

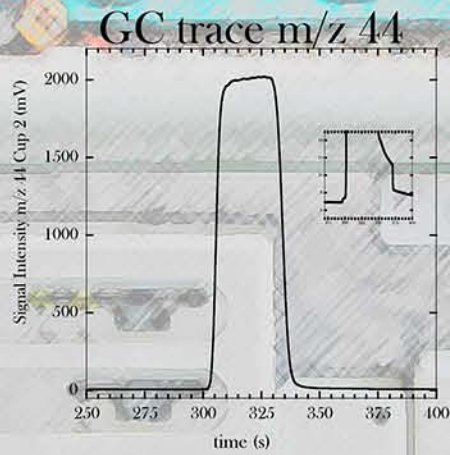
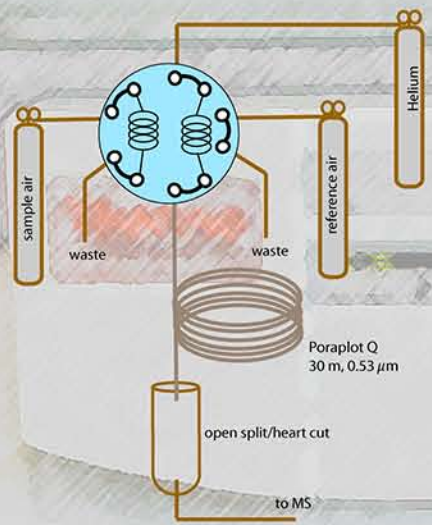
High precision isotopic analysis of CO₂ in air, using a non-cryogenic GC-IRMS approach



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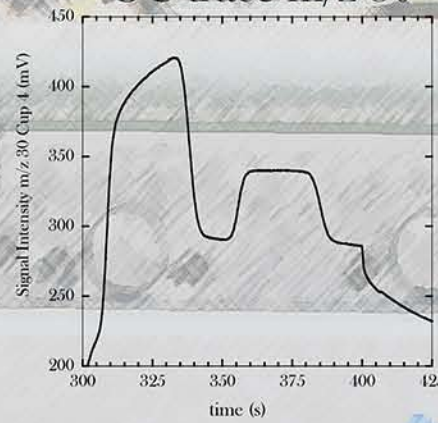
Below is a description of our attempt to use a Finnigan Delta V Plus and a modified Gas Bench for measuring the isotopic composition of CO₂ in air without the need for liquid nitrogen or a dual inlet system. The goal is to create a highly precise and accurate method with the results comparable to the classical dual inlet techniques and capable of a moderate to high throughput.

Schematics of air injector



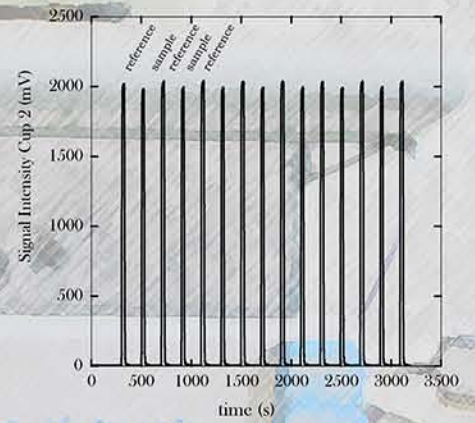
The setup is relative simple; it is based around a 10 port Valco valve enabling identical treatment of both standard and sample. The valve is equipped with two 1 ml stainless steel loops, one continuously flushed with standard air and the other with sample air.

GC trace m/z 30



m/z 30 trace, presumably NO, during elution of the CO₂ peak. The first peak is likely to be NO formed on the filament while the CO₂ pressure is high while the second is NO formed from N₂O. Comparing the elution time for N₂O with that of CO₂ shows a sufficient separation for the CO₂ ratio to be free interference from N₂O.

Repeated injections of reference and sample



A typical sample run. The sample peaks are flanked on both sides by a reference peak allowing for a normalization similar to the Dual Inlet.

Calculating one flask result

| Peak to Peak: (raw) | Averages | Stdev's | $\delta^{13}C$ raw | $\delta^{18}O$ raw | $\delta^{13}C$ - sample normalized | $\delta^{18}O$ - sample normalized |
|-----------------------------|----------|---------|--------------------|--------------------|------------------------------------|------------------------------------|
| sample-air $\delta^{13}C$: | -9.037 | 0.032 | -9.515 | -2.62 | | |
| ref-air $\delta^{13}C$: | -9.490 | 0.016 | -9.024 | -2.57 | -9.0385 | -2.5795 |
| sample-air $\delta^{18}O$: | -2.553 | 0.016 | -9.486 | -2.601 | | |
| ref-air $\delta^{18}O$: | -2.599 | 0.033 | -9.054 | -2.56 | -9.073 | -2.5915 |
| | | | -9.506 | -2.576 | | |
| | | | -8.974 | -2.539 | -8.989 | -2.559 |
| | | | -9.494 | -2.624 | | |
| | | | -9.034 | -2.53 | -9.057 | -2.5315 |
| | | | -9.49 | -2.613 | | |
| | | | -9.068 | -2.546 | -9.1075 | -2.5875 |
| | | | -9.461 | -2.544 | | |
| | | | -9.036 | -2.575 | -9.0815 | -2.6115 |
| | | | -9.478 | -2.623 | | |
| | | | -9.067 | -2.555 | -9.0975 | -2.539 |
| | | | -9.491 | -2.649 | | |
| | | | | | Average: (normalized) | Average: (normalized) |
| | | | | | -9.063 | -2.571 |
| | | | | | Stdev: (normalized) | Stdev: (normalized) |
| | | | | | 0.040 | 0.029 |

