

Finnigan™ GasBench II



Universal On-line Gas Preparation
and Introduction System for
Isotope Ratio MS

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The Finnigan GasBench II is an innovative solution for high precision on-line isotope and molecular ratio determination of headspace samples, including water equilibration, carbonates, and atmospheric gases (e.g. CO₂, O₂/N₂). The precision and accuracy of the dual viscous flow inlet system are achieved using modern “continuous flow” techniques.

The Finnigan GasBench II is not only an alternative to dual inlet system techniques but it significantly extends the practice of isotope ratio mass spectrometry (IRMS).

- Multiple loop injection leads to high precision
- Automation leads to high sample throughput
- High sensitivity results in low sample consumption
- GC separation delivers pure analyte from gas mixtures
- Automatic range recognition and autodilution leads to the largest dynamic range of sample size
- Extreme flexibility leads to very high versatility



Finnigan™ GasBench II
On-line gas preparation
Multiple loop injection

The range of applications includes, but is not limited to:

- D/H in water through equilibration with H₂/Pt
- ¹⁸O/¹⁶O in water through equilibration with CO₂
- ¹⁸O/¹⁶O and ¹³C/¹²C from carbonates
- ¹³C/¹²C of dissolved inorganic carbon (DIC)
- ¹³C/¹²C and ¹⁸O/¹⁶O of CO₂ in air
- ¹⁸O/¹⁶O and ¹⁷O/¹⁶O of O₂ in air and water
- ¹⁵N/¹⁴N of N₂ in air

In combination with the PostCon cryotrapping options or the PreCon:

- ¹³C/¹²C of CO₂ in air (sub-ambient concentrations)
- ¹⁵N/¹⁴N and ¹⁸O/¹⁶O of N₂O in air (300 ppb)
- ¹³C/¹²C of CH₄ in air (1.7 ppm)
- ¹⁵N/¹⁴N and ¹⁸O/¹⁶O of N₂O
- ¹⁵N/¹⁴N and ¹⁸O/¹⁶O of nitrate using the Sigman technique
- ¹⁵N/¹⁴N of N₂ from micro-preparation systems

Flexible design allows use with lasers and Elemental Analyzers

- Sampling of CO₂ and SO₂ from laser combustions and decarbonation
- Post-combustion concentration of CO₂, N₂, SO₂ from elemental analyzers

Due to the versatility of the Finnigan GasBench II the list of gas species, isotope ratios, and experiments that can be performed with the Finnigan GasBench II is constantly being extended.

Wide range
of applications



Technical Details

Universal On-line Gas Preparation and Introduction System for Isotope Ratio MS

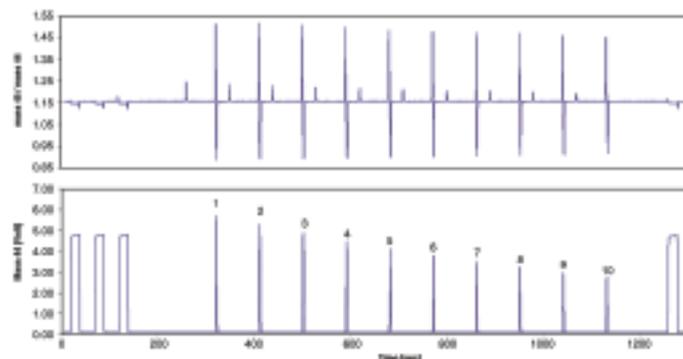
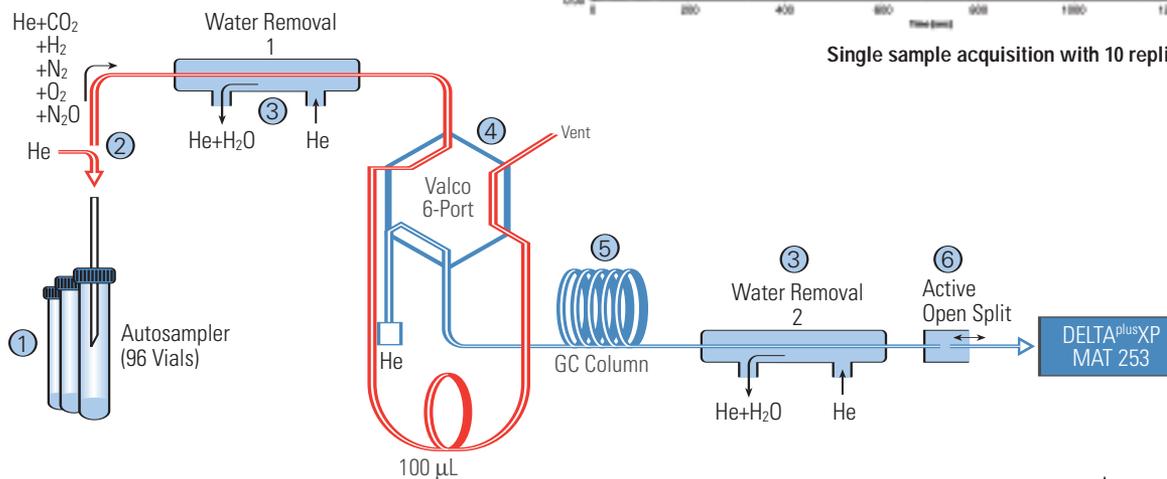
The Finnigan GasBench II consists of a user-programmable autosampler (1), a gas sampling system (2), a maintenance-free water removal system (3), a loop injection system (4), an isothermal gas chromatograph (GC) (5), an active open split interface (6), a reference gas injection system with three reference ports (7), and one or two optional LN2 traps for cryofocusing.

