

Progress towards atmospheric isotope ratio carbon dioxide and nitrous oxide reference materials that meet the WMO-GAW data quality objectives for compatibility

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Low uncertainty traceable reference materials required for monitoring atmospheric greenhouse gas amount fraction

The precise measurement of amount fraction of atmospheric greenhouse gases is required to understand global emission trends.

The WMO-GAW has published a compatibility goals for amount fraction and isotope ratio for CO₂ and amount fraction for N₂O

Data Quality Objectives for GHGs



Component	Compatibility goal	Extended compatibility goal	Range in unpolluted troposphere	Range covered by the WMO scale
CO ₂	± 0.1 ppm (Northern hemisphere) ± 0.05 ppm (South. hemisphere)	± 0.2 ppm	360 – 450 ppm	250 – 520 ppm
CH ₄	± 2 ppb	± 5 ppb	1700 – 2100 ppb	300 – 2600 ppb
CO	± 2 ppb	± 5 ppb	30 – 300 ppb	20 – 500 ppb
N ₂ O	± 0.1 ppb	± 0.3 ppb	320 – 335 ppb	260 – 370 ppb
SF ₆	± 0.02 ppt	± 0.05 ppt	6 – 10 ppt	1.1 – 9.8 ppt
H ₂	± 2 ppb	± 5 ppb	450 – 600 ppb	140 – 1200 ppb
δ ¹³ C-CO ₂	± 0.01‰	± 0.1‰	-7.5 to -9‰ vs. VPDB	
δ ¹⁸ O-CO ₂	± 0.05‰	± 0.1‰	-2 to +2‰ vs. VPDB	
Δ ¹⁴ C-CO ₂	± 0.5‰	± 3‰	0-70‰	
Δ ¹⁴ C-CH ₄	± 0.5‰		50-350‰	
Δ ¹⁴ C-CO	± 2 molecules cm ⁻³		0-25 molecules cm ⁻³	
δ ¹³ C-CH ₄	± 0.02‰	± 0.2‰		
δD-CH ₄	± 1‰	± 5‰		
O ₂ /N ₂	± 2 per meg	± 10 per meg	-250 to -800 per meg (vs. SIO scale)	

Improving analytical uncertainty and preparation processes is necessary for achieving such challenging compatibility goals.



