

Automated H₂/H₂O Equilibration for δD Determination on Aqueous Samples Using Thermo Scientific GasBench II

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Introduction

The measurement of the D/H ratio of water is one of the most important applications of isotope ratio mass spectrometers. Very diverse applications, ranging from studies of variations in natural abundance in the hydrologic cycle to authenticity control of beverages or the use of D-enriched tracers in human and animal metabolic studies, demand a general analytical solution, which provides high precision/ high accuracy/high throughput analysis of D/H in an enormous range of aqueous substrates.

Continuous flow techniques, in which the sample is entrained in a carrier gas, have been shown to allow high throughput from elemental analyzers and gas chromatographs, but for high precision isotope analysis, the dual inlet system has remained the instrument of choice. The development of the technique of repetitive loop injection has enabled us to close the gap between the dual inlet system and continuous flow inlet systems.

The Thermo Scientific 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 H₂/H₂O water equilibration, a small amount of H₂ in the headspace of a sample vial is isotopically equilibrated with the H of H₂O in a liquid sample (H₂/H₂O < 1:1000) on a platinum catalyst. With the GasBench II, water samples > 200 μL can be routinely analyzed with a precision and accuracy < 1 ‰.

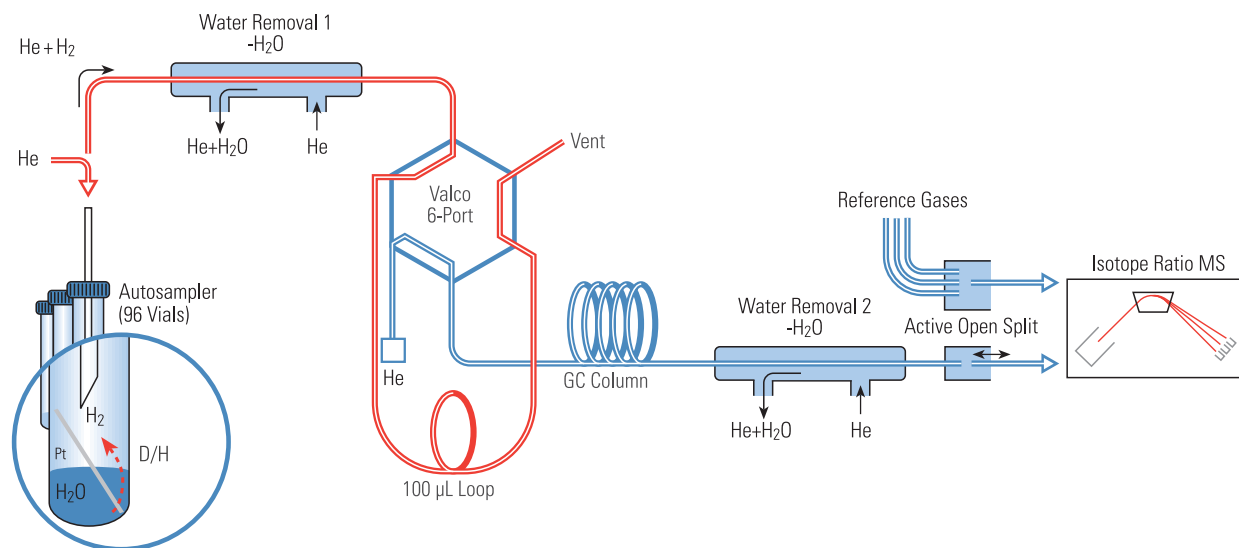


Figure 1: Schematic diagram of the Thermo Scientific GasBench II.