The autosampler can be equipped with a variety of sample trays. A precisely thermostated sample tray is used for carbonates and water equilibration.

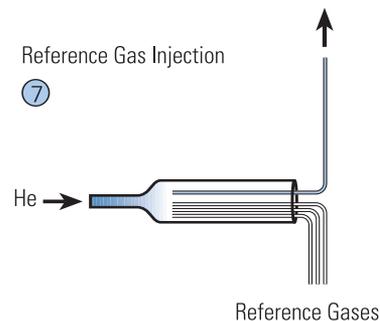
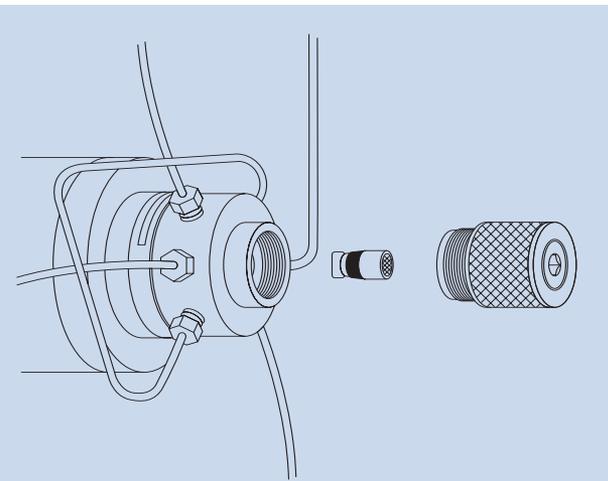
The gas sampling system includes a two port needle which adds a gentle flow of He into the sample vial, thus diluting and displacing sample gas. Water is removed from the sample gas through diffusion traps. The loop injector aliquots the sample gas onto the GC column, which separates the molecular species. The reference gas injection system allows accurate referencing of each sample aliquot to isotopic standards. The system is designed for unattended measurements with high throughput, ensuring high productivity and high reliability.

The Finnigan GasBench II can be used for the isotopic characterization of CO₂, N₂O, O₂ or N₂ between 200 nmol and 20 μmol of total sample size. The CO₂ can be in the original gas sample (air or breath), be released through a preparation step (carbonates, DIC) or be added to the original liquid sample (water-CO₂ equilibration).

GasBench Scheme



Single sample acquisition with 10 replicates



The GasBench Principle

The Finnigan GasBench II allows the precision and accuracy of the dual inlet system to be realized on a CF-IRMS system. The dual inlet principle of repetitive measurements of sample and standard gas is not only retained, it is generalized. The sample volume is the sample vial (instead of a metal bellows), and the reference gas volume is a pressurized gas tank. Reference gas pulses are introduced under computer

control into the carrier gas stream from the reference injection system.