CO₂ and N₂O reference materials: delta value and amount fraction stability



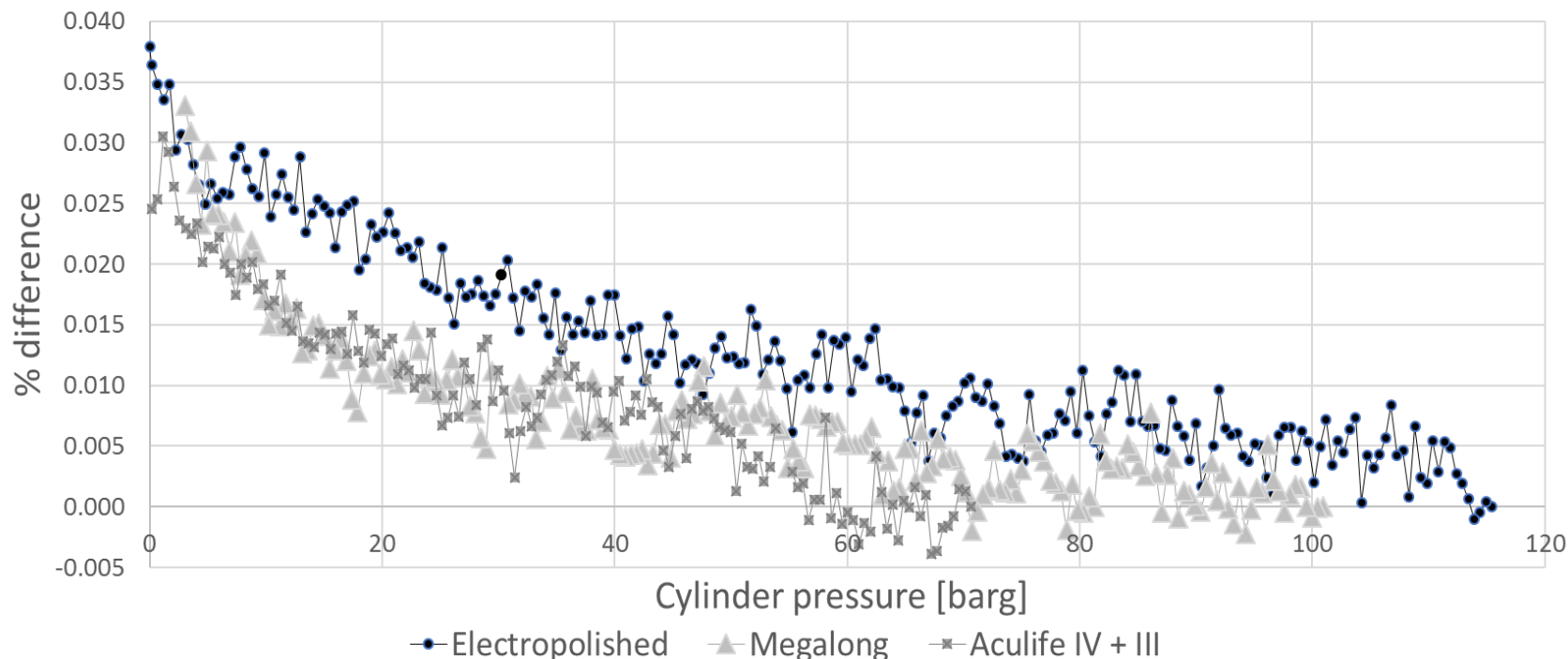
- CO₂ and N₂O reference materials are required with a known delta value for calibration of instruments which cannot discriminate between the major isotopologues and for discrimination between emission sources.
- The preparation of reference materials with well formulated uncertainties in amount fraction and delta value is required to give confidence in atmospheric measurements
- Improving analytical uncertainty and preparation processes is necessary for achieving the WMO-GAW challenging compatibility goals. These include gravimetry, purity analysis, validation, stability, passivation of storage media, and matrix effects.
- We present the stability of the amount fraction and delta value of reference materials on decant, with pressure and with varying cylinder passivation chemistries



CO₂ reference materials: Stability of amount fraction with passivation chemistry

The effect of pressure on the amount fraction of nominally 400 μmolmol^{-1} CO₂ in synthetic air prepared in cylinders with different cylinder passivation or surface treatments.

The plot below shows 5 minutes of data averaged against the average pressure over 5 minutes

