perspective

IRMS

Application Note **AN65**

High Resolution Clumped Isotope Analysis of O_2

- **Unprecedented long-term precision of simultaneous Δ36 and Δ35 analysis**
- **Resolving power 4 x standard IRMS**
- **Elimination of ^{36}Ar corrections**
- **Reduction in sample preparation**
- **Δ36 and Δ35 scale compression ≈ 1**
- **Measured Δ36 and Δ35 independent of isotopic composition**

The Nu Perspective IS is a stable isotope ratio mass spectrometer designed to measure multiple gas species including both the isotopologues of carbon dioxide at masses 44 to 49 and oxygen at masses 32 to 36. Enhancements to the ion source allow the 'mass resolving power' (MRP, m/δm, 5% - 95% of peak) of the instrument to be increased from ≈1000 to ≈4000 while maintaining the high ion currents (40 nA mass 32, O_2) necessary for clumped isotope analysis, with only a sacrifice of 50% sensitivity. This high resolution is ideal for applications where both fast measurement time and the ability to separate isobaric interferences are required.

Enhanced Resolving Power: Δ36 and Δ35 measurement of O_2 gas

One application for this enhanced configuration is the determination of Δ36 and Δ35 in oxygen. This involves measurement of $^{18}O^{18}O$ (≈ mass 36) and $^{18}O^{17}O$ (≈ mass 35) in O_2 gas. This is a challenging application because of the low abundance of these "clumped" signals which not only have contributions from isobaric interferences but require good abundance sensitivity.

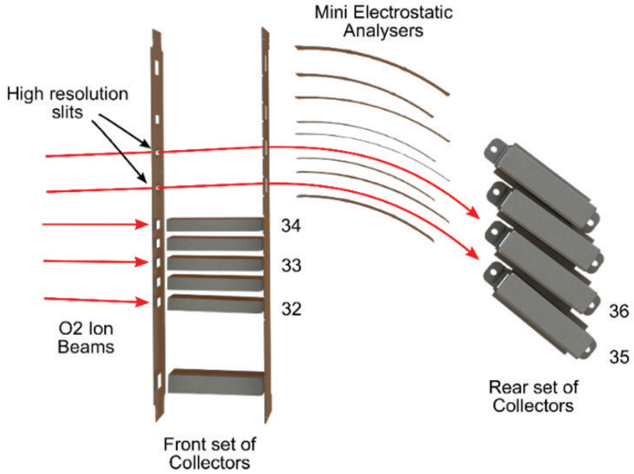

Figure 1. Schematic view of the Perspective IS collector array showing the O_2 masses 32 to 36. Low abundance "clumped" signals mass 35 and 36 enter the collector array through high resolution slits and are filtered through "mini-ESA"s.

The Perspective IS is tailored to meet these challenges. O_2 masses 32 to 34 are measured in standard deep Faraday collectors, whereas the low abundance mass 35 and 36 are filtered through "mini-ESA"s (patent applied for) to greatly improve abundance sensitivity and practically eliminate the contribution of scattered electrons and ions within the analyser. A schematic view of the Perspective collector array is shown in Figure 1.

The issue of isobaric interferences is addressed using the high-resolution option. There are several isobars that interfere: at mass 36; $^{1}H^{35}Cl$ and ^{36}Ar where Ar is present in oxygen samples derived from air. For mass 35; ^{35}Cl. Due to these interferences being mass deficient compared to O_2 they can be "edge resolved". See Figure 2 below:

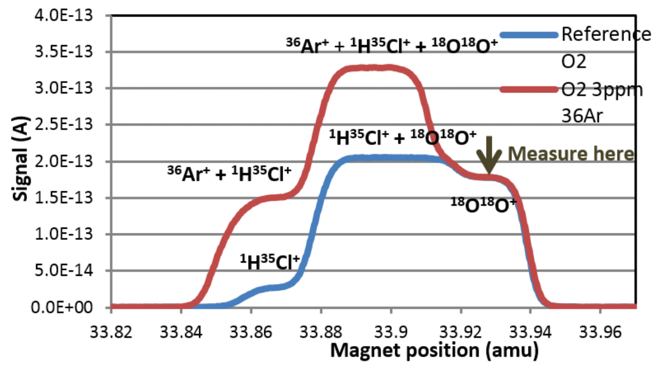

Figure 2. Mass 36 ion signal at MRP ≈ 3600; comparison between pure oxygen reference gas (blue) and oxygen containing 3 ppm $^{36}Ar/^{16}O^{16}O$ (red). IRMS measurement takes place on the right shoulder ($^{18}O^{18}O$ only). Mass 32 $^{16}O^{16}O$ ion current ≈ 4 x 10^{-8} A (8 V).

