

Finnigan GasBench II: ^{18}O -Equilibration on Water, Fruit Juice, and Wine

Andreas W. Hilkert, Hairigh Avak, Thermo Electron Corporation, Bremen, Germany

Key Words

- Finnigan™ GasBench II
- Continuous Flow
- Isotope Ratio MS
- ^{18}O Water Equilibration

Introduction

The measurement of the $^{18}\text{O}/^{16}\text{O}$ ratio of water is one of the most important applications of isotope ratio mass spectrometry. Very diverse applications, ranging from studies of variations in natural abundance in the hydrologic cycle to authenticity control on beverages to the use of ^{18}O enriched tracers in human and animal metabolic studies, demand a general purpose analytical solution which can provide high precision / high accuracy / high throughput analysis of $^{18}\text{O}/^{16}\text{O}$ in an enormous range of substrates.

Continuous flow techniques, in which the sample is entrained in a carrier gas, have been shown to allow high throughput analysis from elemental analyzers and gas chromatographs, but for high precision work, the dual inlet system has remained the instrument of choice.

The development of the technique of repetitive loop injection has allowed us to close the gap between the dual inlet system and continuous flow inlet systems. The Finnigan GasBench II is a continuous flow interface with autosampler-assisted loop injection in which the precision attainable with the dual inlet system is realized by modern continuous flow technology. In CO_2 -water equilibration, a small amount of CO_2 in the headspace of a sample vial is isotopically equilibrated with the water entrained in a liquid sample. The very small amount of CO_2 in the headspace ensures complete transfer of the ^{18}O information during equilibration ($\text{CO}_2/\text{H}_2\text{O} < 1:3000$). With the Finnigan GasBench II, water samples $< 500 \mu\text{l}$ can be routinely analyzed to a precision and accuracy of $< 0.06 \text{‰}$.

