

Isotope Analysis of Water, Fruit Juice and Wine Using the Thermo Scientific GasBench II IRMS

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Key Words

GasBench II, Continuous Flow, Isotope Ratio MS, ^{18}O Water Equilibration

Goal

Demonstrate the capabilities of the Gas Bench II IRMS for isotope studies on a wide range of water-bearing substrates.

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 Thermo Scientific™ GasBench II Isotope Ratio Mass Spectrometer (IRMS) 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 GasBench II IRMS, water samples $< 200 \mu\text{L}$ to $500 \mu\text{L}$ can be routinely analyzed to a precision and accuracy of $< 0.06 \%$. For special applications the sample volume can be reduced as much as down to $50 \mu\text{L}$ or even lower.

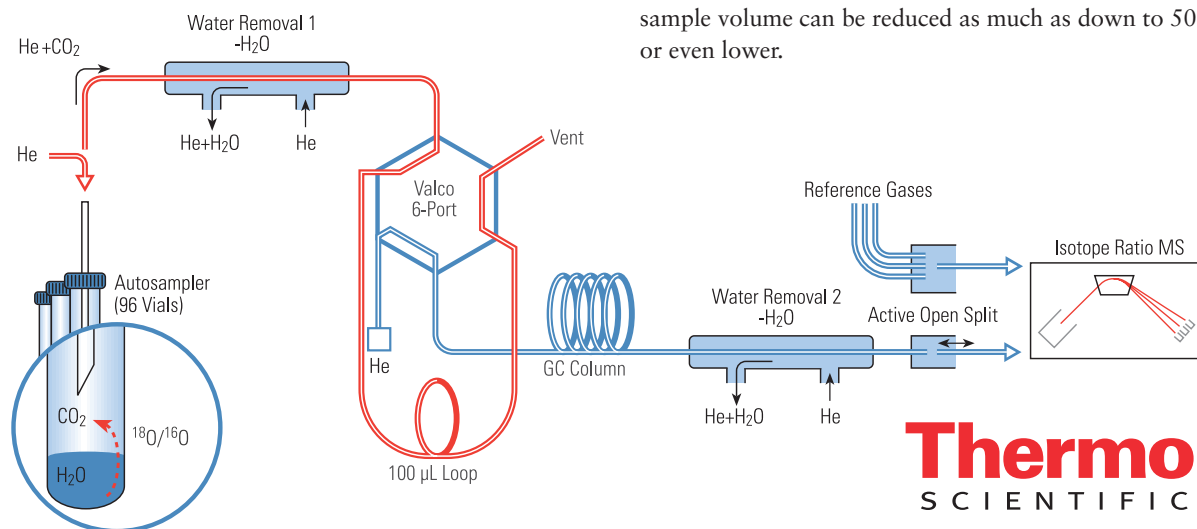


Figure 1. Schematic diagram of the Thermo Scientific GasBench II IRMS.

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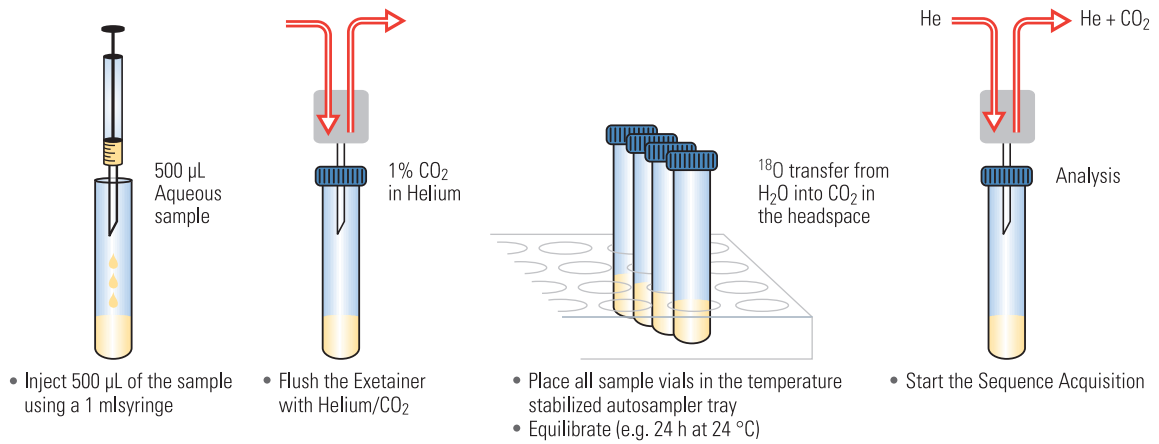


Figure 2. Sample preparation.

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 GasBench II IRMS and on the HDO II water equilibrator. The Thermo Scientific 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 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 GasBench II IRMS (Table 1).

Table 1. Comparison of GasBench II IRMS and HDO II water equilibrator.