The sample gas is entrained in He, which allows GC separation and facilitates fractionation-free viscous flow transport of the sample aliquots. In a typical experiment, ten aliquots of the sample will be taken from the sample vial, dried and cleaned on-line, and measured against reference gas pulses. The sample consumption is much

lower than for the dual inlet system, while comparable precisions are achieved, including an analysis of internal reproducibility.

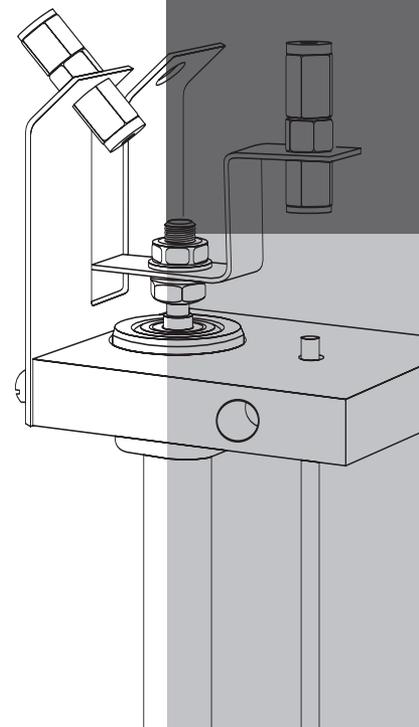


The combination of “Repetitive Loop Injection” and Reference Gas Injection is a generalization of the analytical procedure of sample-standard comparisons performed with a dual viscous flow inlet system.

Comparison to the “classical” Dual Inlet System

During a dual inlet measurement, sample and reference gases confined in variable volumes close to the ion source are sampled alternately and repeatedly through a changeover valve. This measurement strategy leads to high analytical precision and accuracy. Internal reproducibility of the

individual measurements is a commonly used measure of analytical quality which, up to now, has been missing from CF-IRMS inlet systems. The drawbacks of the dual inlet system include off-line sample preparation and purification, ineffective use of the sample gas, lengthy data acquisitions, and cost.

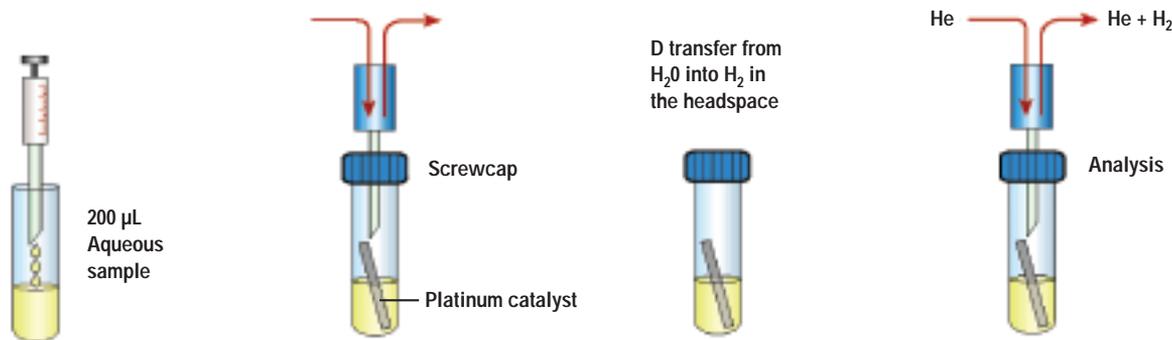


H₂/H₂O and CO₂/H₂O equilibration for δD and δ¹⁸O determination of water

The measurement of the D/H and ¹⁸O/¹⁶O ratios of water is one of the most important applications of isotope ratio mass spectrometry. There is a very diverse range of applications ranging from studies of variations in natural isotope abundance in the hydrologic cycle, to authenticity control on beverages, to metabolic studies using D- or ¹⁸O-enriched tracers in humans and animals. This extreme range of sample types demands a flexible general purpose analytical solution, which can provide high precision / high accuracy / high throughput analysis of ¹⁸O/¹⁶O and D/H.