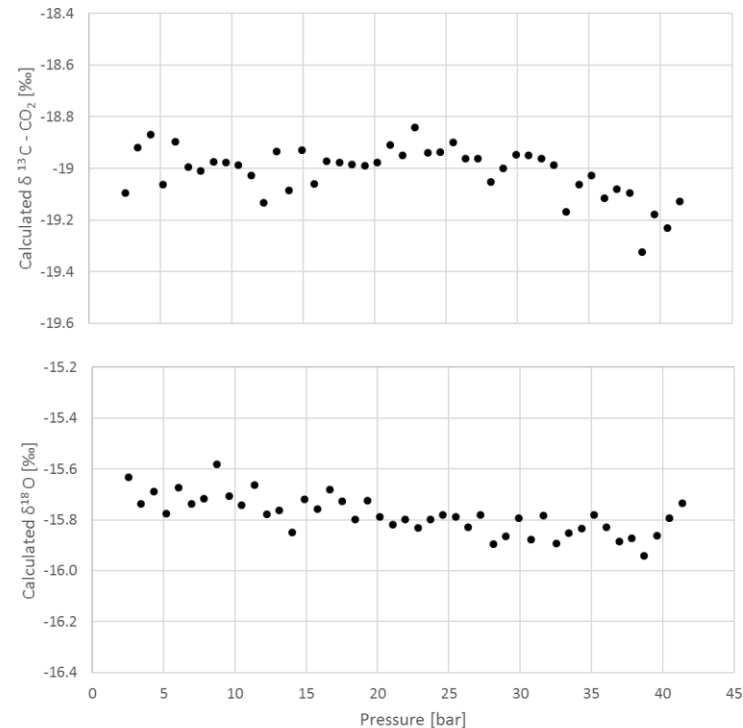
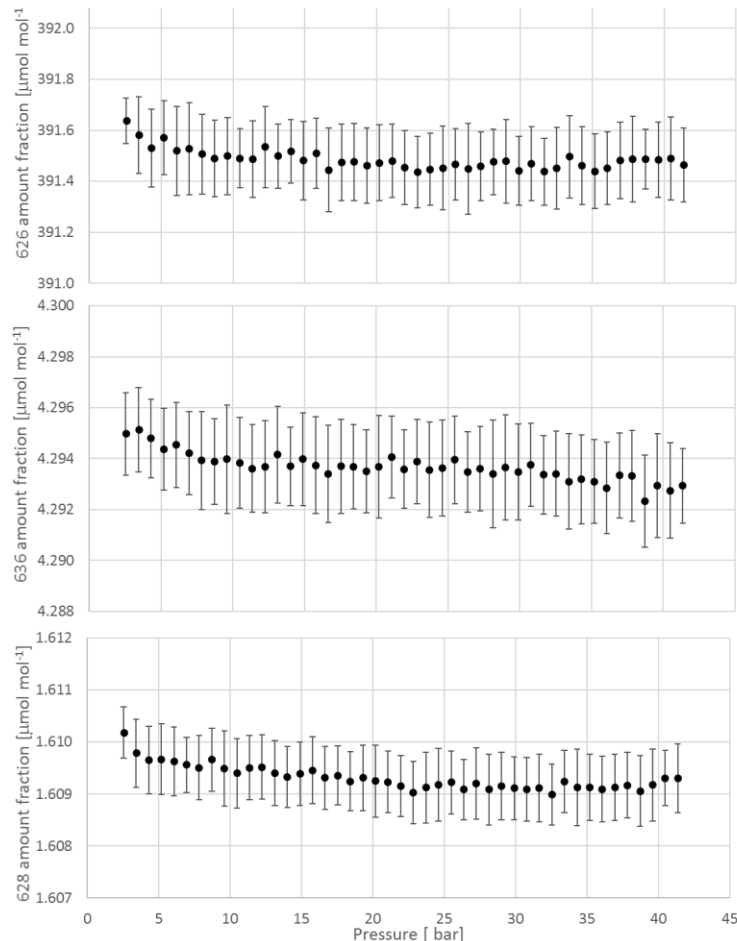


A 0.035 percent increase in amount fraction was observed with reducing pressure to zero bar and 0.015 percent on reducing the pressure to 20 bar cylinder for treated cylinders.

No statistically relevant difference was observed between different cylinder passivation or surface treatments

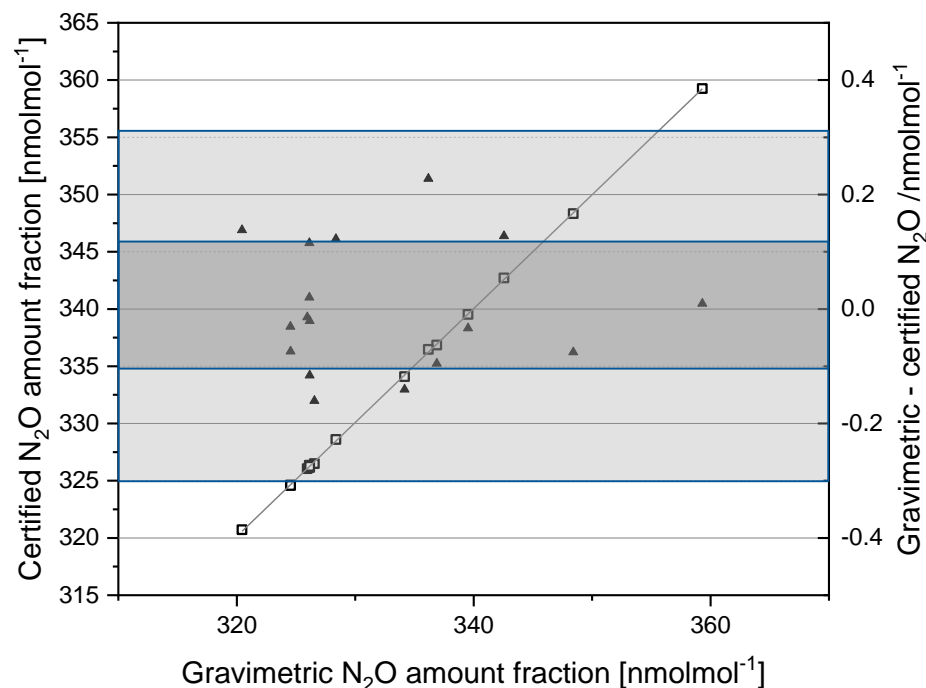
CO₂ reference materials: delta value and amount fraction stability with pressure

