

# $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ Determination of Carbonates Using Thermo Scientific GasBench II

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## Introduction

For more than 50 years,  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  measurements of carbonates have been used to determine paleo-environmental conditions. The principal application has been the analysis of  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  of foraminifera, for which the requirements are high precision and high throughput. In the past, this could only be achieved with a Kiel Carbonate device connected to the IRMS via the dual viscous flow inlet system. The Thermo Scientific GasBench II with the Carbonate-Option, an autosampler assisted sample preparation and loop injection interface, now offers a fast and flexible alternative using modern continuous flow technology coupling to the Thermo Scientific isotope ratio mass spectrometers DELTA V Advantage, DELTA V Plus and MAT 253 as well as MAT 252 and DELTA series mass spectrometers.

The GasBench II in carbonate mode uses the principle of individual acid baths. Phosphoric acid is added dropwise into individual sample vials by a fully automated acid dosing system. The evolved  $\text{CO}_2$  is slowly passed through a sampling loop in a trickling stream of helium. Repetitive loop injections onto an isothermal GC column create a series of pulses of pure  $\text{CO}_2$  in He, which enter the IRMS via an open split. 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.

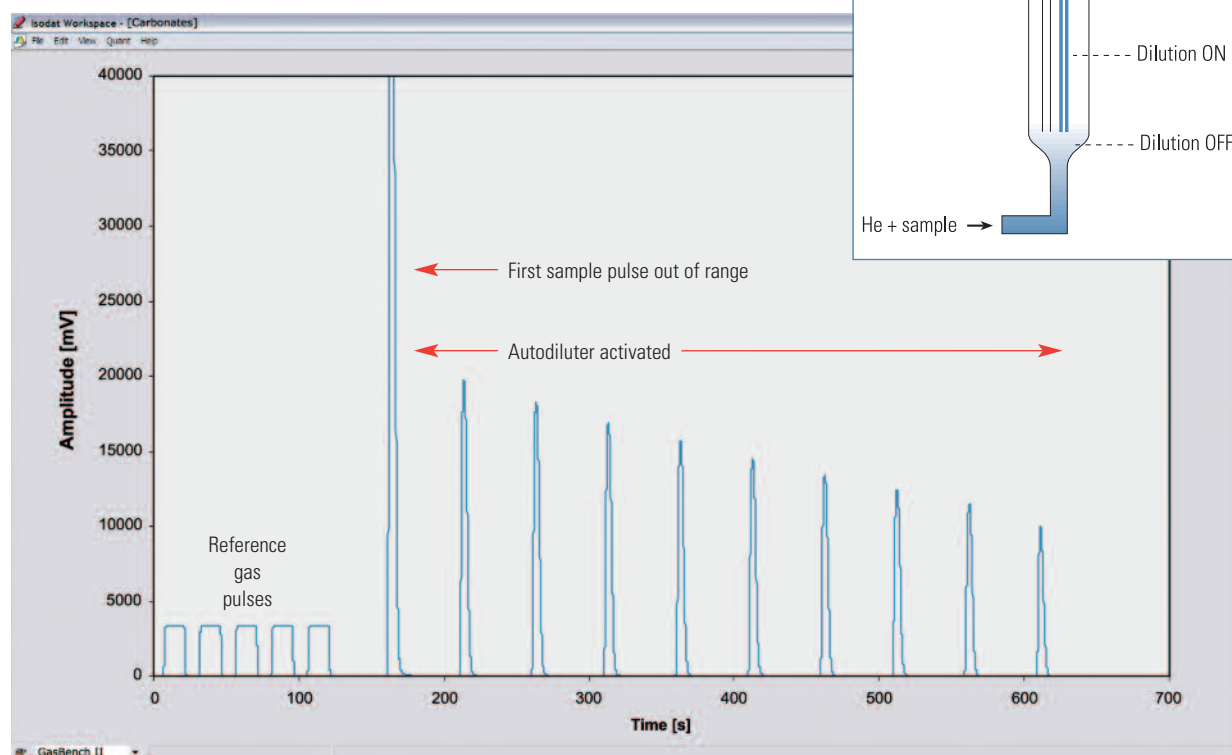


Figure 1: Thermo Scientific GasBench II data acquisition, 10 sample pulses, Autodiluter activated by first sample pulse.

## Key Words

- GasBench II
- Carbonates
- Continuous Flow
- Isotope Ratio MS

## The Carbonate Option

The carbonate option contains a microliter pump that allows injection of anhydrous phosphoric acid (103%) into the sample vial under computer control, a stainless steel acid capillary (acid needle), a double needle holder for the CTC GC PAL or CombiPAL auto sampler (Figure 2), reference material ( $\text{CaCO}_3$ , Merck KGaA) and pre-cleaned reusable borosilicate vials.