The aqueous samples are placed in 10 ml screw top vials using disposable pipettes. For D/H, a platinum catalyst is added. The vials are sealed with septa and all air is removed from the sample vials by an automated, autosampler-assisted flushing procedure which uses a mixture of either H₂ or CO₂ in He. The H₂ or CO₂ in the flushing He stream is used as equilibration gas. After the required equilibration time (D: 40 min, ¹⁸O: 20 h) the whole batch of samples is analyzed. The use of repetitive loop injection (1-2 min per replicate) achieves analytical precisions comparable to those from a dual inlet system.

Alternatively, the Finnigan TC/EA, the quantitative high temperature carbon reduction Elemental Analyzer, can be integrated with the GasBench II for high precision analysis of D/H and ¹⁸O from a single sub-μL injection of water.



- Place 200 μL of the sample in the vial

- Place all sample vials in the autosampler tray
- All vials are automatically flushed

- Equilibrate for 40 min

- Start the Sequence Acquisition

Dissolved Inorganic Carbon

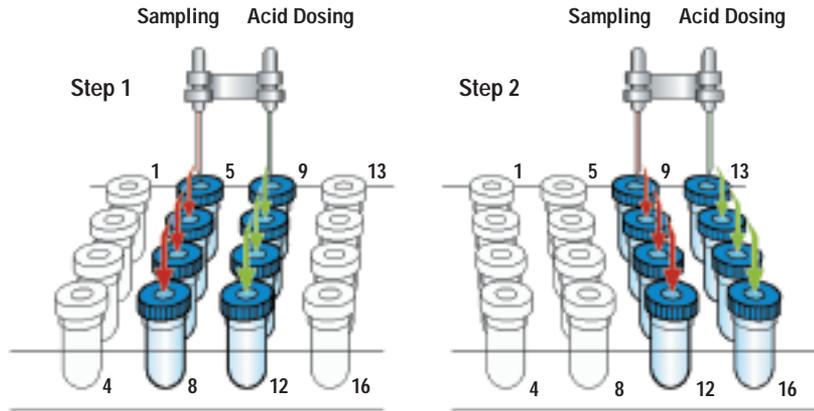
A request to replace the laborious manual preparation of ¹³C of DIC for dual inlet analysis with a fast, reliable and accurate continuous flow method is, in fact, what led to the development of the Finnigan GasBench II. The requirement of < 0.1 ‰ precision was readily exceeded, with precisions of 0.03 – 0.05 ‰ being shown by users. It is safe to say that the Finnigan GasBench II has revolutionized DIC analysis.

The risk of adsorption of CO₂ from air into the sea water during sample handling requires a different preparation of the sample vials. 3 drops of phosphoric acid (ca. 3 μL) are placed in the empty vials. After sealing the vials with septa, all vials are automatically flushed with pure helium. The sea water samples are injected using gastight, disposable syringes. After a short reaction time, the CO₂ in the headspace of each vial is automatically

analyzed using the same acquisition process as for all other Finnigan GasBench II applications.

$\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ determination of carbonates

For more than 50 years, $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ measurements of carbonates have been one of the major applications of stable isotopes. The analysis of foraminifera, in particular, is one of the most demanding applications, requiring both high precision and high throughput.



The Carbonate Reaction Kit

The Finnigan GasBench II in carbonate mode uses the principle of individual acid baths using a fully automated acid dosing system. The carbonate option contains a microliter pump that allows injection of anhydrous

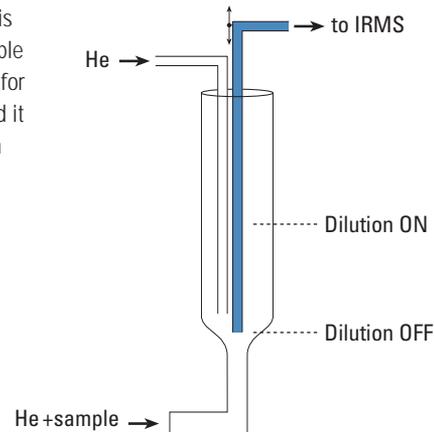
phosphoric acid (103 %) into the sample vials. The double needle setup ensures identical reaction and analysis conditions for each sample. Laboratories have shown that 80 samples per day (including 14 standards for quality control) can be

processed in routine operation. An overall precision of 0.08 ‰ for $\delta^{18}\text{O}$ and of 0.06 ‰ for $\delta^{13}\text{C}$ has been achieved.