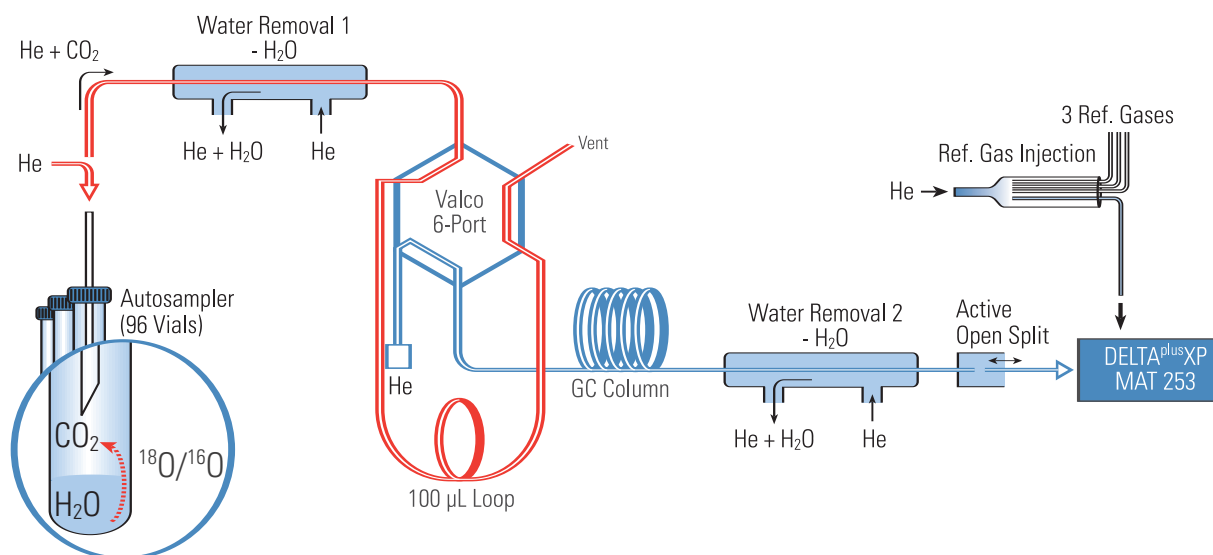


Figure 1: Schematic diagram of the Finnigan GasBench II

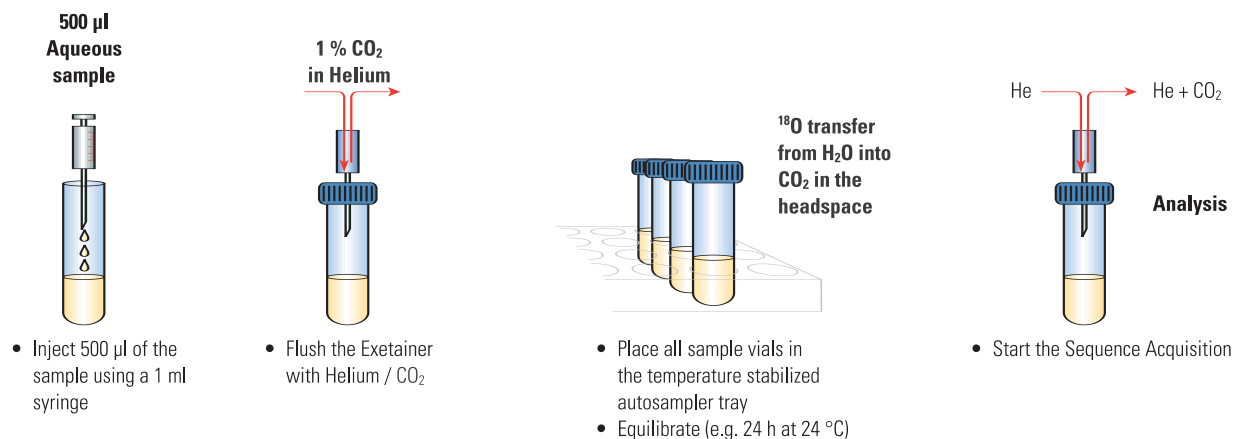


Figure 2: Sample preparation

Experimental conditions

Borosilicate sample bottles are washed with diluted acid, then washed twice with deionized water and dried overnight at 70 °C. After adding 500 µL of sample into the open vials using a disposable syringe they are sealed with new septa. Residual air in the vials is removed from the sample vials by an automated autosampler-assisted flushing procedure, which uses a mixture of 0.3 % to 0.5 % CO₂ in He. Flushing is carried out at a flow of 100 ml/min for 5 minutes. The 0.3 % to 0.5 % CO₂ in the flushing He stream is used as equilibration gas. Measurement is carried out after an equilibration time of 24 h at 24 °C. The temperature stability required for ¹⁸O equilibration is ± 0.1 °C (the temperature dependence is ~ 0.25 ‰ per 1 °C). By helium the sample is moved through the water trap, filling the sample loop and leaving to vent. Water vapor is quantitatively removed on-line from the gas stream. The sampling loop aliquots 100 µl samples of the headspace into an isothermal gas chromatograph, where CO₂ is separated from any other gas species. The use of repetitive loop injection (1-2 min per replicate) allows to approach a precision comparable to that of a dual inlet system. Some of the analysis presented have been prepared by an older, manual method injecting 500 µl of aqueous sample through the septum into 10 ml screwcap Exetainers, prefilled with a commercial mixture of 0.2 % up to 1 % CO₂ in helium (99.996 % purity).

Referencing to VSMOW

In order to perform VSMOW / VSLAP scaling, required for reporting the data relative to VSMOW, each set of samples includes two reference water samples of different composition. For the samples analyzed here, the scaling corrections are in the range of the analytical error (~ 0.02 ‰).

Sample size:	500 µl of water
CO ₂ /He:	1 %
Equilibration:	20 h at 24 °C
Sampling loop:	10 µl
Replicates (loop switches):	10
GC column:	PoraPLOT Q 25 m (24 °C)
SMOW/SLAP scaling factor:	0.9946

Water: Accuracy, memory, precision

Three natural water laboratory standards were analyzed on both the Finnigan GasBench II and on the Finnigan HDO II water equilibrator. The Finnigan HDO II and its predecessor, the HDO I, are dual inlet peripherals and are the accepted standard for automated high precision water equilibration in 100 laboratories worldwide. Comparison with the Finnigan HDO II results shows that the two data sets are in very close agreement, with an offset of 0.03 ‰, validating the accuracy of the Finnigan GasBench II (Table 1).

	GASBENCH II Δ ¹⁸ O _{VSMOW} (‰)	HDO II Δ ¹⁸ O _{VSMOW} (‰)	ΔΔ (‰)
PAK	- 37.34	- 37.37	0.03
ANST	- 28.32	- 28.35	0.03
Vostok	- 56.60	- 56.64	0.04

Table 1: Comparison of Finnigan GasBench II and Finnigan HDO II water equilibrator

The Vostok sample, which is significantly depleted in ¹⁸O relative to VSMOW, is used to demonstrate the complete absence of memory effects in the Finnigan GasBench II (Figure 3).

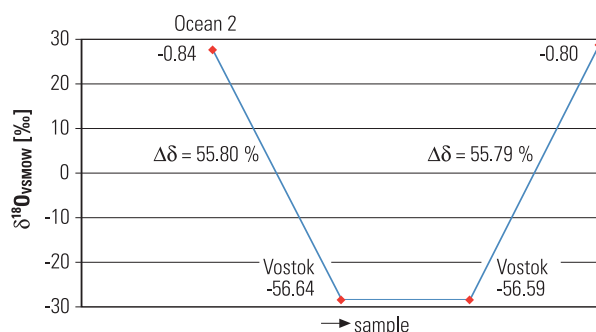


Figure 3: Absence of memory effects

The average external precision of replicate analyses on the Finnigan GasBench II was < 0.05 ‰.