Key Words

- GasBench II
- Continuous Flow
- H₂/H₂O Water Equilibration
- Isotope Ratio MS

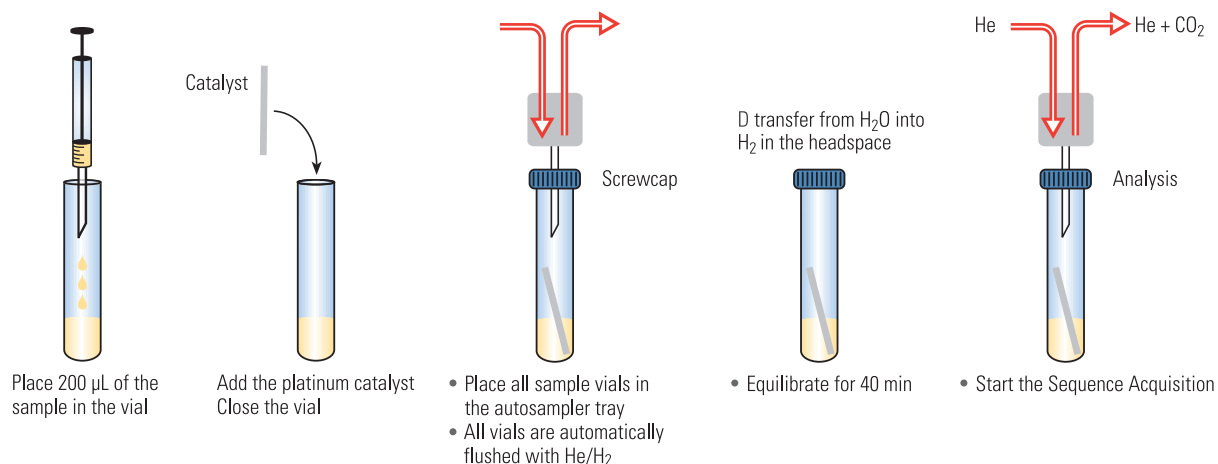


Figure 2: Automated sample preparation and analysis.

Experimental Conditions

Borosilicate sample bottles are washed with diluted acid, then washed twice with deionized water and dried overnight at 70 °C. After adding 200 µL of sample using a disposable syringe and inserting the platinum catalyst (Part # 1091831) into the open vials, 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 2% H₂ in He. Flushing is carried out at a flow of 100 ml/min for 5 minutes. The 2% H₂ in the flushing He stream are used as equilibration gas. Measurement is carried out after an equilibration time of 40 minutes using the settings outlined in Table 1.

Tray temperature	28 °C
Equilibration time	40 min
Loop volume	100 µL
GC temperature	60 °C
GC column flow	1.5 ml/min
Sampling needle flow	0.8 ml/min
Software	Isodat 2.0
Peak detection	Low pass filtered background
	Start Slope 20 mV/s
	End Slope 30 mV/s
Measurement timing	5 reference peaks
	10 sample peaks
Time per sample	630 s
Samples per day	80

Table 1: Experimental details.

To perform oxygen equilibration on the same samples, the caps and septa are replaced with fresh ones and the samples are flushed with 0.5% CO₂ in He.

Data Handling

All δ values and sample related data are extracted to an Microsoft® Excel file using the Isodat Software Suite Excel export utility. Further calculations are carried out using a predefined Excel worksheet. Final data are related to VSMOW for offset and to SLAP for slope corrections^[1].

Precision and Reproducibility

The precision and accuracy of D/H water equilibration with the GasBench II is demonstrated by a series of internationally certified water standards and secondary standards. The course of the analyses covers the natural abundance range from 0 ‰ to - 440 ‰. The samples are analyzed with replicates to evaluate memory effects. Figure 3 shows the final results of the first four sample sets with isotope differences of more than 400 ‰. The data prove the absence of any memory effect for water samples in the natural range.

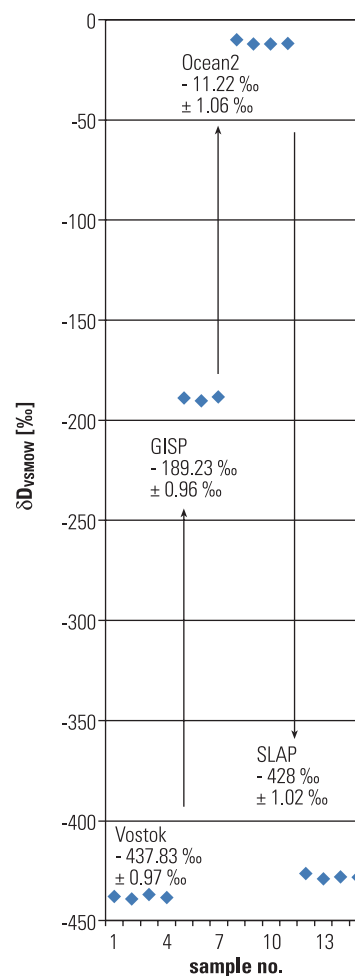


Figure 3: Memory test.