- Several aluminium cylinders (0.85 L, Luxfer) were filled to 40-45 bar with nominally 325 nmolmol⁻¹ N₂O in synthetic air reference material and emptied through a CRDS (LGR 43-r)
- The amount fraction of 626 and 636 and 628 CO₂ was recorded and the $\delta^{13}\text{C-CO}_2$ and $\delta^{18}\text{O-CO}_2$ was calculated, an example is shown below
- The $\delta^{13}\text{C-CO}_2$ and $\delta^{18}\text{O-CO}_2$ values were not observed to change with pressure



N₂O reference materials: Gravimetric production and certification

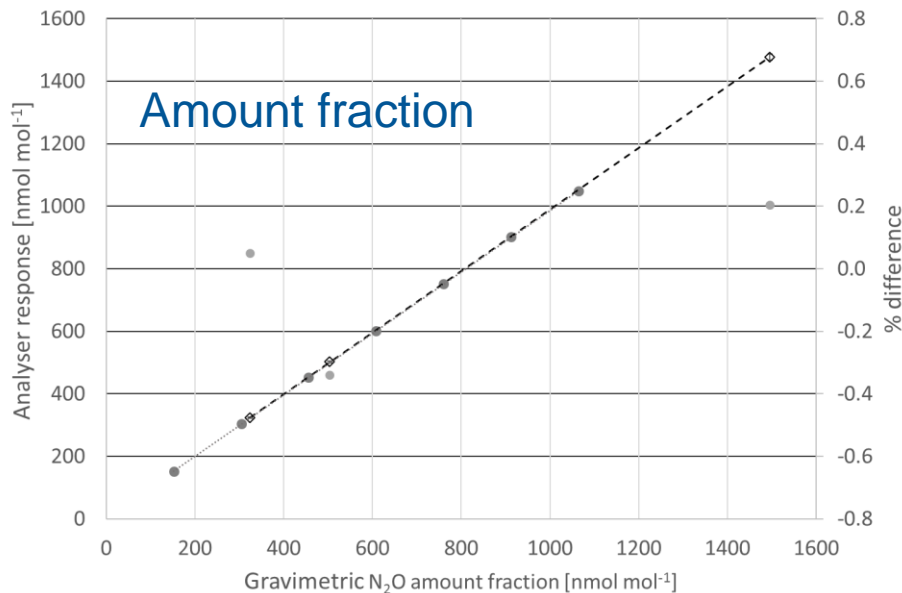
- N₂O reference materials in the range 320 – 360 nmolmol⁻¹ was gravimetrically prepared from pure N₂O with a gravimetric uncertainty on the order of the extended WMO-GAW compatibility goal of 0.3 nmolmol⁻¹
- A CRDS (Picarro G53101-*i*) was used to certify a range of reference materials with amount fractions in the range 320 – 360nmolmol⁻¹
- All reference materials were certified against a 325 nmolmol⁻¹ reference material
- All certified within the WMO extended DQO
- Demonstrating the linearity of the CRDS for amount fraction in this range