Oxygen spiking with argon; dual inlet measurement

To prove the technique can effectively remove Ar interference, a dual inlet zero enrichment test was run using identical oxygen reference gas in the sample and reference bellows. The sample gas was then progressively spiked with argon and the test re-run. The results are shown below:

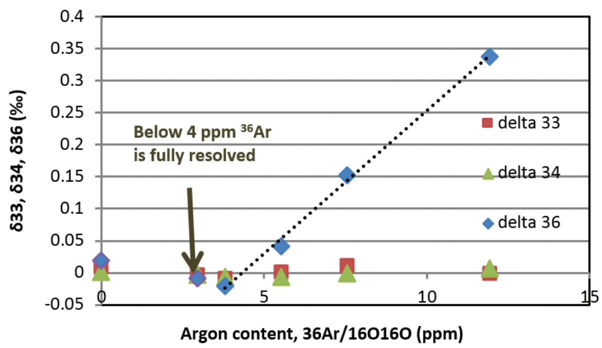

Figure 3. Dual inlet measurement: δ33, δ34 and δ36 of O_2 reference gas spiked with argon with respect to pure oxygen reference gas, plotted against ^{36}Ar content of the spiked oxygen gas.

Below 4 ppm ^{36}Ar / $^{16}O^{16}O$ the presence of argon has no effect on δ36. Air purified through a single gas chromatograph (GC) cycle to yield oxygen typically has a concentration << 1 ppm ^{36}Ar, therefore high resolution eliminates both the need for Ar data corrections and time consuming multiple GC clean-up steps. The result is a measurement of higher accuracy.

Simultaneous Δ35 and Δ36 measurement

By using a pair of narrow slits on the 35 and 36 collectors, isobaric interferences on the 'clumped' O_2 isotopologues can be resolved using "edge" or "pseudo" resolution. The "Zoom Optics" of the Perspective allow the peaks to be precisely aligned and focused electrostatically without physically moving the collectors.

Δ35 and Δ36 linearity with respect to isotopic composition

O2 gas standards with a range of isotopic compositions were photochemically and thermally equilibrated at a range of known temperatures [1]. These gases were processed on a custom-built oxygen preparation line [1] and analysed on the Perspective IS using the 'edge resolution' technique as displayed in Figure 2. The results are presented below:

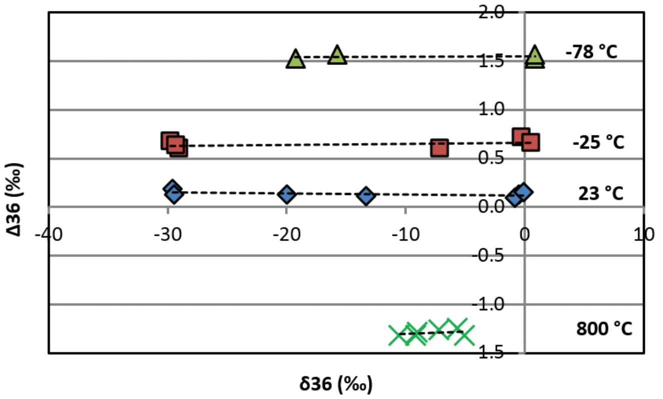

Figure 4. Linearity plots of raw Δ36 against raw measured δ36. Values are relative to the working gas. No linearity or scale compression corrections have been applied.

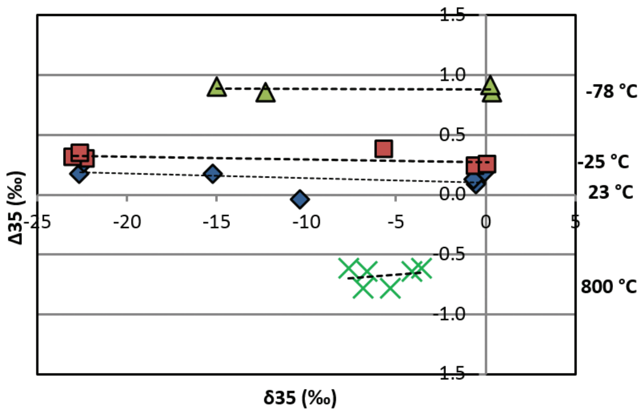

Figure 5. Linearity plots of raw Δ35 against raw measured δ35. Values are relative to the working gas. No linearity or scale compression corrections have been applied.

Measured Δ36 and Δ35 were found, within error, to be independent of δ36 and δ35 respectively, negating the need for any linearity corrections in the data. The improved abundance sensitivity provided by the Perspective IS mini-ESA filters allows for this additional processing step to be discarded.

The theoretical values of Δ36 [2] and Δ35 [1] for the O_2 gases with known equilibration temperatures were plotted against the mean raw measured value of Δ36 and Δ35 (relative to the working gas). See Figure 6 and Figure 7 below:

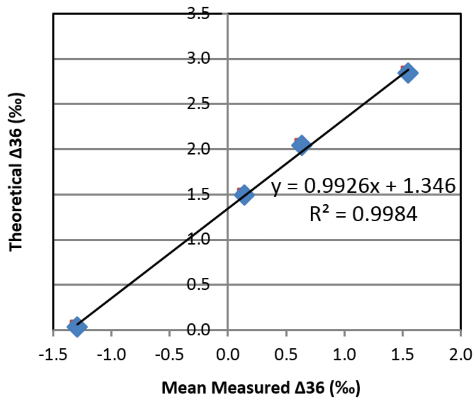

Figure 6. Theoretical Δ36 of O_2 gas standards against mean measured Δ36 (no corrections applied).

