Direct air measurements using the high resolution Thermo Ultra mass spectrometer

O_2/N_2 and Ar/N_2 ratios, and O_2, N_2 and Ar isotopic composition

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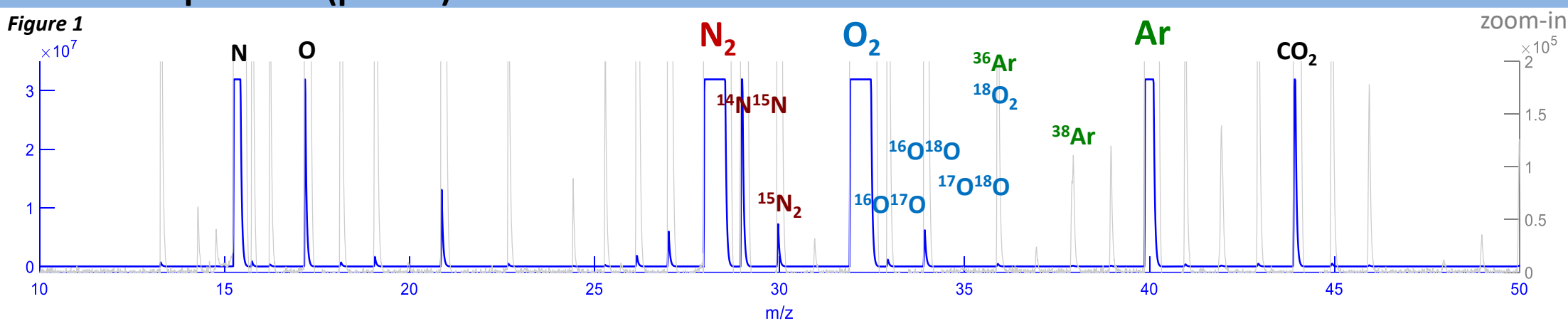
Whole air spectrum (partial)

Figure 1



N_2: $\delta^{15}N$, $\delta^{15}N_2$ ($\Delta^{15}N_2$)

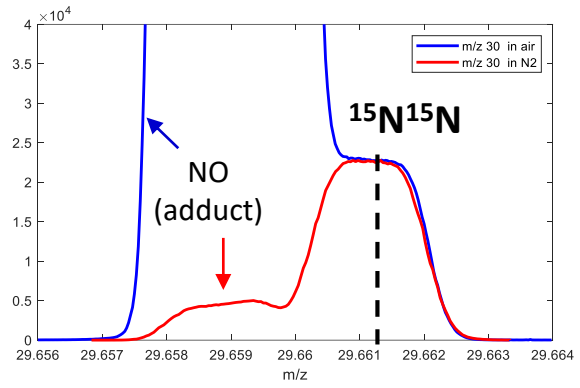


***Figure 2**: Mass scan around m/z 30, showing the NO and $^{15}N^{15}N$ peaks. The dashed line indicates the measurement location.*

- $^{15}N^{15}N$ visible both in air and in pure N_2
- $^{15}N^{15}N$ main interference: NO adduct
- $^{15}N^{15}N$ not sensitive to (small) changes in adduct size
- $\delta^{15}N$: good when measured on air; not (yet) good enough in extracted N_2