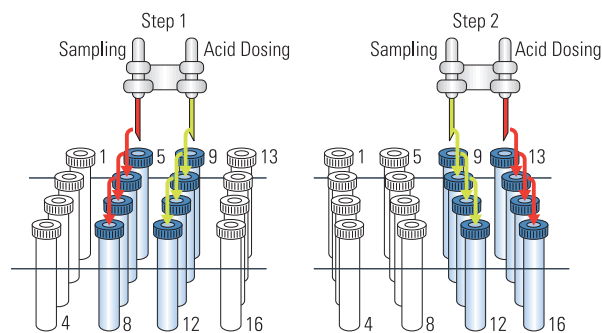


Figure 2: Simultaneous sampling and acid dosing. Step 1: Sample 5 is analyzed while sample 9 is prepared. Every 630 s another pair of samples is processed (6 to 8, 10 to 12). Step 2: After 4 x 630 s sample 9 is analyzed while sample 13 is prepared.

## Principle of Operation

The double needle setup allows fully automated acid dosing and sample analysis to be performed during one sequence. The sequence is designed to ensure identical reaction times (60 minutes) and analysis conditions for each sample (Figure 2). A trickling stream of He delivered through the double needle dilutes and displaces gas in the headspace of the vial onto a sample loop (100  $\mu\text{l}$ ) of a VALCO 8-port valve. The sample loop is repetitively emptied onto a GC column, where  $\text{CO}_2$  is chromatographically separated from other components of the gas sample, and this peak of  $\text{CO}_2$  is sent through the open split into the ion source. In a typical analysis, ten sequential aliquots of pure  $\text{CO}_2$  are delivered to the mass spectrometer. 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 (Figure 1).

## The Autodiluter

The GasBench II in carbonate mode offers a unique computer controlled Autodiluter capability. If the signal height of the first sample peak exceeds a predefined threshold (e.g. 30 V), the diluter is activated, resulting in a 3 fold reduction in signal height for the subsequent sample peaks (Figure 1). 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 because the  $\text{CO}_2$  signals would exceed the 50-V range of the electronics (10 V on old amplifiers).

The accessible range of sample sizes is enhanced by a factor of three, allowing analysis of samples larger than 700  $\mu\text{g}$  of carbonate in the same sequence with samples < 100  $\mu\text{g}$ . 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).

Tray temperature	72 °C
Acid dosing	3 drops $\text{H}_3\text{PO}_4$
Reaction & equilibration time per sample	60 min
Loop volume	100 $\mu\text{l}$
GC temperature	68 °C
GC column flow	1.5 ml/min
Sampling needle flow	0.8 ml/min
Software	Isodat Software Suite
Peak detection	Individual Background
	Start Slope 20 mV/s
	End Slope 30 mV/s
Measurement timing	5 reference peaks
	10 sample peaks
Time for one sample	630 s
Samples per day	80

Table 1: Experimental details.

## Experimental Conditions

Borosilicate sample bottles are washed in diluted acid, then twice in de-ionized water and overnight dried at 70 °C. After adding the samples to the vials open to air, they are sealed using unused septa. Residual air is removed from the sample vials by automated autosampler-assisted flushing with He, using a flow of 100 ml/min of He for 5 minutes. The phosphoric acid, which is maintained at the reaction temperature, is added dropwise under computer control to each individual reaction vessel. In these experiments, 3 drops of acid were added to each sample prior to measurement. A reaction time of 60 minutes was used. Both the amount of the acid and the reaction time are controlled by the software.

## Corrections Applied for Different Sample Sizes

Data was extracted to an Microsoft® Excel file by using the Isodat Software Suite Excel export utility and further calculation steps were carried out using a predefined Excel Worksheet. Figure 3 shows analyses of synthetic  $\text{CaCO}_3$  obtained during two measurement runs on two different days. Sample size ranged from 11  $\mu\text{g}$  to 420  $\mu\text{g}$ . The mean  $\delta$ -value is the same for all samples within statistical boundaries. The small linear dependence of  $\delta^{18}\text{O}$  on increasing peak intensities (within the linearity specifications of the DELTA<sup>plus</sup>) was corrected using a linearity factor (the slope of a line in m/z 44 intensity vs.  $\delta^{18}\text{O}$ ). The slope determined is small for  $\delta^{18}\text{O}$  (0.015 ‰/nA). For  $\delta^{13}\text{C}$  no slope correction was applied.