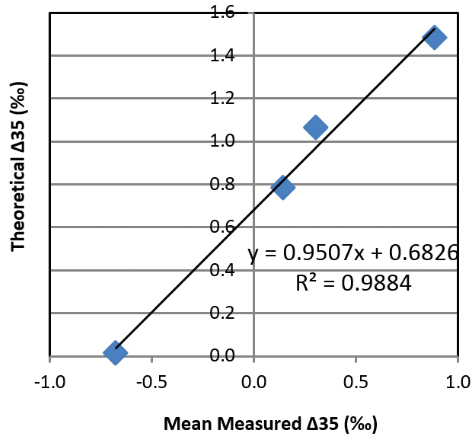

Figure 7. Theoretical Δ35 of O_2 gas standards against mean measured Δ35 (no corrections applied).

Theoretical Δ36 and Δ35 of O_2 gas standards plotted against mean measured Δ36 and Δ35 both yielded a gradient ≈ 1 (within error) showing that the Perspective IS ion source exhibits negligible clumped isotope scale compression in oxygen gas (via scrambling of the isotopic ordering).

Long term measurements of Δ36 and Δ35 in air

Oxygen from air, processed on the same custom-built preparation line used for linearity measurements (Figure 4 – 7), was measured over an extended period on the Perspective IS. Δ36, Δ35, $\delta^{18}O^{air}$ and $\delta^{17}O^{air}$ over a period of 5 months (n = 17) are shown in Figure 8 below:

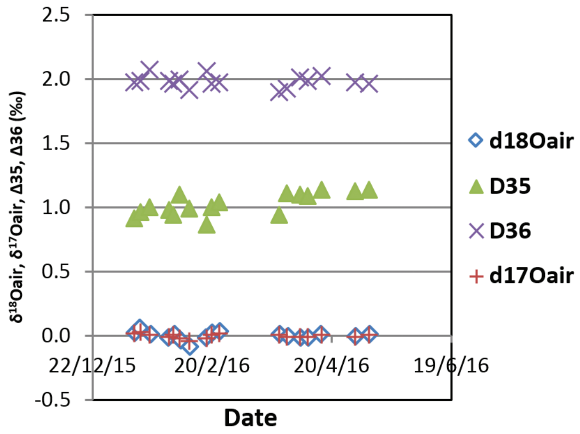

Figure 8. Δ36, Δ35, $\delta^{18}O_{air}$ and $\delta^{17}O_{air}$ of air measured over a 5-month period.

Each data point represents a dual inlet analysis consisting of 2000 s integration time (approx. 1.5 hours instrument time) at 40 nA (8 V) O_2 mass 32 signal. The plots show the exceptional stability of the Perspective IS without the need for isotopic linearity corrections or ^{36}Ar corrections. Statistics of the 17 data points are shown in the following table:

	$\delta^{18}O_{air}$ (‰)	$\delta^{17}O_{air}$ (‰)	Δ35 (‰)	Δ36 (‰)
Average	-7.6E-05	-0.0002	1.025	1.979
1σ	0.0324	0.0170	**0.086**	**0.047**

The Δ36 external precision of ±0.047 ‰ (n = 17) achieved on the Perspective IS is a significant advance compared to the previous best published precision of ±0.17 ‰ on a competing SIRMS instrument (based on replicate analysis of air) [1]. Similarly, the Δ35 external precision of ±0.086 ‰ (n = 17), also represents a leap in precision when compared to prior work on a competitor's instrument (±0.25 ‰ [4]).

Further comments and conclusion

The external precision presented in this long-term experiment has already been surpassed in further measurements of air performed on the Perspective IS presented in Yeung et al. 2016 [3] where a Δ36 external reproducibility of ±0.038 ‰ (1σ) in 11 air samples was obtained.

In conclusion the Perspective IS high resolution option offers fast clumped isotope analysis with high ion currents, while simultaneously offering high resolution spectroscopic removal of interfering masses. The result is unprecedented stability and precision in the measurement of clumped isotopes.

References

[1] Yeung, L. Y., J. L. Ash, and E. D. Young (2014), Rapid photochemical equilibration of isotope bond ordering in O_2, J. Geophys. Res. Atmos., 119, 10,552–10,566, doi:10.1002/2014JD021909.

[2] Wang, Z., E. A. Schauble, and J. M. Eiler (2004), Equilibrium thermodynamics of multiply substituted isotopologues of molecular gases, Geochim. Cosmochim. Acta, 68(23), 4779–4797

[3] Yeung, L. Y., et al. (2016), Isotopic ordering in atmospheric O_2 as a tracer of ozone photochemistry and the tropical atmosphere, J. Geophys. Res. Atmos., 121, 12,541–12,559, doi:10.1002/ 2016JD025455.

[4] Yeung, L. Y., E. D. Young, and E. A. Schauble (2012), Measurements of $^{18}O^{18}O$ and $^{17}O^{18}O$ in the atmosphere and the role of isotope-exchange reactions, J. Geophys. Res., 117, D18306, doi:10.1029/2012JD017992.

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