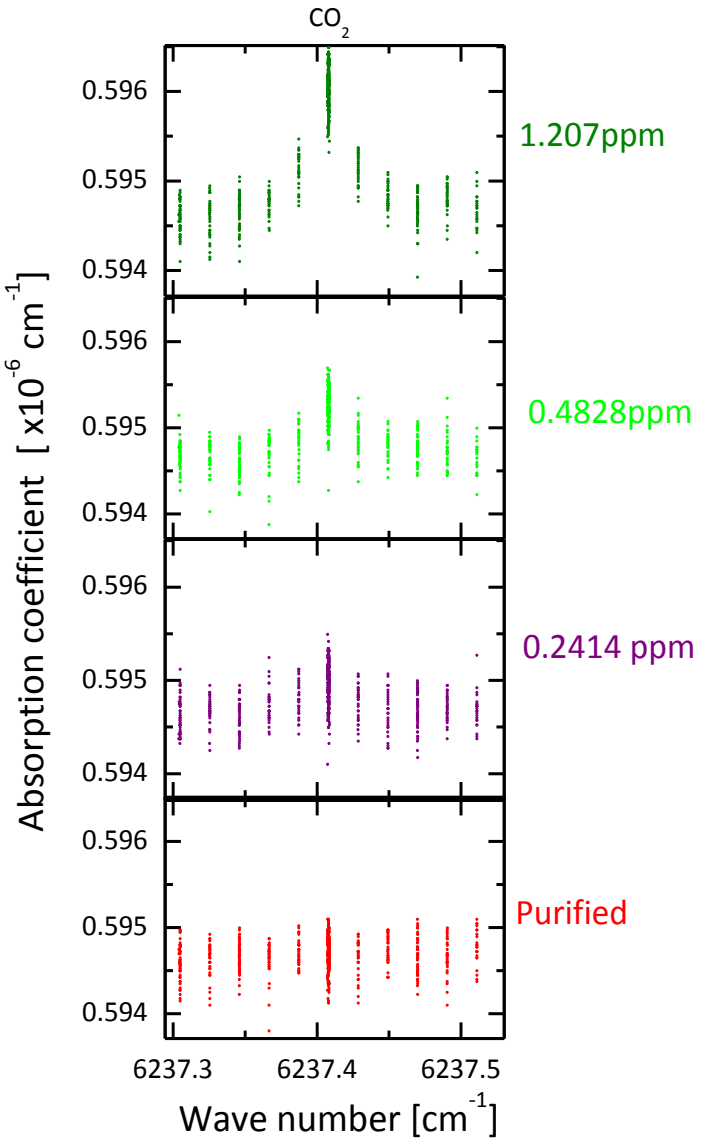
Purity


300 nmol/mol standard diluted in steps of 150 pmol/mol
whole air
zero reference
4.0
3.0
2.0
1.0
0.0
Amount Fraction (nmol/mol)
Measurement Number