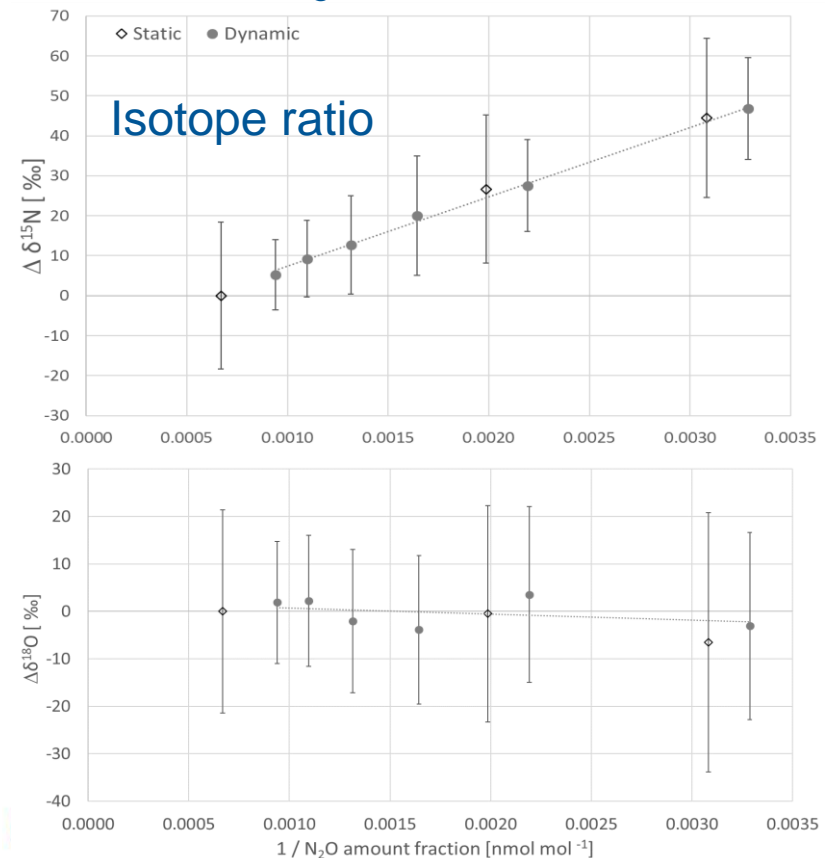
Certified amount fraction with increasing gravimetric amount fraction for ambient N₂O reference standards (open squares) with differences between the gravimetric and certified amount fractions (filled triangles). The WMO-GAW DQO is indicated with light grey shading and extended DQO is indicated with dark grey shading

N₂O reference materials: Agreement between static and dynamic reference materials

- Static reference materials compared to dynamically generated reference materials with agreement of 0.05% at nominally 325 nmol mol⁻¹
- $\delta^{15}\text{N}$ varied with amount fraction with good agreement between static and dynamically generated values indicating no difference in fractionation in standard preparation.
- $\delta^{15}\text{N}$ was not observed to vary within statistical significance for increasing amount fraction.



