

EA-IRMS: Accurate and Precise Weight% O and $\delta^{18}\text{O}$ Analysis of Nitrogen-rich Samples using the EA IsoLink IRMS System

Christopher Brodie, Oliver Kracht,
Charles Douthitt
Thermo Fisher Scientific, Bremen,
Germany

Key Words

$\delta^{18}\text{O}$, EA IsoLink, N_2 -CO Separation, Precision, Pyrolysis, Weight% Oxygen

Goal

Demonstrate high precision weight% O and $\delta^{18}\text{O}$ analysis on nitrogen-rich sample matrices with complete N_2 and CO peak separation using continuous flow gas chromatography.

Introduction

Oxygen isotope ratio ($\delta^{18}\text{O}$) analysis of organic and inorganic sample matrices has become increasingly common in food authenticity and control, forensics, geosciences, ecology and archaeology.



A known challenge to $\delta^{18}\text{O}$ analysis by pyrolysis EA-IRMS is the production of accurate and precise values from nitrogen-rich sample matrices^{1,2,3}. N_2 and CO are formed in the reactor during the pyrolysis of nitrogen-rich sample matrices. However, without complete chromatographic separation of any tailing N_2 peaks, N_2 masses will be collected during isotopic analysis of CO, because the molecules have the same mass, and therefore adversely affect the accuracy and precision of the measured $\delta^{18}\text{O}$ values^{1,2,3}.



Figure 1. Thermo Scientific EA IsoLink IRMS System.

One prerequisite to accurate and precise $\delta^{18}\text{O}$ analysis of nitrogenous compounds is the complete *baseline separation* of N_2 and CO peaks, meaning that the detector response returns to baseline between the N_2 and CO peaks. Because caffeine, with 4 nitrogen atoms and 2 oxygen atoms per molecule (Figure 2), is a common reference material available in a range of well specified $\delta^{18}\text{O}$ values, it is an ideal compound to evaluate N_2 and CO peak separation, weight% Oxygen (wt% O) determinations and $\delta^{18}\text{O}$ values on the Thermo Scientific™ EA IsoLink™ IRMS System (Figure 1).

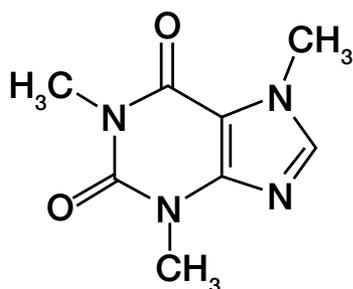


Figure 2. Caffeine molecule.

Analytical configuration

Between 100 and 200 μg of caffeine or benzoic acid, corresponding to 22–35 μg of oxygen in the sample, was weighed into silver containers and introduced into the reactor from the Thermo Scientific™ MAS Plus Autosampler. The reactor consists of an outer ceramic tube and an inner glassy carbon reactor filled with glassy carbon chips and a helium carrier gas flow via a bottom feed connector between them. During analysis, the reactor was held at 1450°C. The N_2 and CO gases were separated using a 1m 5Å molecular sieve packed GC column that was held isothermally at 70°C. After separation, wt% O was determined using a Thermal Conductivity Detector and the helium stream was then transferred into a Thermo Scientific™ Delta V™ Isotope Ratio MS for isotope ratio measurements via the open split of the Thermo Scientific™ ConFlo IV™ Universal Interface.

Baseline separation of N_2 and CO by gas chromatography

Baseline separation of the N_2 and CO peaks is achieved by continuous flow gas chromatography using a packed GC column (Figure 3). The analysis demonstrates that there is no interference evident on the mass 28 trace, which would be caused by overlapping N_2 and CO peaks^{1,2}, meaning the detector response returned to baseline between the peaks. Furthermore, there is no interference on the mass 30 trace, which can be caused by secondary pyrolysis products on the CO peak^{2,3}. However, it should be noted that pyrolysis byproduct formation can vary between different organic and inorganic sample matrices³.