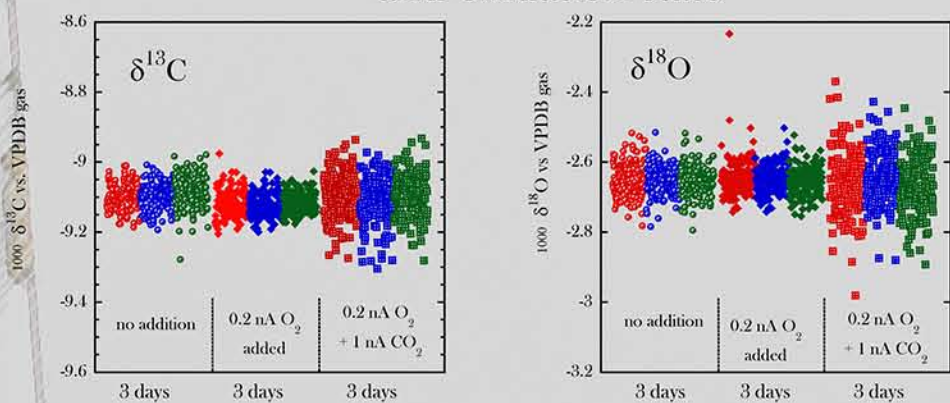
$$S_n = \frac{(R_{n-1} + R_{n+1})}{2} + R_{true} + S_n$$

Normalization of sample S_n relative to the two adjacent measured references R_{n-1}, R_{n+1}, with the assigned value R_{true}.

As the valve turns, 1 ml aliquots of standard or sample are injected onto a Poraplot Q column (0.53 μ m, 30 m). The CO₂ contained in the air is here separated from the main constituents (nitrogen and oxygen) as well as N₂O, and is introduced into the mass spectrometer by using the open split to perform a heart cut. With the alternating injection of standard and sample gas, the CO₂ peak from each sample gas injection is flanked by two standard peaks analogous to a Dual Inlet analysis. The normalization of the sample ratios can therefore be done in the similar manner as with the Dual Inlet minimizing the time between assigned and measured ratios and, to some extent, also account for instrument drift.

Although we have been using the least challenging of all samples - a pressurized air tank, the preliminary results from this setup are very promising; For $\delta^{13}C$, the run to run precision is ~ 0.01 ‰ while the results for $\delta^{18}O$ have a precision ~ 0.05 ‰. The precision of the repeatability of the daily averages is better than 0.01 ‰ for $\delta^{13}C$ and ~ 0.02 ‰ for $\delta^{18}O$.

Testing for ion source surface chemistry and oxidation state



The consistency of this setup has allowed us to explore several basic properties which can interfere with the accuracy and robustness of the system. Inter alia we tried to assess the "Chemical State" of the ion source on the measurement precision. The surfaces of the ion source and, in particular the presence of the hot tungsten wire ($\sim 2300^\circ C$) interact with the sample gas entering and can leave residues from chemical reactions that interfere with the next sample peak. By introducing a small background of CO₂, O₂ or a combination of the two we have been able to compare the results over a few days of repeated analysis. While conclusions cannot be drawn rigorously we see effects that need to be taken care of in a systematic fashion for making this technique as robust as required for the targeted precision level.

"Day to Day" performance

| n=4x (7 x 7) | $\delta^{13}C$ | $\delta^{18}O$ |
|-----------------|----------------|----------------|
| "48 h" Average: | -9.0771 | -2.5648 |
| Stdev (corr): | 0.0029 | 0.0173 |
| Loop Offset: | -0.0031 | 0.0792 |

| August 19, 3 pm, n=7 (x7) | $\delta^{13}C$ | $\delta^{18}O$ |
|---------------------------|----------------|----------------|
| Run-to-Run Average: | -9.0729 | -2.5469 |
| Stdev (corr): | 0.0132 | 0.0155 |
| offset: | 0.0011 | 0.0731 |

| August 20, 6 am, n=7 (x7) | $\delta^{13}C$ | $\delta^{18}O$ |
|---------------------------|----------------|----------------|
| Run-to-Run Average: | -9.0783 | -2.5543 |
| Stdev (corr): | 0.0143 | 0.0170 |
| offset: | -0.0043 | 0.0657 |

| August 20, 12 pm, n=7 (x7) | $\delta^{13}C$ | $\delta^{18}O$ |
|----------------------------|----------------|----------------|
| Run-to-Run Average: | -9.0797 | -2.5845 |
| Stdev (corr): | 0.0078 | 0.0898 |
| offset: | -0.0057 | 0.0355 |

| August 20, 8 pm, n=7 (x7) | $\delta^{13}C$ | $\delta^{18}O$ |
|---------------------------|----------------|----------------|
| Run-to-Run Average: | -9.0775 | -2.5736 |
| Stdev (corr): | 0.0082 | 0.0443 |
| offset: | -0.0035 | 0.0464 |

Reference:
Ferretti, D. F., D. C. Lowe, R. J. Martin, and G. W. Brailsford (2000). A new gas chromatograph-isotope ratio mass spectrometry technique for high-precision, N₂O-free analysis of $\delta^{13}C$ and $\delta^{18}O$ in atmospheric CO₂ from small air samples. *J. Geophys. Res.*, 105(D5), 6709-6718.