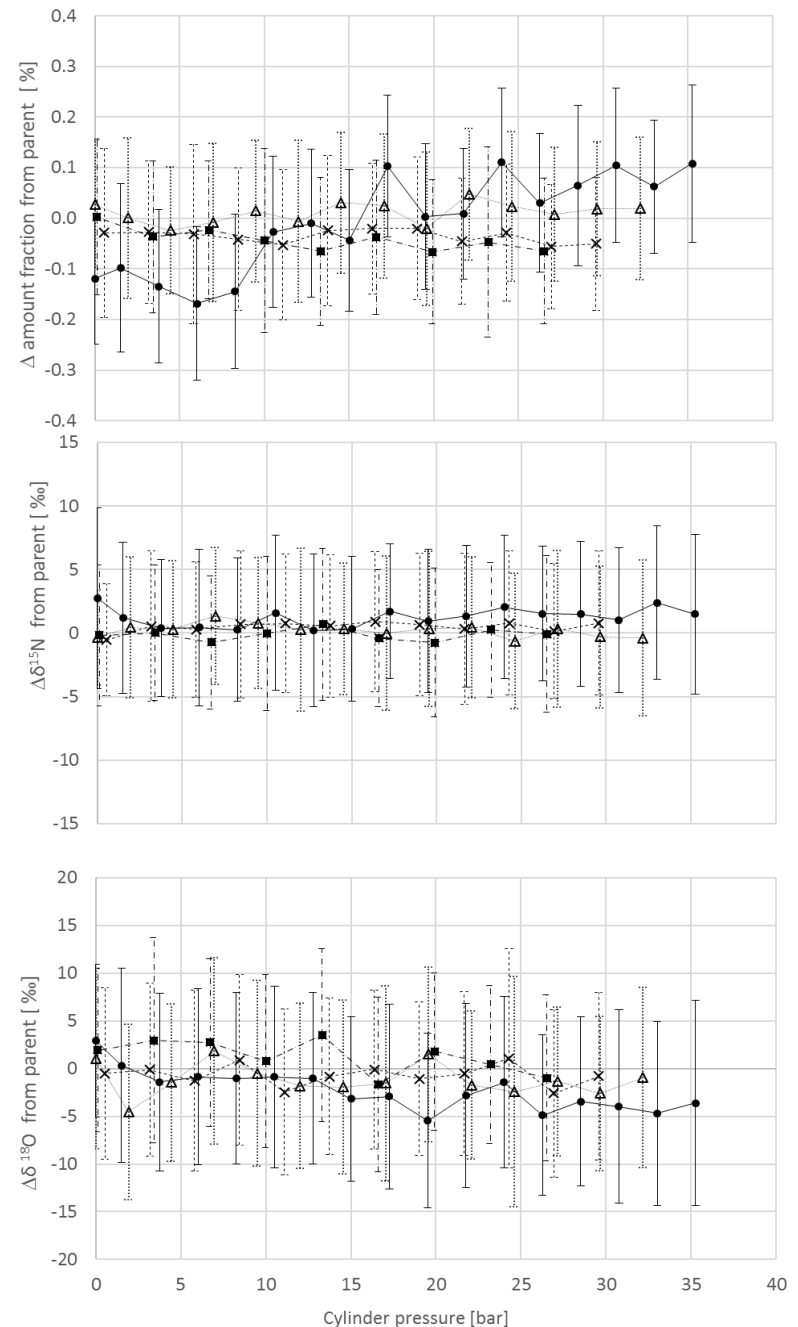
N₂O static (open rectangles) and dynamic (filled circles) reference materials (above) change in $\delta^{15}\text{N}$ with amount fraction (top right) change in $\delta^{18}\text{O}$ with amount fraction (lower right). Each data point represents four repetitions of a five minute average. Error bars represent 1 standard deviation. Error bars are plotted but are not visible on the plot above.