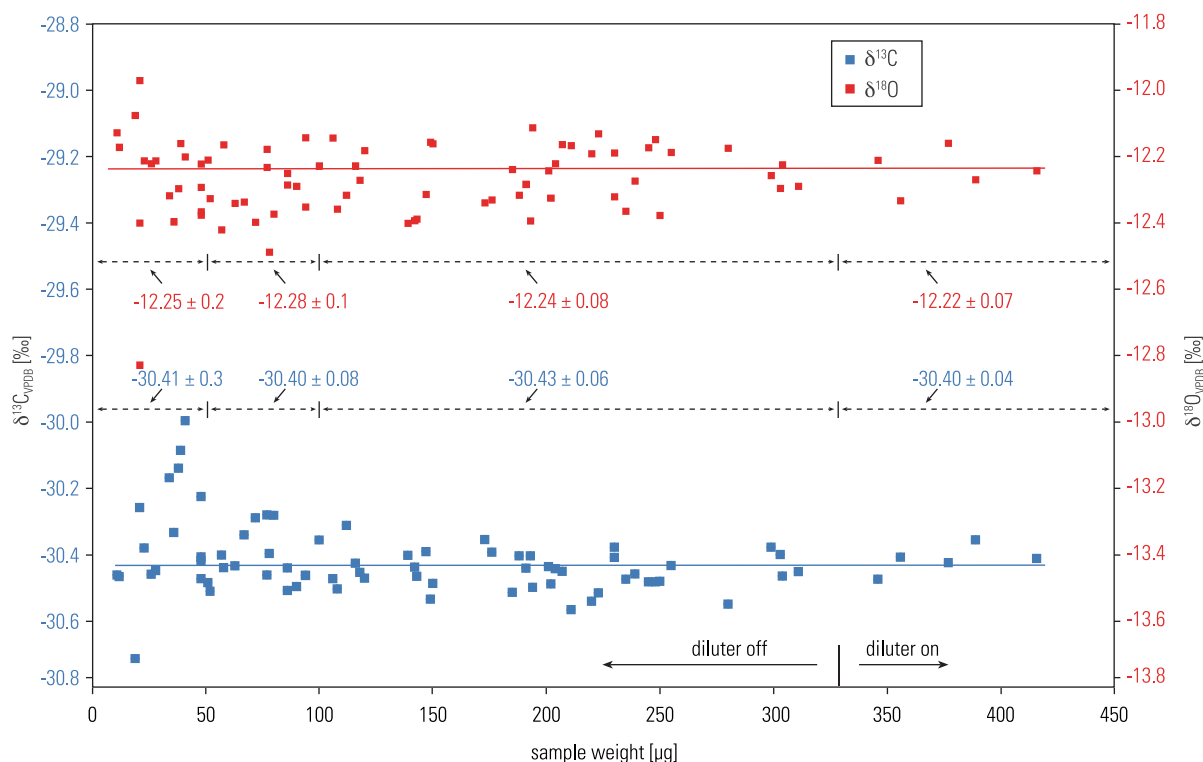


Figure 3: The graph shows the large dynamic range of the GasBench II. The  $\delta$ -values after linearity correction are independent of sample weight. Note that the Autodiluter has no effect on the  $\delta$ -values.

### Analysis of Reference Materials

A comparison of internationally certified reference materials with GasBench II measurements was performed analyzing 2 sets of samples on 2 different days. Table 2 shows mean values and 1  $\sigma$  standard deviation of the measurements as compared to the values given by the International Atomic Energy Agency (IAEA).

	$\delta^{13}\text{C}_{\text{VPDB}} [\text{‰}]$			$\delta^{18}\text{O}_{\text{VPDB}} [\text{‰}]$		
	IAEA	SET1 (N=6)	SET2 (N=6)	IAEA	SET1 (N=6)	SET2 (N=6)
NBS 18	-5.008 $\pm 0.058$	-5.02 $\pm 0.15$	-4.99 $\pm 0.10$	-22.97 $\pm 0.067$	-23.00 $\pm 0.06$	-22.88 $\pm 0.05$
NBS 19	1.95 $\pm 0.12$	1.77 $\pm 0.05$	1.95 $\pm 0.05$	-2.2 $\pm 0.07$	-2.01 $\pm 0.06$	-2.09 $\pm 0.06$
CO-9	-47.119 $\pm 0.296$	-47.16 $\pm 0.08$	-46.75 $\pm 0.11$	-15.282 $\pm 0.093$	-15.28 $\pm 0.04$	-15.35 $\pm 0.07$
CO-8	-5.749 $\pm 0.255$	-5.63 $\pm 0.23$	-5.71 $\pm 0.07$	-22.667 $\pm 0.187$	-22.96 $\pm 0.19$	-22.56 $\pm 0.15$
CO-1	2.48 $\pm 0.068$	2.47 $\pm 0.19$	2.79 $\pm 0.07$	-2.437 $\pm 0.073$	-2.37 $\pm 0.05$	-2.44 $\pm 0.10$

Table 2: Calibrated results (vs. VPDB) of two data sets measured on 2 different days compared to IAEA accepted values.