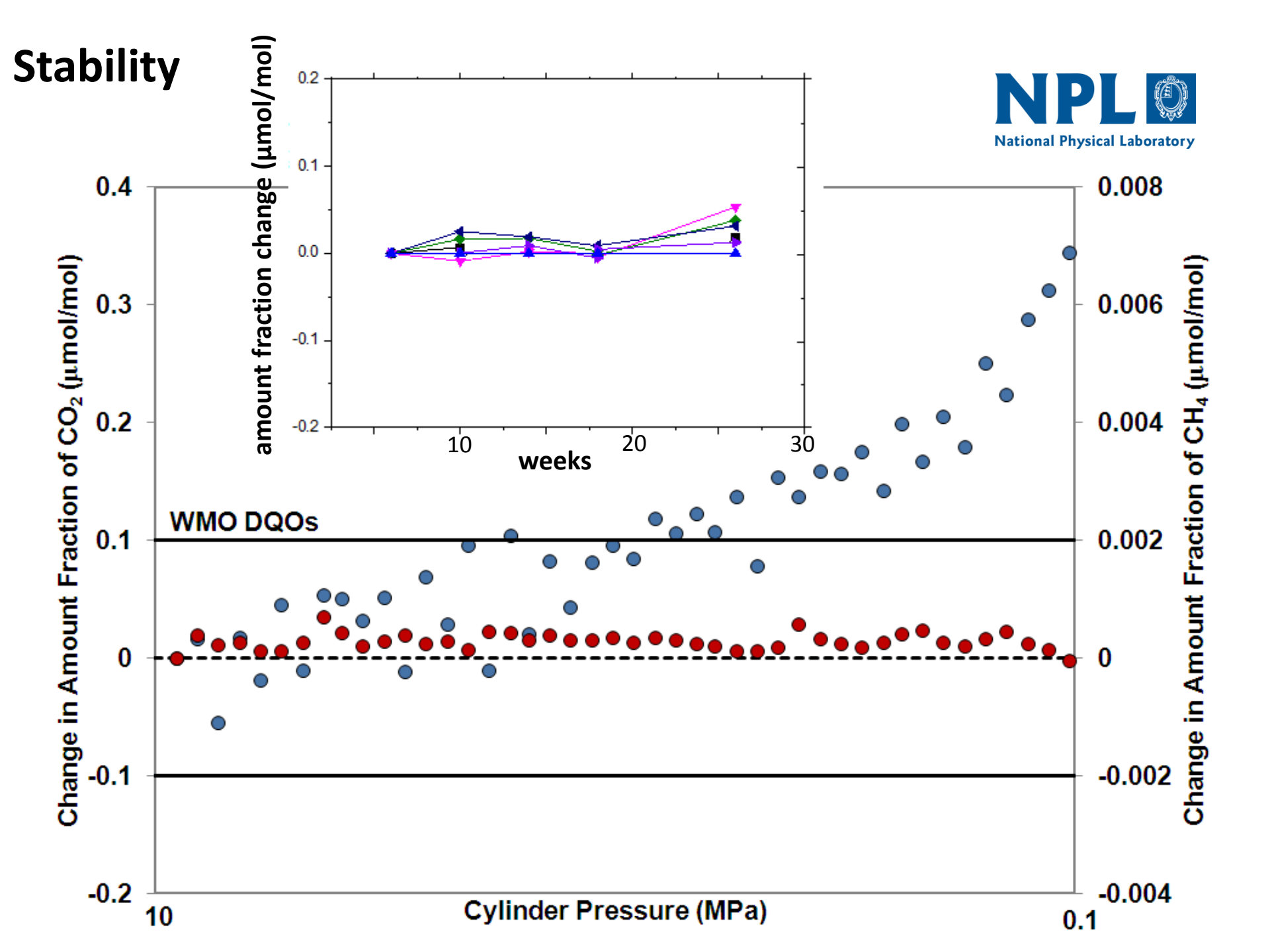
Zero air standards

- More cost effective
- More control over the amount fraction of impurities
- Gravimetric information

CO_2: 60 nmol/mol
CH_4: 2 nmol/mol
CO: 4 nmol/mol
H_2O: 500 nmol/mol
N_2, O_2, Ar blended to natural abundance