Fruit Juices: Detection of adulteration

Sample size:	500 µl of fruit juice
CO ₂ /He:	0.2 %
Equilibration:	20 h at 28 °C
Sampling loop:	100 µl
Replicates (loop switches):	10
GC column:	PoraPLOT Q 25 m (24 °C)
SMOW/SLAP scaling factor:	1.0024

¹⁸O determination of water in fruit juice is widely used to establish whether a juice has been reconstituted from concentrate using local water. As part of a larger study defining baseline data, apple and orange juices of different origin were analyzed. For purposes of comparison, samples of mineral water and local drinking water were analyzed (Figure 4). Adulteration of orange juice is clearly demonstrated. The average external precision achieved on replicate analyses was < 0.06 ‰.

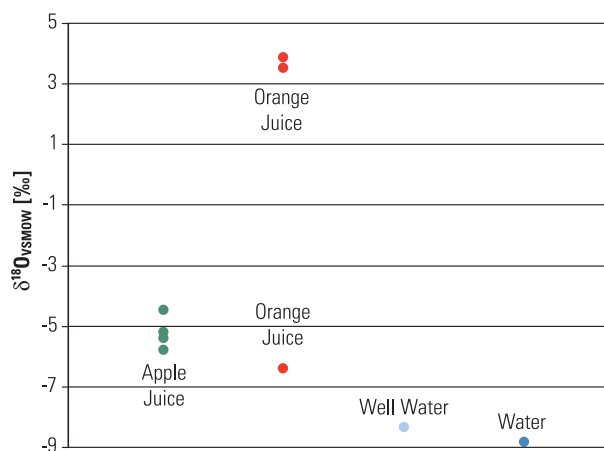


Figure 4: Fruit juices

Wine: Authenticity control

Sample size:	500 µl of wine
CO ₂ /He:	1 %
Equilibration:	20 h at 24 °C
Sampling loop:	10 µl
Replicates (loop switches):	10
GC column:	PoraPLOT Q 25 m (24 °C)
SMOW/SLAP scaling factor:	0.9980

¹⁸O isotopic analysis of wine has been a topic of increasing interest, and is now the subject of EU regulation. In order to validate the Finnigan GasBench II for this application, samples of wine were run on both the Finnigan GasBench II and the Finnigan HDO II water equilibrators. The wine samples were analyzed directly, without distillation. Comparison with the results from Finnigan HDO II (Table 2) shows that the two data sets are in very close agreement within < 0.03 ‰.

	GASBENCH II Δ ¹⁸ O _{VSMOW} (‰)	HDO II Δ ¹⁸ O _{VSMOW} (‰)	ΔΔ (‰)
Wine A	0.18 ‰	0.16 ‰	0.02
Wine B	- 1.34 ‰	- 1.37 ‰	0.03
Wine C	1.53 ‰	1.54 ‰	- 0.01

Table 2: Analysis of wine with the Finnigan GasBench II

The natural CO₂ in wine was analyzed directly, which opens the possibility to eliminate the addition of CO₂ to the headspace for equilibration. To show the ease and precision of this method, the δ¹⁸O of Wine C was analyzed with and without addition of CO₂ (Table 3); no difference was seen between the two approaches, and the overall precision was 0.035 ‰.

	Δ ¹⁸ O _{VSMOW}	EQUILIBRATION	DATE
EQ1a	1.534 ‰	1 % CO ₂ / He	4 / 27
EQ1b	1.517 ‰	1 % CO ₂ / He	4 / 27
EQ2	1.494 ‰	CO ₂ from wine	4 / 27
EQ3	1.577 ‰	CO ₂ from wine	4 / 28
Mean:	1.531 ‰	± 0.035 ‰	

Table 3: Analysis of δ¹⁸O of wine with the Finnigan GasBench II without addition of CO₂

The high sensitivity of the Finnigan GasBench II coupled with any DELTA^{plus} Isotope Ratio MS opens the possibility of using the CO₂ already present in the beverage as the equilibration gas, which could lead to a significant simplification of sample preparation procedures.

Conclusions

The Finnigan GasBench II can be used for highly precise measurements of the oxygen isotopic composition of waters. Analysis of the same samples on the Finnigan HDO II water equilibrators (a dual inlet system peripheral) shows very close agreement, with a Δδ (Finnigan GasBench II - Finnigan HDO II) < 0.03 ‰, serving to validate the technique and the device. Successful analysis of natural waters, fruit juices, and wines shows that the Finnigan GasBench II can be used for isotope studies on a wide range of water-bearing substrates. Measuring a suite of natural waters which included a very depleted antarctic water establishes that the Finnigan GasBench II has no memory, and that there is no cross talk between samples as is often the case for water preparation devices. It is also shown that for samples with natural CO₂ concentration, it is possible to measure the water oxygen composition without any addition of CO₂ for equilibration.

Literature

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- ² Stephen T. Nelson, Rapid Commun. Mass Spectrom. 14, 293-297 (2000)

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