**Data referring to:** Reference and Intercomparison Materials for Stable Isotopes of Light Elements, IAEA, Vienna, 1995, IAEA-TECDOC-825, ISSN 1011-4289

### Conclusions

The GasBench II with the carbonate option can be used for precise ( $\delta^{13}\text{C}$ :  $\pm 0.06$  ‰,  $\delta^{18}\text{O}$ :  $\pm 0.08$  ‰) and accurate measurements of samples containing in excess of 100  $\mu\text{g}$  of carbonate. Smaller samples can be measured with somewhat lower precision:

	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$
50 - 100 $\mu\text{g}$ :	$\pm 0.08$ ‰	$\pm 0.10$ ‰
10 - 50 $\mu\text{g}$ :	$\pm 0.30$ ‰	$\pm 0.20$ ‰

Accuracy is not affected by the sample size. Comparison of the measured  $\delta$ -values of carbonate reference materials with the internationally accepted values shows excellent agreement. The large dynamic range eliminates the need for sample weighing and therefore speeds up sample handling. Up to 80 samples per day can be measured on a continuous basis.

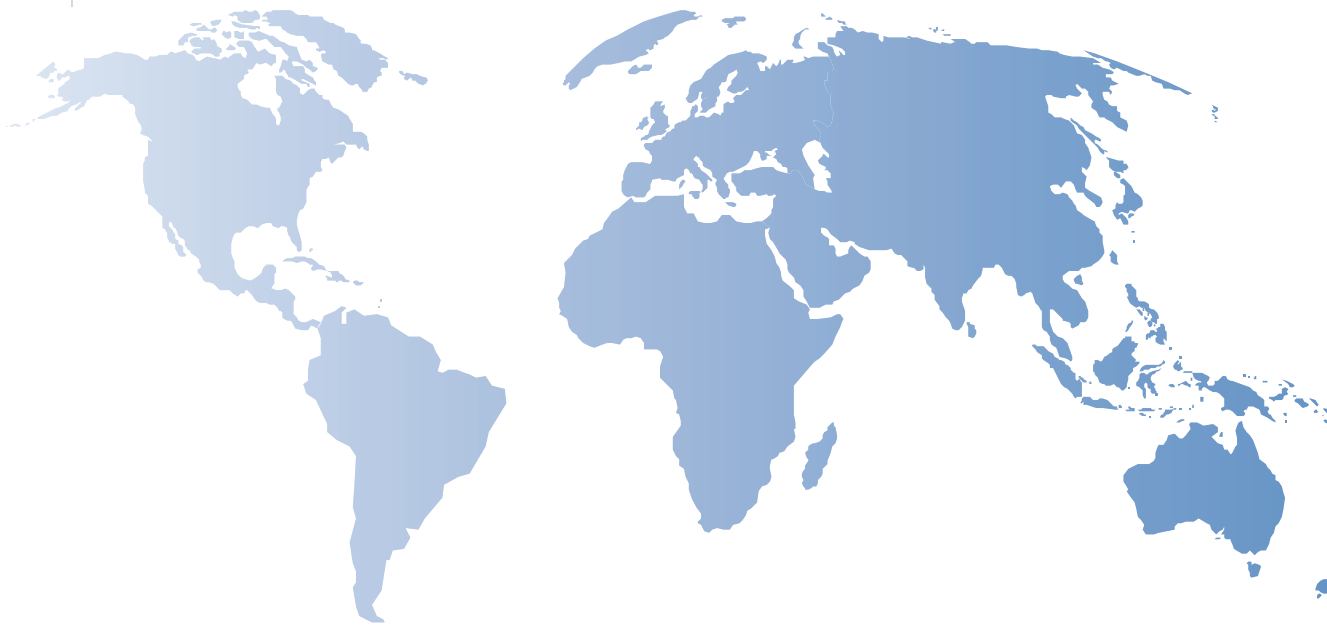
### Literature

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