Table 2 lists the results for the series of consecutive samples. They show that every sample analysis is within a precision range of ± 1 ‰ (1σ) or better. This relates to a precision of the raw delta values of ± 0.25 ‰ (1σ) or better. The accuracy for D/H equilibration using the GasBench principle is in accordance with the achieved precision.

	IAEA ACCEPTED VALUE [‰]	GASBENCH II RESULTS	
		MEAN [‰]	S.D. [‰]
Vostok Snow		- 437.9	0.97
IAEA GISP	- 189.73	- 189.2	0.97
OCEAN 2		- 11.2	1.06
IAEA SLAP	- 428	given	1.02
ANST 4		- 224.3	0.62
HBW-2 Tap		- 58.6	0.93
IAEA VSMOW	0	given	0.82
HL-1		- 363.3	0.96
PAN 5		- 293.3	0.49
GISP 379		- 192.3	0.89

Table 2: Comparison of δD results versus VSMOW for recognized standards. The IAEA-accepted values are listed in the second column1.

Application of the Method to D-Enriched Samples

One application of the H_2 -equilibration technique is biochemical tracer studies, in which highly enriched samples (up to a $\Delta\delta$ of 2000 ‰) are measured. When handling enriched samples, it is crucially important to avoid or eliminate any memory effects that would affect the results of other samples with natural abundance levels. We measured a series of D-enriched urine samples from a tracer study^[2] together with the VSMOW and GISP standards. The samples were arranged in the autosampler tray in such a way as to maximize the isotopic differences between samples, followed by repetition of the same sample to measure the memory effect. Table 3 shows the results listed in the order of measurement.

Sample	Mean [‰]	S.D. [‰]
135 KM PD2	1393.9	1.7
GISP	- 192.1	1.2
TAP + Albumin 50 g/L	- 41.8	1.4
SLAP	- 429.4	1.0
135-KM Day 8	644.7	2.1
135-KM PD1	1588.9	1.4
Tap + Glucose 1 g/L	- 39.6	2.1
143 ZP PD2	1061.6	1.5
VSMOW	- 0.2	0.6
143 ZP PD1	1410.6	1.6
DLW diluted	1429.1	0.9
SLAP	- 426.6	2.1

Table 3: δD results versus VSMOW obtained from a series of D-enriched urine samples.

Each result is the average of three or four individual measurements. The memory effect was calculated as the difference of the first sample measurement and the mean of the subsequent measurements. The weighted (harmonic) mean of the memory effect is 1 ‰ per 1000 ‰ of the isotopic difference.

Conclusions

The GasBench II is a continuous flow interface for the Thermo Scientific isotope ratio mass spectrometers DELTA V Advantage, DELTA V Plus, and MAT 253 as well as for MAT 252 and all DELTA series mass spectrometers equipped for continuous flow technology. Coupled to a DELTA V, DELTA^{plus} XP, DELTA^{plus} XL or MAT 253, the GasBench II can be used for precise δ_2H measurements of water samples (± 1 ‰). Comparison of the measured values with internationally accepted values shows excellent agreement. Investigation of the applicability of this method for tracer studies reveals that the memory effect is quite small: in the range of 1 ‰ for an isotopic difference of 1000 ‰. Using the GasBench II, Δ of H_2O can be measured of up to 80 samples per day continuously.

Acknowledgements and References

- ^[1] Reference and Intercomparison Materials for Stable Isotopes of Light Elements, IAEA, Vienna, 1995, IAEA-TECDOC-825, ISSN 1011-4289
- ^[2] Samples courtesy of Prof. D. Schoeller, University of Wisconsin Medical School

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