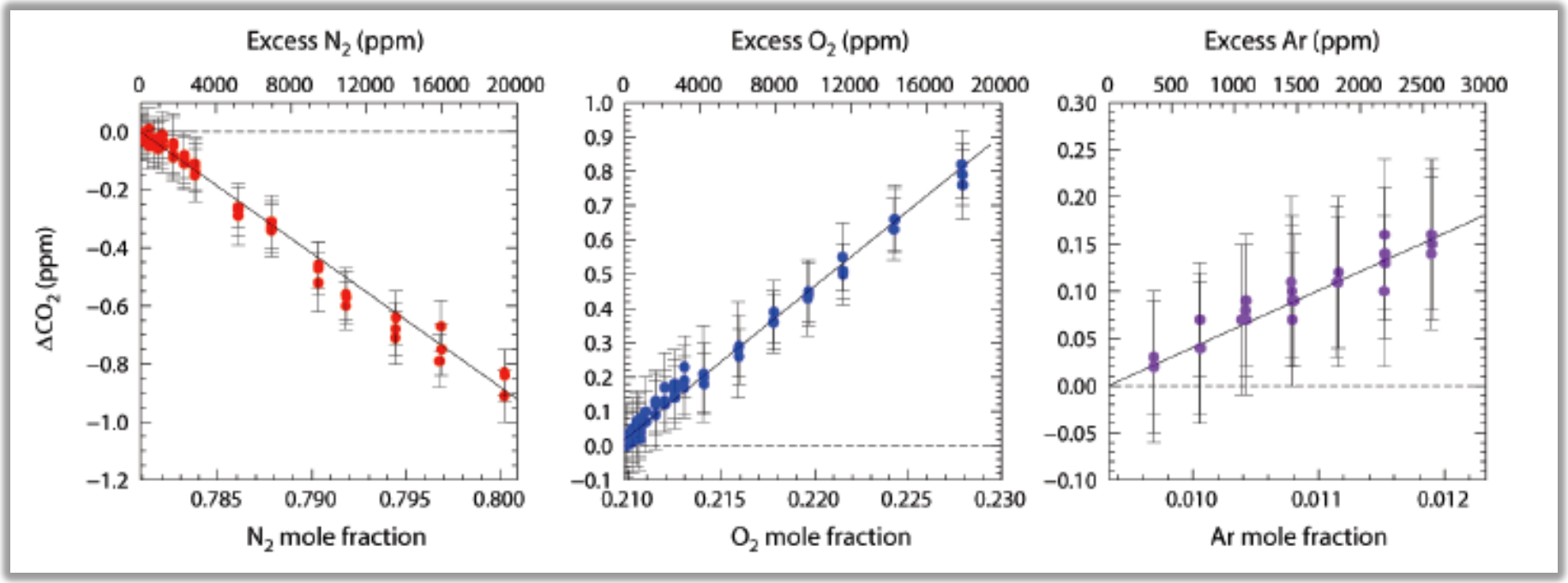


Stability


amount fraction change (µmol/mol)
0.2
0.1
0.0
-0.1
-0.2
10
20
30
weeks
WMO DQOs
0.4
0.3
0.2
0.1
0
-0.1
-0.2
Change in Amount Fraction of CO_2 (µmol/mol)
0.008
0.006
0.004
0.002
0
-0.002
-0.004
Change in Amount Fraction of CH_4 (µmol/mol)
10
Cylinder Pressure (MPa)
0.1