	GASBENCH II $\Delta^{18}\text{O}_{\text{VSMOW}} (\text{‰})$	HDO II $\Delta^{18}\text{O}_{\text{VSMOW}} (\text{‰})$	$\Delta\Delta (\text{‰})$
PAK	-37.34	-37.37	0.03
ANST	-28.32	-28.35	0.03
Vostok	-56.60	-56.64	0.04

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

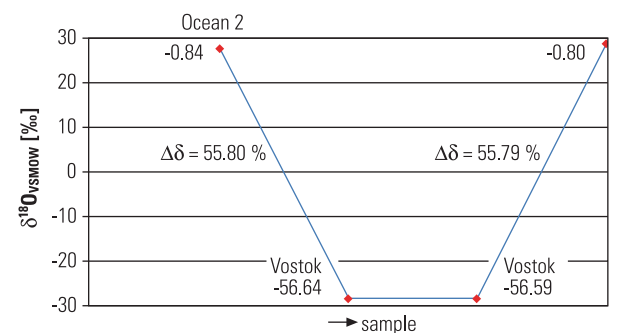


Figure 3. Absence of memory effects.

The average external precision of replicate analyses on the GasBench II IRMS 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 $^\circ\text{C}$
Sampling Loop:	10 μL
Replicates (Loop Switches):	10
GC Column:	PoraPLOT Q 25 m (24 $^\circ\text{C}$)
SMOW/SLAP Scaling Factor:	1.0024

^{18}O 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 $< 0.06 \text{ ‰}$.

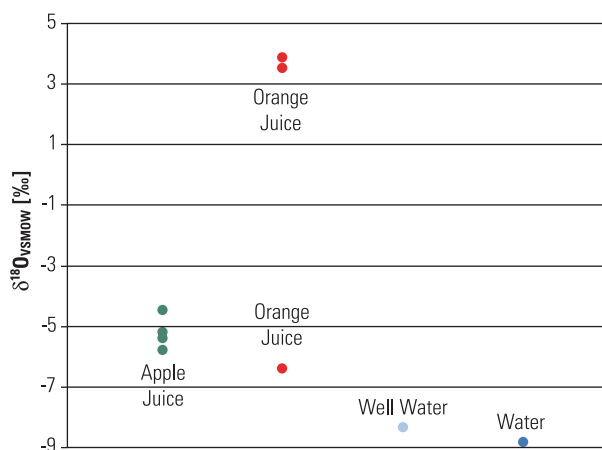


Figure 4. Fruit juices.

Wine: Authenticity Control

Sample Size:	500 μL of fruit juice
CO_2/He :	1%
Equilibration:	20 h at 24 $^\circ\text{C}$
Sampling Loop:	10 μL
Replicates (Loop Switches):	10
GC Column:	PoraPLOT Q 25 m (24 $^\circ\text{C}$)
SMOW/SLAP Scaling Factor:	0.9980

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

Table 2. Analysis of wine with the GasBench II IRMS.

	GASBENCH II $\Delta^{18}\text{O}_{\text{VSMOW}} \text{ (‰)}$	HDO II $\Delta^{18}\text{O}_{\text{VSMOW}} \text{ (‰)}$	$\Delta\Delta \text{ (‰)}$
Wine A	0.18 ‰	0.16 ‰	0.02
Wine B	-1.34 ‰	-1.37 ‰	0.03
Wine C	1.53 ‰	1.54 ‰	-0.01

The natural CO_2 in wine was analyzed directly, which opens the possibility to eliminate the addition of CO_2 to the headspace for equilibration. To show the ease and precision of this method, the $\delta^{18}\text{O}$ of Wine C was analyzed with and without addition of CO_2 (Table 3); no difference was seen between the two approaches, and the overall precision was 0.035 ‰ .

Table 3. Analysis of $\delta^{18}\text{O}$ of wine with the GasBench II IRMS without addition of CO_2 .

	$\Delta^{18}\text{O}_{\text{VSMOW}}$	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 ‰	$\pm 0.035 \text{ ‰}$	

The high sensitivity of the GasBench II IRMS coupled with a Thermo Scientific™ DELTA V Advantage IRMS, DELTA V Plus IRMS opens the possibility of using the CO_2 already present in the beverage as the equilibration gas, which could lead to a significant simplification of sample preparation procedures.

Conclusion

The GasBench II IRMS can be used for highly precise measurements of the oxygen isotopic composition of waters. Analysis of the same samples on the HDO II water equilibribrator (a dual inlet system peripheral) shows very close agreement, with a $\Delta\delta$ (GasBench II IRMS – HDO II) < 0.03 ‰, served here to validate the technique and the device. Successful analysis of natural waters, fruit juices, and wines shows that the GasBench II IRMS 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 GasBench II IRMS has no memory, and that there is no cross talk between samples as is so 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.

References

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