N₂O reference materials: Stability with reducing pressure

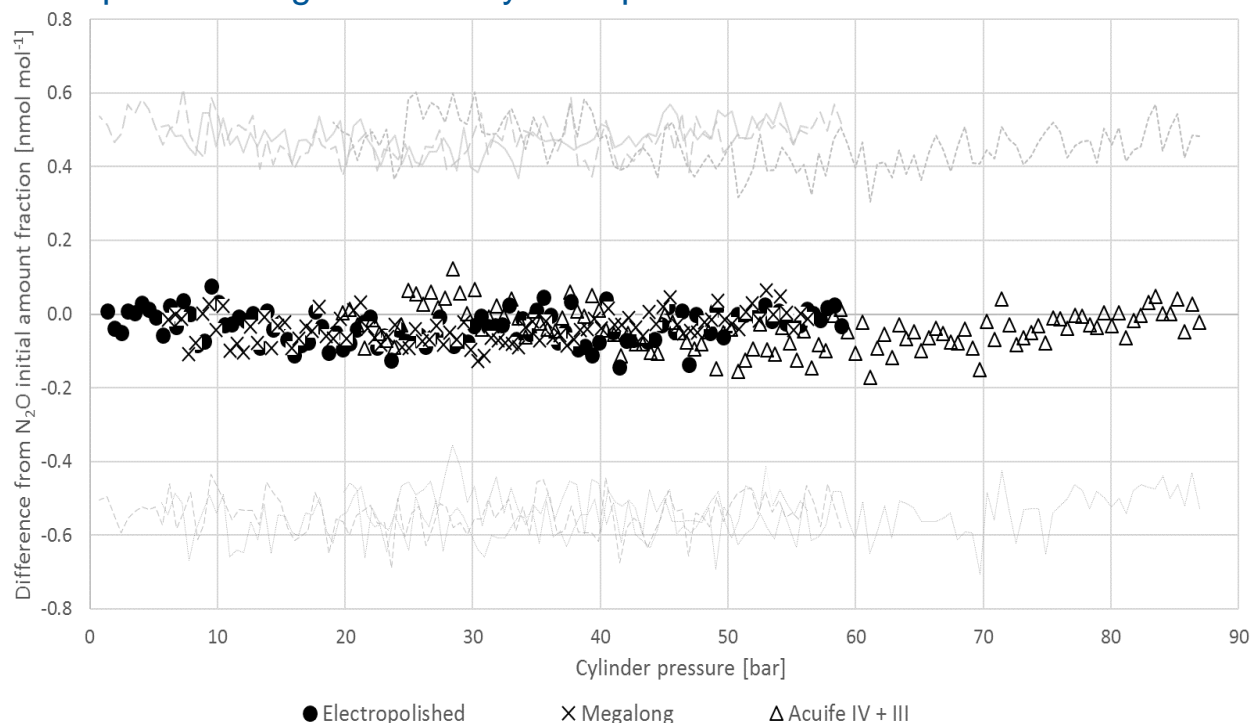
- Aluminium cylinders (0.85 L, Luxfer) were filled to 30-35 bar with nominally 325 nmolmol⁻¹ N₂O in synthetic air reference material and emptied through the CRDS
- No statistically relevant trend for N₂O amount fraction or delta value was observed as the cylinder pressure reduces
- There is good agreement between the four cylinders
- The data indicates that adsorption onto cylinder walls causes negligible changes in amount fraction and delta value with pressure.

Figure shows the effect of reducing cylinder pressure on (top) percentage difference in amount fraction from N₂O parent cylinder, (middle) difference in $\delta^{15}\text{N}$ from N₂O parent cylinder, (lower) difference in $\delta^{18}\text{O}$ from N₂O parent cylinder. Error bars represent one standard deviation.



N₂O reference materials: Stability with cylinder passivation chemistry

- The effect of passivation chemistry and cylinder treatment on the stability of the reference materials with pressure was measured.
- No statistically relevant difference in amount fraction was observed with reducing cylinder pressure regardless of cylinder passivation treatment