O_2: $\delta^{17}O$, $\delta^{18}O$, $\delta^{17}O^{18}O$, $\delta^{18}O_2$

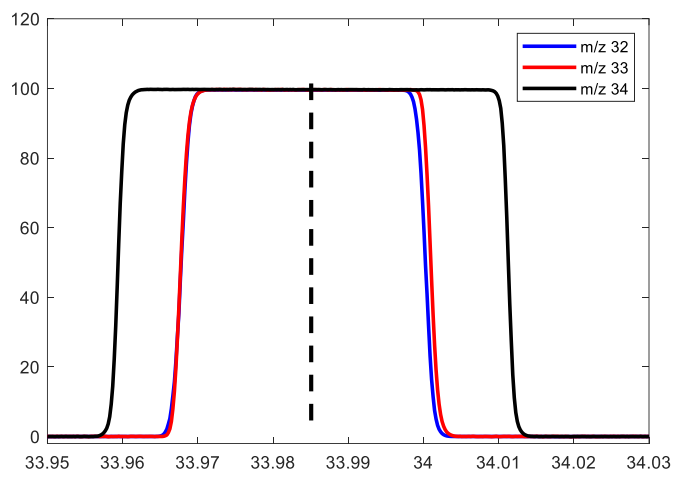


***Figure 3**: Overlayed mass scans of the O_2 peaks at m/z 32, 33 and 34. The dashed line indicates the measurement location (clumped traces not shown)*

- precision slightly lower than when measuring pure (extracted) O_2
- BUT: possible extraction artefacts avoided

Ar: $\delta^{38}Ar$, $\delta^{40}Ar$

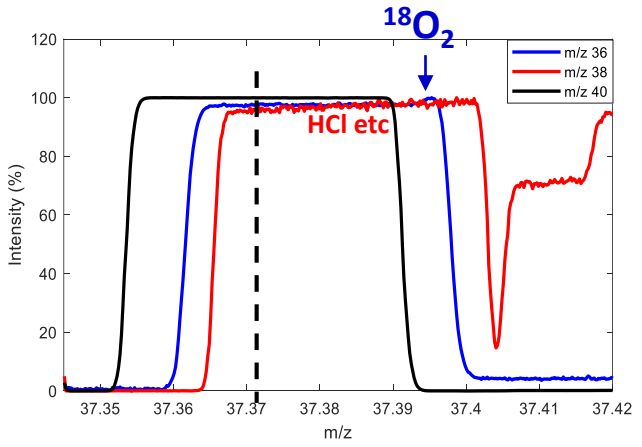


***Figure 4**: Overlayed mass scans of the Ar peaks at m/z 36, 38 and 40. The dashed line indicates the measurement location - set on the left side of the m.z 36 and 38 peaks in order to avoid some small interferences.*

- several (minor) interfering compounds not well separated in medium resolution
- next: test high resolution

Species	m/z	Internal precision	Notes
$\delta O_2/N_2$	28, 32	1 permeg	main meas. error: sample transfer
$\delta Ar/N_2$	40, 28	10 permeg	peak hopping; main meas. error: sample transfer
O_2 iso: $\delta^{17}O$	33, 32	10 permeg	medium resolution
O_2 iso: $\delta^{18}O$	34, 32	3 permeg	medium resolution
O_2 iso: δ17-18	35, 32	0.2 per**mil**	medium resolution
O_2 iso: δ18-18	36, 32	0.1 per**mil**	medium resolution
N_2 iso: $\delta^{15}N$	29, 28	2 permeg	better in air than in extracted N_2
N_2 iso: δ15-15	30, 28	0.6 per**mil**	high resolution
Ar iso: $\delta^{38}Ar$	38, 36	40 permeg	medium resolution
Ar iso: $\delta^{40}Ar$	40, 36	20 permeg	medium resolution

Method (dis)advantages

\+
- **extraction** / separation not needed
  → associated artifacts avoided
- no **isobaric interferences** (high resolution)
- all species measured in the **same sample**
- measurement possible for **low abundance** species, e.g. clumped isotopologues (high sensitivity)
- **flexible** m/z combinations (movable detectors)

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- narrow **dispersion** range (+/- 5%)
  → use peak hopping
- other **interferences and nonlin** still possible

The MAT-253 Ultra instrument

- **9 detectors**
  - 1 fixed, 8 movable
  - all with Faraday cups
  - 4 with ion counters
  - including 10^{13} Ohm amplifier
- **Mass resolution**: adjustable to low, medium or high (M/ΔM ~40000)

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