Commutability

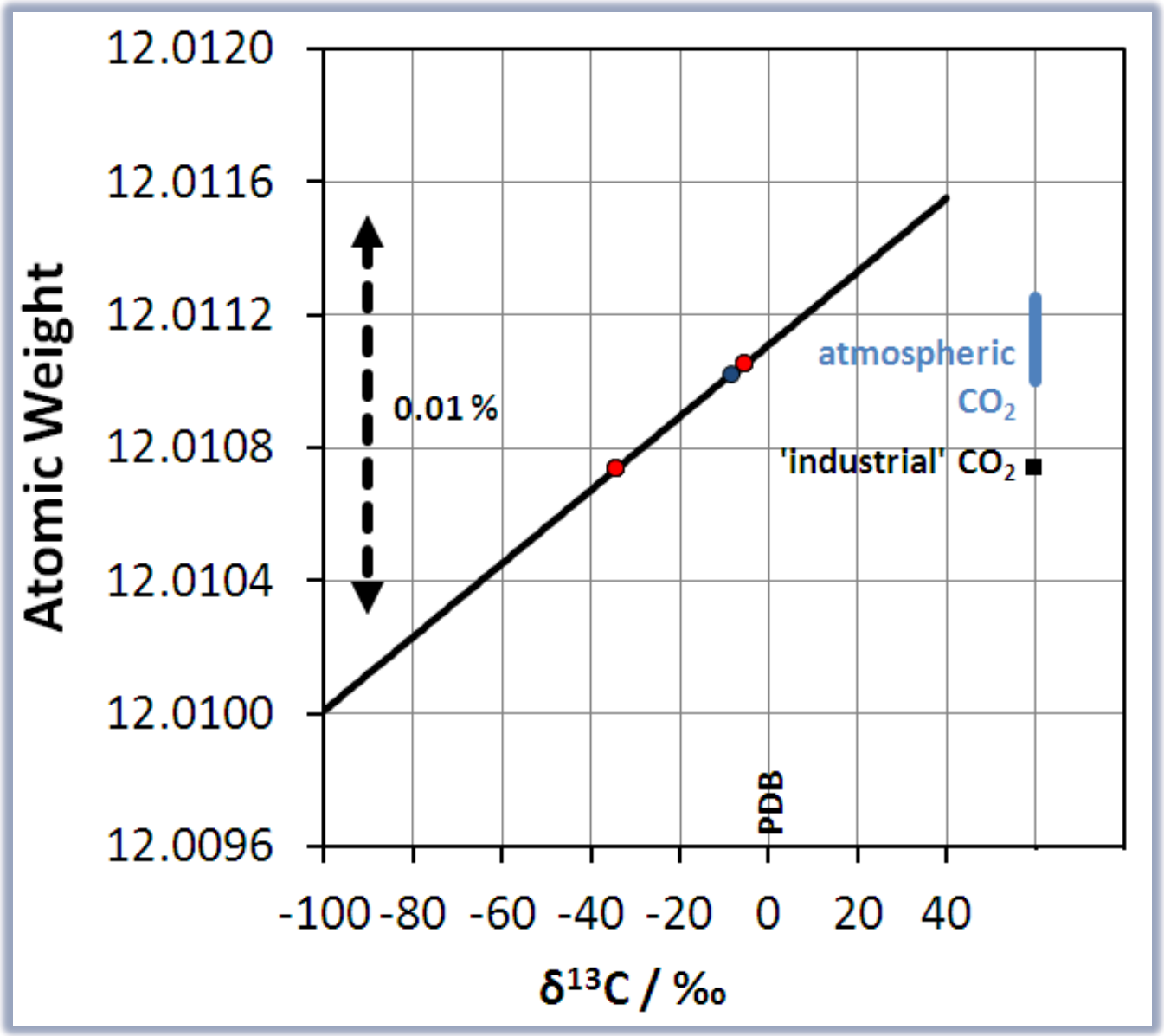
- **Influence of the matrix composition on the spectroscopy**
- **More pronounced for CO_2**
- **NPL focussing on preparation of synthetic air standards**