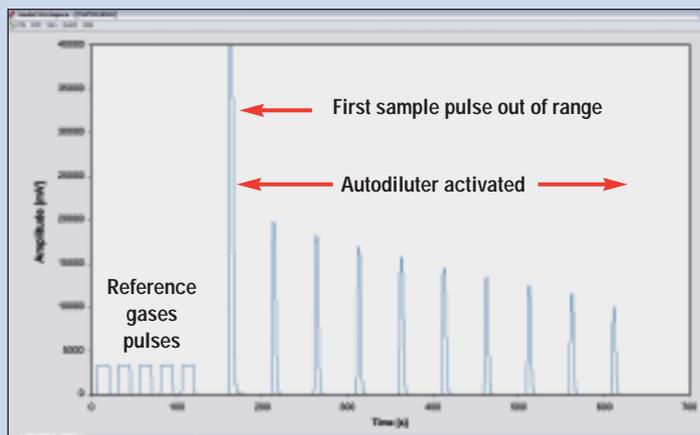
The Autodiluter

The Finnigan GasBench II offers a unique computer-controlled Autodiluter capability. If the signal height of the first sample peak exceeds a pre-defined threshold (e.g. 20 V), the diluter is activated resulting in a 3-fold reduction in signal height for the subsequent sample peaks. The dilution is performed in the open split, just before transfer into the ion source, eliminating any possible effects on the integrity of the sample gas. The Autodiluter capability allows analysis of samples that would

normally be too large to be measured. This capability offers clear advantages in sample preparation, because it reduces the need for time-consuming weighing of samples, and it allows analysis of samples with unknown amounts of carbonates (e.g. whole rock samples with carbonate cements).



Finnigan GasBench II data acquisition, 10 sample pulses, Autodiluter activated by first sample pulse

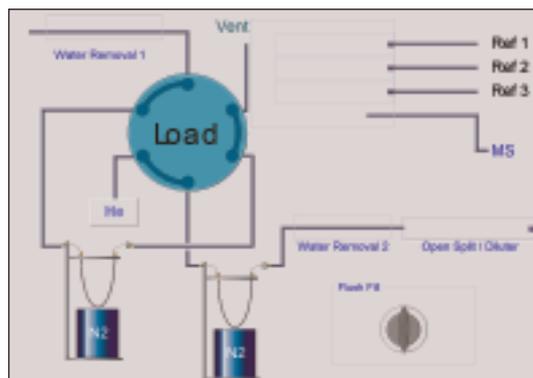


Finnigan GasBench II Combinations

GasBench II Options

- Carbonate Reaction Kit
The carbonate option contains a micro-liter pump that allows injection of anhydrous phosphoric acid (103 %) into the sample vials and a dual needle array for dosing and sampling
- 96 Sample tray (ambient temperature)
- 96 Sample tray (temperature controlled)
- Single cryotrap
Trapping option with a single fused silica trap for sub ambient gas concentration (e.g. 100 ppm CO₂)
- Dual cryotrap (PostCon)
Trapping option with two traps, one 1/16" nickel-wire filled stainless steel trap for trapping ppm amounts of analyte from a fast He gas stream, and one fused silica trap for cryo-focusing onto the GC column head