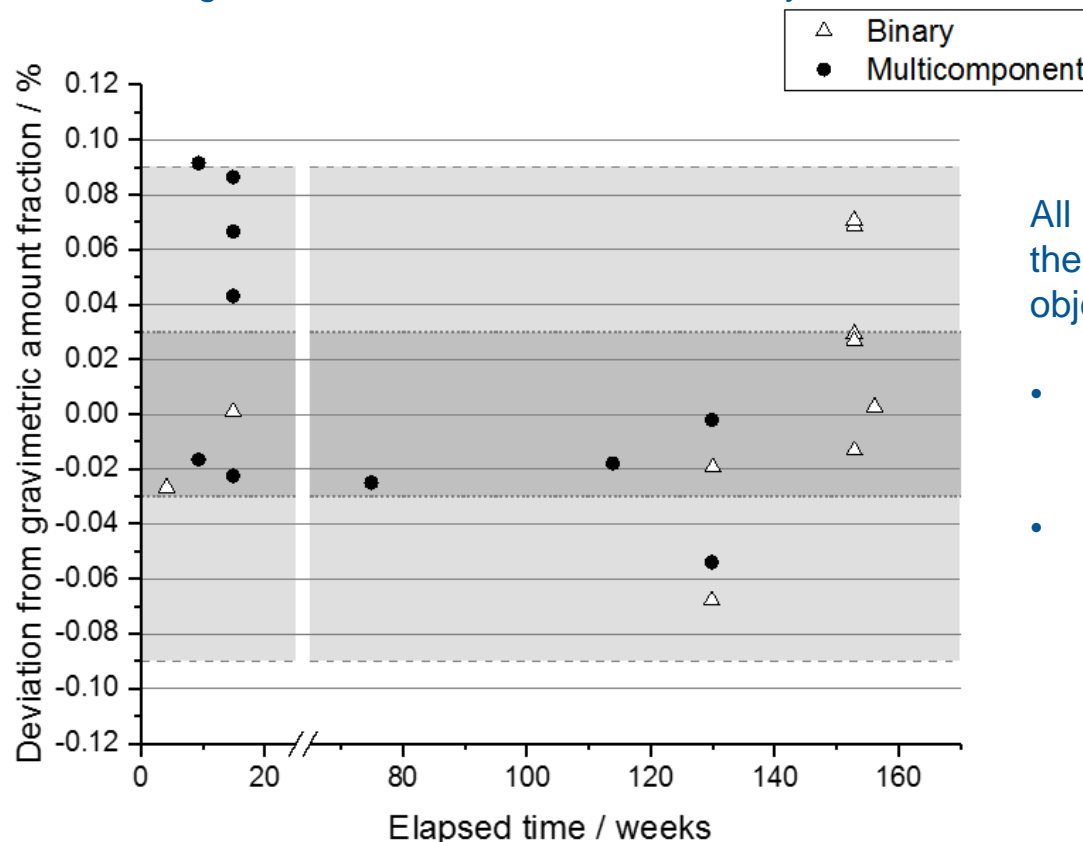


Difference from initial N₂O amount fraction with reducing cylinder pressure for three nominally 325 nmol mol⁻¹ N₂O in synthetic air standards produced in 10 L cylinders with three different cylinder passivation processes: Electropolished (filled circles), Air Liquide Megalong (crosses), Air Liquide Aculife IV + III (open triangles). The uncertainty (one standard deviation) is plotted as dotted lines (Aculife), dashed lines (electropolished) and a solid line (Megalong)



N₂O reference materials: Stability through time

Freshly prepared reference materials in the amount fraction range 320 – 360 nmolmol⁻¹ N₂O in synthetic air and N₂O with atmospheric amount fraction of CO₂, CH₄ and CO were certified against a reference standard over 3 years.



All reference materials certified to within the extended WMO-GAW data quality objectives indicating;

- The stability of the N₂O reference materials over a period of three years
- The comparability of N₂O binaries and multicomponent reference standards for amount fraction

Certified N₂O amount fraction as a function of the gravimetric amount fraction for ambient N₂O reference standards (open squares), with differences in certified and gravimetric values (filled triangles). The WMO – GAW compatibility goal is indicated on the plot in dark grey shading and the extended compatibility goal is indicated by lighter grey shading



Summary

- We have gravimetrically produced a range of CO₂ and N₂O atmospheric amount fraction reference materials
- For CO₂ reference materials we demonstrated the stability of both $\delta^{13}\text{C}$ - CO₂ and $\delta^{18}\text{O}$ - CO₂ isotopologues with reducing pressure despite a small increase in total CO₂ amount fraction observed for all tested cylinder passivation chemistries. This indicates no preference of adsorption of one isotopologue.
- For N₂O the change in amount fraction of the reference materials with reducing cylinder pressure was shown to be negligible regardless of cylinder passivation chemistry and the stability of the mixtures over three years was within the expanded WMO-GAW uncertainty goals of $\pm 0.3 \text{ nmolmol}^{-1}$
- The $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ value of the N₂O reference materials was also demonstrated to be stable with reducing pressure, and agreement of amount fraction and delta value was achieved between production of reference materials statically and dynamically.