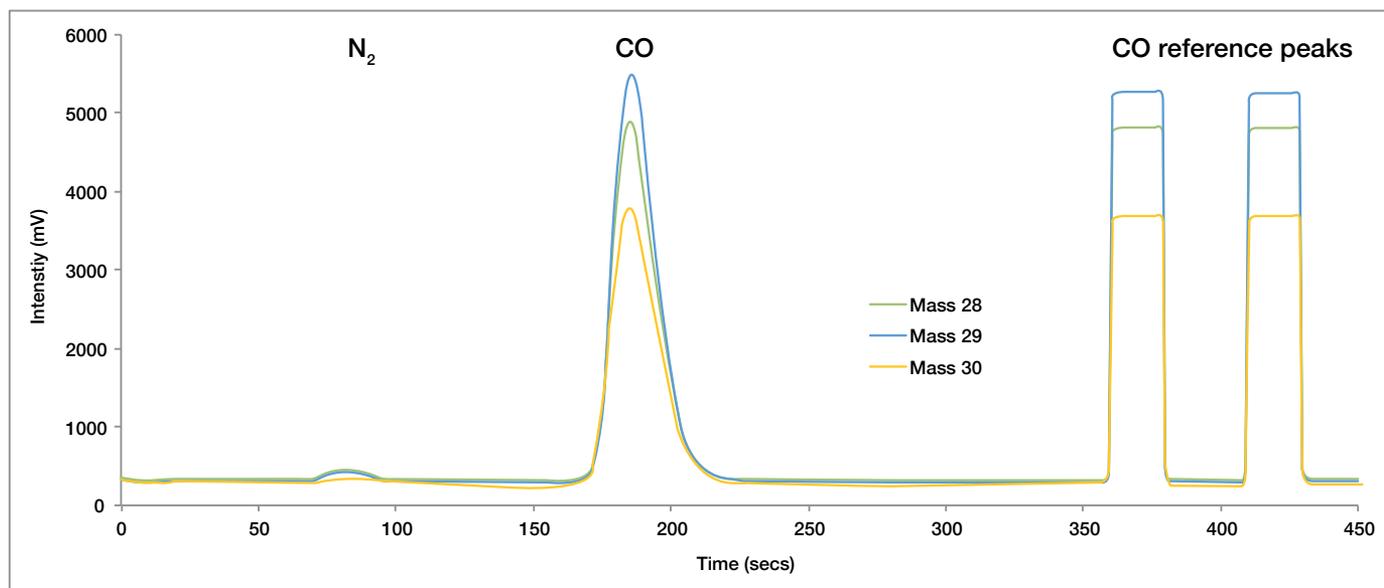


Figure 3. Complete baseline separation of N_2 and CO peaks on the EA IsoLink IRMS System.

EA IsoLink IRMS System performance for $\delta^{18}\text{O}$ analysis of caffeine

Table 1 shows weight% O and $\delta^{18}\text{O}$ data for 30 sequential measurements of five isotopically distinct caffeine samples and two benzoic acid sample. The precision of measured $\delta^{18}\text{O}$ values is outstanding, less than or equal to 0.21‰ for individual samples across a range of 22–35 $\mu\text{g O}$, excluding IAEA 602. Although the precision on IAEA 602 is very high, which is believed to be the result of sample contamination affecting reproducibility, the accuracy is excellent.

In addition, there is no memory effect on $\delta^{18}\text{O}$ values across a 75‰ range (Figure 4). BRE001 was used as the weight % reference material, with a known content of 16.50% oxygen. A 2-point VSMOW calibration was applied to the raw $\delta^{18}\text{O}$ using IAEA 601 and IAEA 602.

The data presented in Table 1 are application data and are not warranted because they exceed product specifications. The guaranteed product specification for $\delta^{18}\text{O}$ is $\pm 0.4\text{‰}$ (1 sd) for 50 μg of oxygen measured on benzoic acid.

Table 1. $\delta^{18}\text{O}$ values for 30 sequential caffeine and benzoic acid samples.

Sample	n	weight% O (measured)	Avg. $\mu\text{g O}$	$\delta^{18}\text{O}_{\text{VSMOW}} (\text{‰})$ (measured)
BRE001 (Caffeine)	3	16.50	34.82	24.21 \pm 0.21
USGS 61 (Caffeine)	5	16.25 \pm 0.51	34.47	16.05 \pm 0.07
USGS 62 (Caffeine)	5	16.11 \pm 0.15	33.12	-4.31 \pm 0.12
USGS 63 (Caffeine)	5	16.36 \pm 0.33	35.22	16.52 \pm 0.08
IAEA 600 (Caffeine)	3	16.48 \pm 0.17	22.14	-4.17 \pm 0.05
BRE001 (Caffeine)	3	16.50	34.82	24.04 \pm 0.08
IAEA 602 (Benzoic Acid)	3	23.55 \pm 0.09	30.14	71.40 \pm 1.93*
IAEA 601 (Benzoic Acid)	3	23.79 \pm 0.51	29.23	23.30 \pm 0.19*

*Certified reference value for IAEA 602 is 71.4 \pm 0.3‰ and IAEA 601 is 23.3 \pm 0.3‰