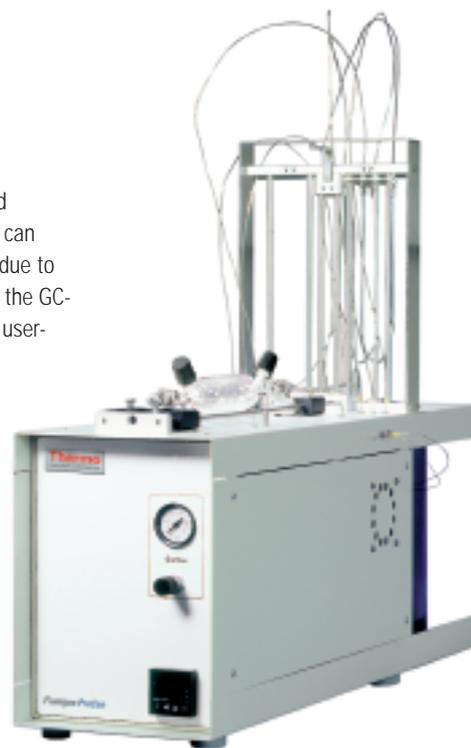
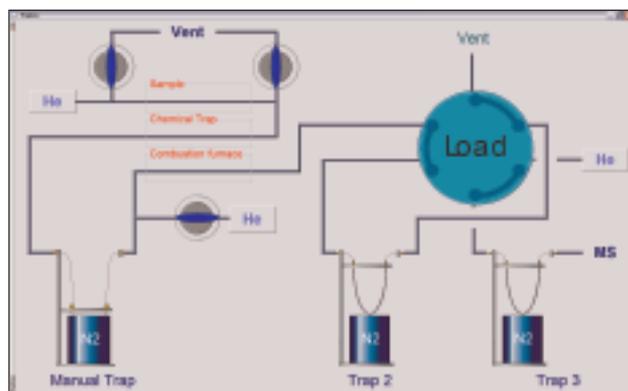
- Autosampler extensions
The Finnigan GasBench II autosampler can be extended to automate a second peripheral device, including the TC/EA, EA, H/Device, and PreCon.



PreCon Integration and Automation

For gas concentrations in the low ppm and ppb range, the Finnigan PreCon gives access to the fully automated preparation and pre-concentration of trace gases such as N₂O (300 ppb) and CH₄ (1.7 ppm) followed by cryogenic focusing in front of the GC column. The Finnigan PreCon can be loaded manually or operated fully automatically using the GC-PAL autosampler of the Finnigan GasBench II with the two line needle for continuous sample transfer.

The GC-PAL can be equipped with a 96 x 12 mL sample tray. User-defined sample trays and sample containers can easily be registered and automated due to the fully object oriented structure of the GC-PAL. All processes are controlled by user-definable Isodat 2.0 scripts.



Analytical Performance

Mass spectrometer:

Thermo Finnigan DELTA series or Finnigan MAT 253

Finnigan GasBench II Basic Performance

10 pulses of reference gas (amplitude 3V, H₂ 5V), δ notation

		Precision (1 σ)	Linearity
CO ₂	¹³ C	0.06 ‰	0.02 ‰/nA
CO ₂	¹⁸ O	0.08 ‰	0.02 ‰/nA
O ₂	¹⁸ O	0.08 ‰	0.02 ‰/nA
N ₂	¹⁵ N	0.06 ‰	0.02 ‰/nA
H ₂	² H	0.50 ‰	0.20 ‰/nA

An ion current range of 2 – 20 nA (0.6 – 6 V) is equivalent to 1.2 μ g – 12 μ g carbon equivalent in the headspace of a 12 mL vial

External precision of isotope ratios C, O, H, using the Finnigan GasBench II with 12 mL vials (n=5), δ notation

Water equilibration (versus V-SMOW & SLAP) ⁽¹⁾			
500 μ l	as CO ₂	δ^{18} O	< 0.08 ‰
200 μ l	as H ₂	δ^2 H	< 2.0 ‰
		δ^2 H	< 0.5 ‰ on raw data ⁽¹⁾
Carbonates			
100 μ g	as CO ₂	δ^{18} O	< 0.1 ‰
		δ^{13} C	< 0.1 ‰
Dissolved inorganic carbon, ocean water			
600 μ l	as CO ₂	δ^{13} C	< 0.08 ‰
CO ₂ in air			
12 ml	as CO ₂	δ^{13} C	< 0.2 ‰

⁽¹⁾ V-SMOW & SLAP scaling: Based on IAEA recommendations all ¹⁸O and D analysis need to be based on V-SMOW and SLAP.

For H₂/H₂O equilibration with platinum catalyst, this referencing results in a scale expansion of up to 4 times from the raw delta values to the final data, which equivalently decreases the precision of measurements.

On ¹⁸O determinations (CO₂/H₂O) this data processing also needs to be performed but the scaling factor usually is almost 1 and therefore has no effect on the performance data.

Acceptance Specification

During installation, the system performance of the Finnigan GasBench II will be demonstrated with a mixture of CO₂ in He ($\geq 0.3\%$), to show an external precision of 0.08 ‰ for δ^{13} C and δ^{18} O (n=5).

A mixture of H₂ in He mixture ($\geq 1.0\%$) is used to show an external precision (n=5) of 2.0 ‰ for δ^2 H.



