Gaseous reference materials to underpin measurements of amount fraction and isotopic composition of greenhouse gases

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Rationale

- Requirement for traceability from the primary realisation of the mole
- Legislation aimed at reducing emissions and their measurement
- Long-term observations based on accurate and stable standards
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

- Gravimetric preparation
- Purity analysis
- Analytical validation

Challenges
- Purity and gravimetry
- Stability
- Commutability
Purity and gravimetry

- New method with lower uncertainty
- NPL Adjustable Gas Standard
- Quantification by standard addition
Commutability

- Influence of matrix composition on spectroscopy (requirement for 0.1 cmol mol\(^{-1}\))
- More pronounced for CO\(_2\)

1 \(\%\) corresponds to \(~ 4 \text{ nmol/mol}\)
Commutability

$\delta^{18}O \text{ (VPDB)}$

$\delta^{13}C \text{ (VPDB)}$

fermentation

natural gas

combustion

NPL blend
Calibration

![Graph showing residual vs. \(\delta^{13}C_{VPDB-CO_2}(\%o)\) and \(\delta^{18}O_{VPDB-CO_2}(\%o)\).]
Influence of the calibration

\[ \delta^{13}C_{VPDB-CO2} \]
Metrology for Stable Isotope Reference Standards (SIRS)

The project will address:

- Limitations in infrastructure to deliver international gaseous CO₂ reference materials
- Absence of international gaseous N₂O reference materials with stated uncertainties
- Advances in optical spectroscopy for traceable field deployable techniques

**New reference materials, calibration methods and instrumentation**

- CO₂ (pure and 400 µmol/mol in air, uncertainties: δ^{13}C-CO₂ 0.1 ‰, δ^{18}O-CO₂ 0.5 ‰)
- Re-measure absolute CO₂ isotope ratios to provide data for SI traceability
- N₂O (pure and 300 – 1000 nmol/mol in air) reference materials (uncertainties 1.0 ‰ (δ^{15}Nα and δ^{15}Nβ) and 0.5 ‰ (δ^{15}N, δ^{18}O))
- Spectroscopic methods for isotope ratio measurements
Conclusions

• Substantial progress made towards developing an infrastructure to provide SI traceability for measurements of CO$_2$, CH$_4$, N$_2$O and CO

• Research required to deliver gaseous reference materials for isotope ratio of CO$_2$ and N$_2$O

Acknowledgements