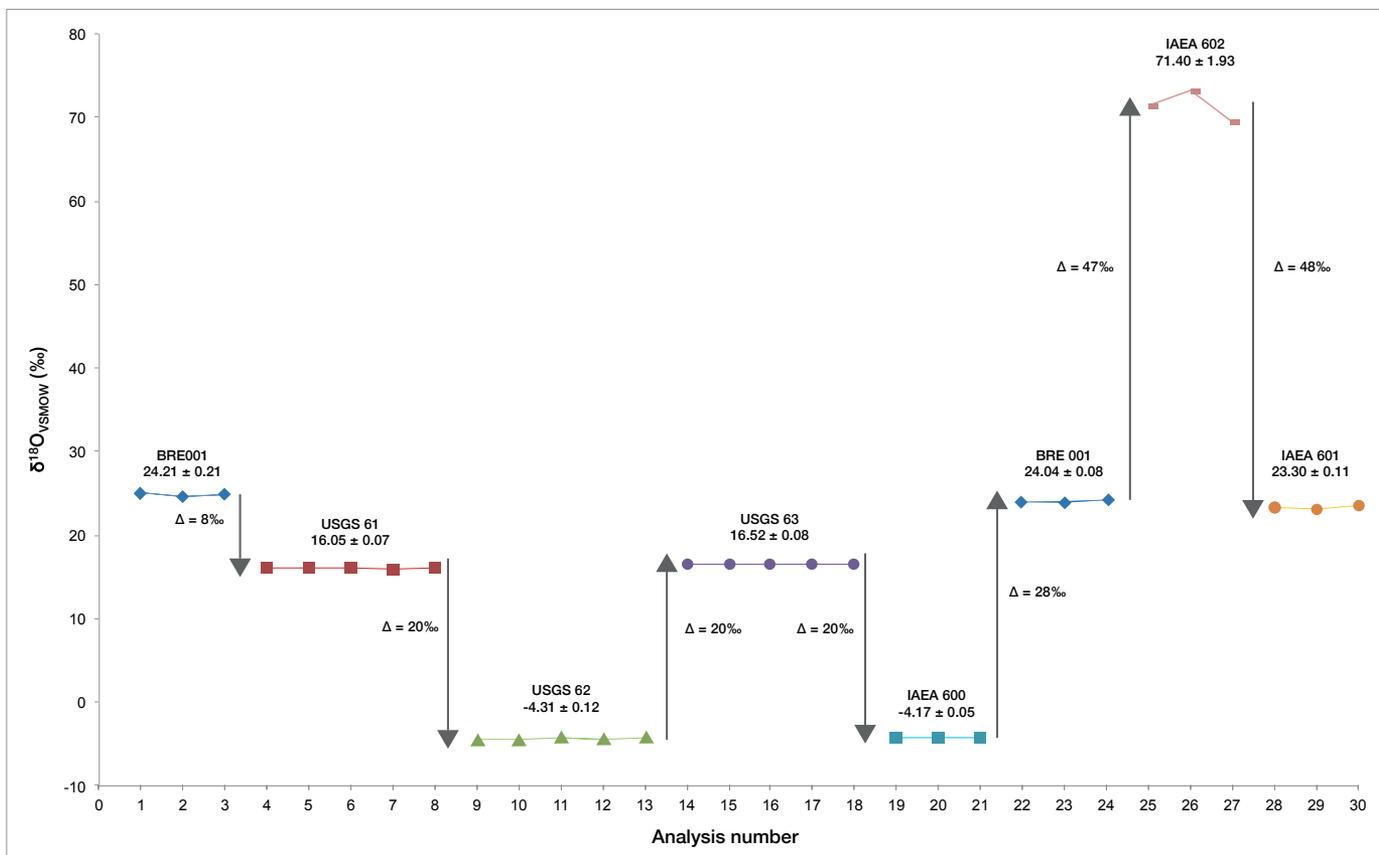


Figure 4. 30 sequential analyses showing no memory on $\delta^{18}\text{O}$ values.

Summary

The EA IsoLink IRMS System ensures accurate and precise weight% O and $\delta^{18}\text{O}$ values on nitrogen-rich materials using continuous flow gas chromatography. Total analysis time per sample was 7.5 minutes, including isotope reference gas peaks. The helium consumption is 1.12 liters per sample thanks to the Helium Management (He^M) Module, which reduces helium consumption without compromise. The analyses here demonstrate:

- Complete baseline separation of N_2 and CO peaks using a packed GC column, with no evidence of N_2 tailing into the CO peak.
- Accurate and precise wt% O and $\delta^{18}\text{O}$ values
- No memory effect across a 75‰ range
- Complete automation from sample introduction through to data evaluation using the Thermo Scientific™ Isodat™ Software Suite

References

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