Installation Requirements

Power

230 V single phase, 8 A

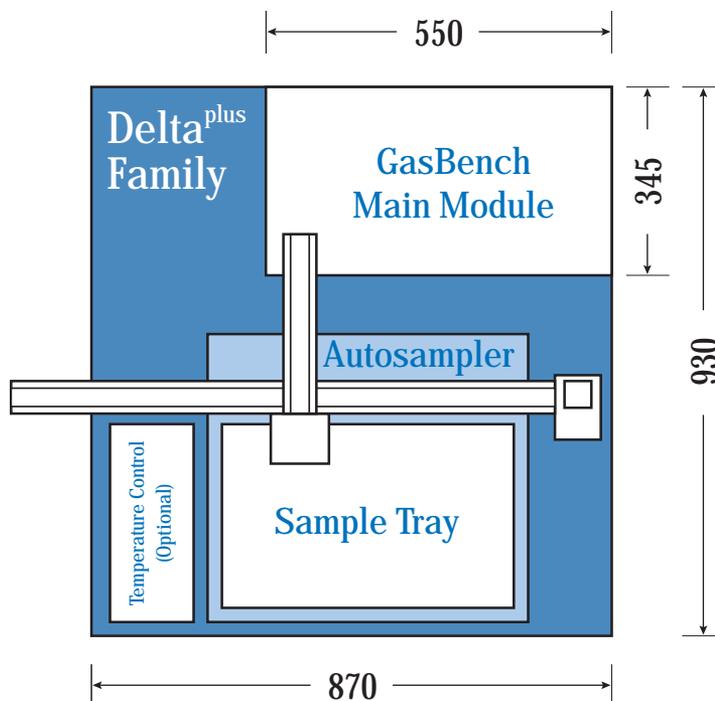
Gases

- He, better 99.999%
- CO₂, better 99.995%
- H₂, better 99.999%
- 0.3% - 1% CO₂, (99.995%) in He (99.999%) for ¹⁸O water equilibration
- 1.0% - 2.0% H₂ (99.999%) in He (99.999%) for ²H water equilibration

Optional items

- PoraPLOT Q capillary column for separation of N₂ and CO₂ (included in the standard Finnigan GasBench II system)
- Carbonate kit with dual needle support, acid pump and needle, phosphoric acid for carbonate analysis
- Temperature stabilized tray with 96 x 12 mL vials for carbonate and water analysis
- Hydrophobic Pt catalyst sticks for H₂/H₂O equilibration
- 5Å PLOT capillary column for good chromatographic resolution and thus high precision isotopic measurements of the molecular components of air (N₂, O₂, Ar, CH₄, CO)
- Single cryo trap for trapping of trace gases from low He flow systems
- PostCon dual cold trap for trapping of trace gases from high He flow systems with subsequent cryofocusing in the second trap

Top view with dimensions in mm



Literature

- A simple, practical methodology for routine VSMOW/SLAP normalization of water samples analyzed by continuous flow methods, S.T. Nelson, *Rapid Commun. Mass Spectrom.* 14, 1044–1046 (2000)
- Sample vial influences on the accuracy and precision of carbon and oxygen isotope ratio analysis in continuous flow mass spectrometric applications, S.T. Nelson, *Rapid Commun. Mass Spectrom.* 14, 293–297 (2000)
- Continuous-flow isotope ratio mass spectrometric analysis of carbonate minerals, Ch. Spötl and T.W. Vennemann, *Rapid Commun. Mass Spectrom.* 17, 1004–1006 (2003)
- A bacterial method for the measurement of the oxygen isotopic composition of nitrate in marine and fresh waters, K.L. Casciotti, D.M. Sigman, M.G. Hastings, J.K. Böhlke, and A. Hilkert, *Analytical Chemistry*, 74, 4905-4912 (2002)
- Using septum-capped vials with continuous-flow isotope ratio mass spectrometric analysis of atmospheric CO₂ for Keeling plot applications, K.P. Tu, P.D. Brooks and T.E. Dawson, *Rapid Commun. Mass Spectrom.* 15, 952-956 (2001)

Documentation of system performance is also available in the Finnigan GasBench II Application Reports.

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