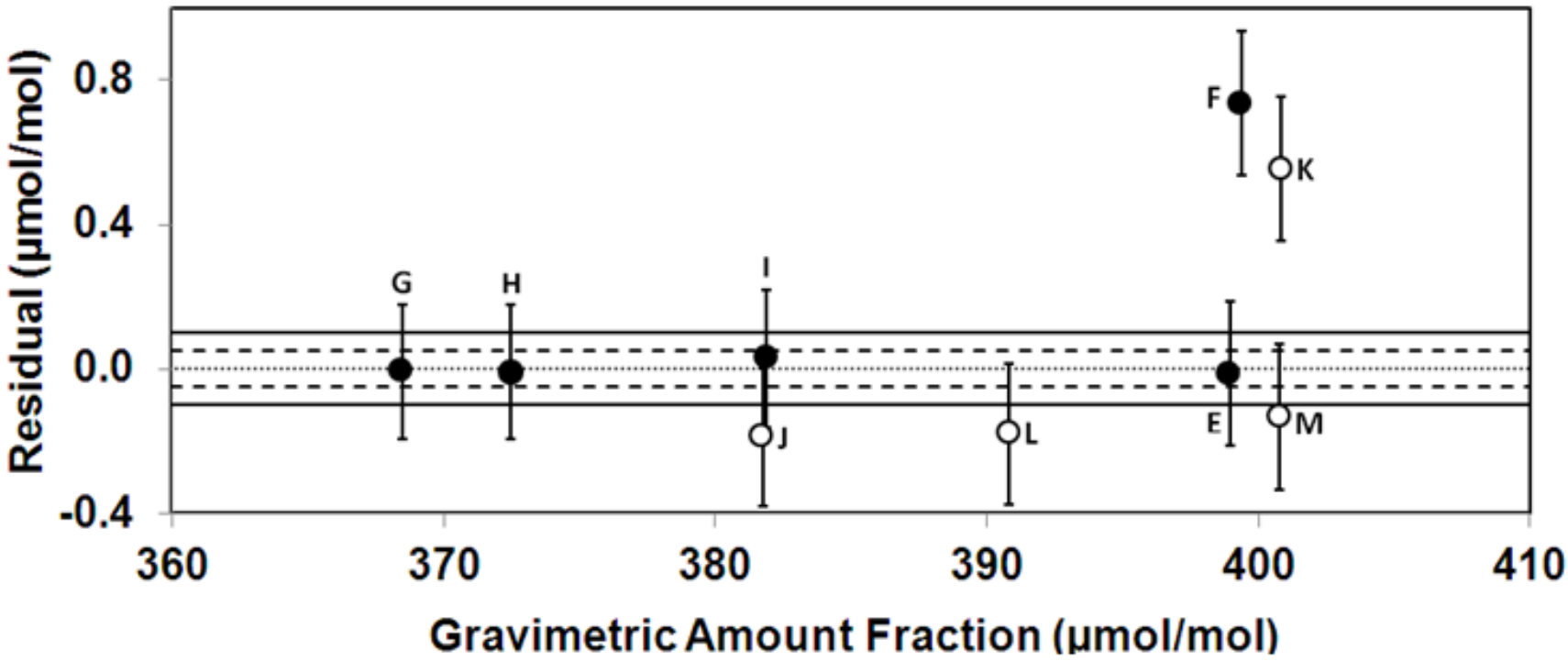
requirement for 0.1 cmol/mol

H. Nara, H. Tanimoto, Y. Tohjima, H. Mukai, Y. Nojiri, K. Katsumata and C. W. Rella, *Atmos. Meas. Tech.*, **5**, 2689–2701, (2012).

Commutability



Commutability

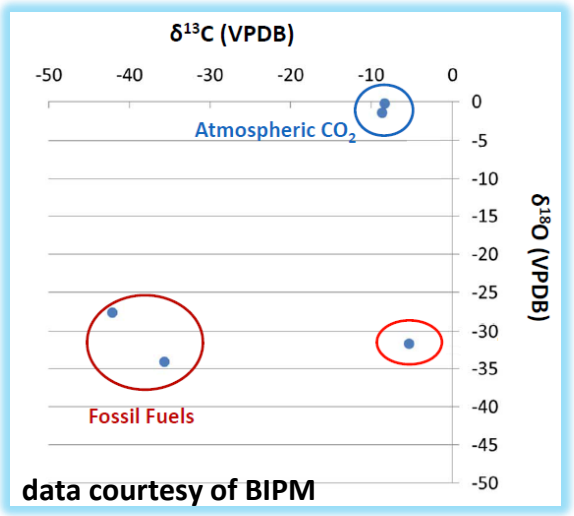


Work confirms differences in the literature (170 nmol/mol)

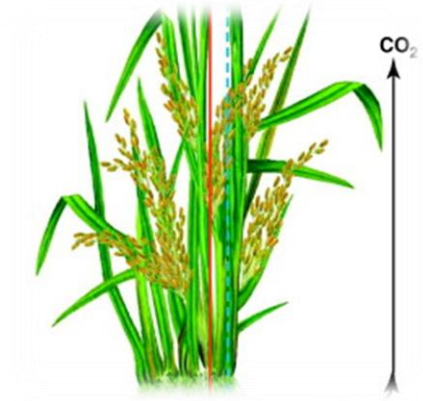
P J Brewer, R J C Brown, M N Miller, M D Minarro, A Murugan, M J T Milton, G C Rhoderick, *Anal Chem*, **86**, 1887, (2013).

Commutability

NPL National Physical Laboratory

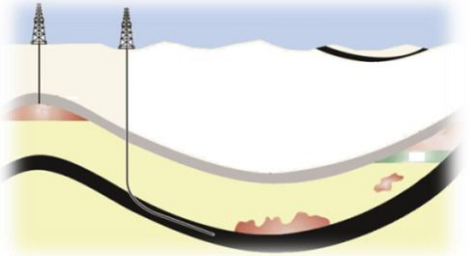


fermentation -20 to -10 ‰

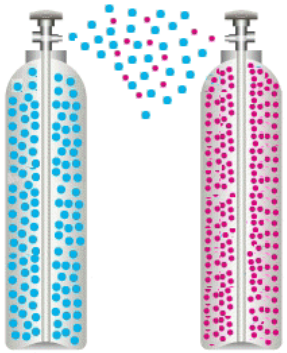


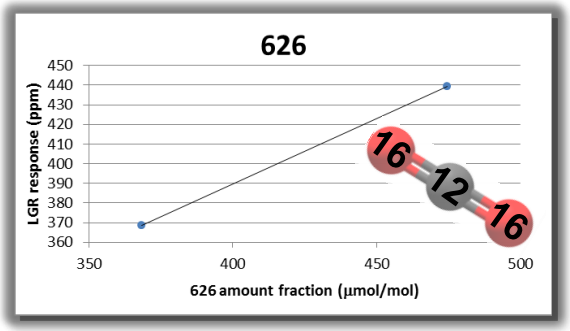
clean air -8 ‰

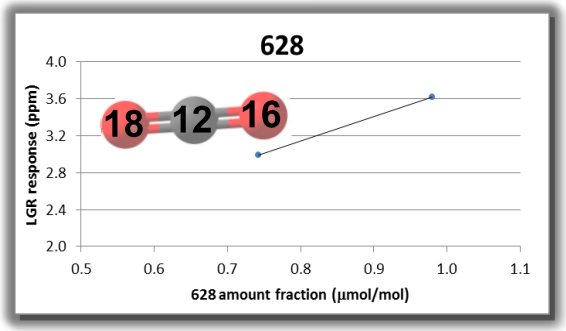
natural gas well -7 to -2 ‰

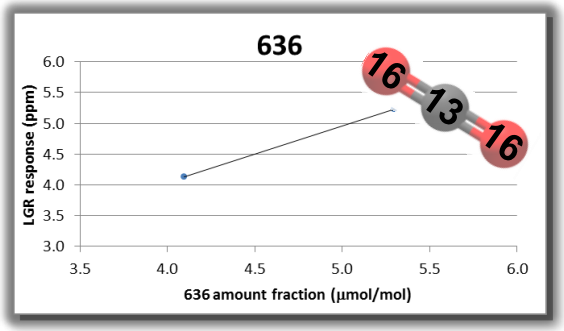


blending access full range









combustion -40 ‰

Reference standards for isotope ratio

National Physical Laboratory

- Support governments to verify emissions and demonstrate national reduction targets we need to **discriminate** between the natural and various manmade sources of greenhouse gases

- No infrastructure to deliver international gaseous CO_2 reference materials to meet demand or international gaseous N_2O reference materials with stated uncertainties to underpin isotope ratio measurements

- Exploit advances in optical spectroscopy for traceable field deployable techniques

New reference materials, calibration methods and instrumentation

- CO_2 (pure and 400 µmol/mol in air, uncertainties: $\delta^{13}C$-CO_2 0.1 ‰, $\delta^{18}O$-CO_2 0.5 ‰)

- Re-measure absolute CO_2 isotope ratios to provide data for SI traceability

- N_2O (pure and 300 – 1000 nmol/mol in air) reference materials (uncertainties 1.0 ‰ ($\delta^{15}N^{\alpha}$ and $\delta^{15}N^{\beta}$) and 0.5 ‰ ($\delta^{15}N$, $\delta^{18}O$))

- Spectroscopic methods for isotope ratio measurements

Conclusions

National Physical Laboratory

- Substantial progress made towards developing an infrastructure to provide SI traceability for measurements of CO_2, CH_4, N_2O and CO
- CO_2 and N_2O most challenging and require propagation of existing scales to meet demand until SI traceability is achieved
- Research required to deliver gaseous reference materials for isotope ratio of CO_2 and N_2O

Acknowledgements

- Funding from the EU and department of UK BEIS
- Dave Worton, Ruth Pearce and Kate Resner (NPL)
- Royal Holloway University
- CCQM-GAWG

EURAMET

EMRP
European Metrology Research Programme
Programme of EURAMET

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

Department for Business, Energy & Industrial Strategy