[1]Thermo Fisher Scientific, Bremen, Germany

Using Isotope Ratio Infrared Spectrometer to determine $\delta^{13}C$ and $\delta^{18}O$ of carbonate samples

Danijela Smajgl[1]*, Nils Stöbener[1], Magda Mandic[1]

ABSTRACT

The automated measurement of $\delta^{13}C$ and $\delta^{18}O$ from solid carbonate samples has been demonstrated using a Thermo Scientific™ Delta Ray™ IRIS with URI Connect. The measurement of certified reference materials confirms the high achievable accuracy and a precision of <0.1‰ for both $\delta^{13}C$ and $\delta^{18}O$.

INTRODUCTION

Stable carbon and oxygen isotopic compositions ($\delta^{13}C$ and $\delta^{18}O$) of carbonates have been widely used for reconstruction of paleoenvironments.

The isotopic signature of carbon, $\delta^{13}C$ is significant as a tracer for the origin of carbon. Variations of $\delta^{18}O$ in oxygen bearing minerals have been used as proxies for various environmental records, especially temperature.

For many decades different instrumental methods involving generations of the Thermo Fisher Scientific isotope ratio mass spectrometers with Kiel Carbonate device, or the continuous flow Gas Bench II with the Carbonate-Option in conjunction with an CTC GC PAL or Combi PAL autosampler, offered the scientifically required high precision, and high throughput of samples for these applications.

The Delta Ray IRIS with URI Connect and TELEDYNE Cetac ASX-7100 autosampler now extends the traditional offerings with a system that can be used in the laboratory or the field and offers high precision and throughput of samples.

Fig 1. Thermo Scientific™ Delta Ray™ IRIS with URI Connect and Cetac ASX-7100 with heated sample rack.

EXPERIMENTAL SETUP

The URI Connect contains a Variable Volume (VV) of up to 100 mL in size. The CO_2 gas released in vials by reaction of samples with phosphoric acid is flushed into the VV through a Nafion based built-in water trap. CO_2 free synthetic air is used as a Carrier. During measurement, the VV is decreased, resulting in a continuous gas flow of diluted sample CO_2 into the measurement cell (Fig 2).
Prior to measurement, a fraction of the VV is used to determine the present CO_2 concentration. The Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software automatically adjusts the dilution of the CO_2 to achieve the desired concentration (e.g., 400 ppm) in the Delta Ray. As part of the workflow, reference gases are regularly measured at the same concentration as the sample to allow for automatic drift correction.

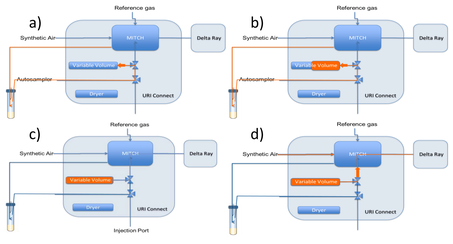

Fig 2. Workflow of the sample handling within the URI Connect.

a) Flushing of the vial headspace into the Variable Volume (VV)
b) VV increases
c) headspace transfer completed
d) release of sample gas from the VV into the Delta Ray and dilution with synthetic air.

METHOD

The preparation of the samples for analysis on the Delta Ray IRIS with URI Connect is similar to the previously mentioned Gas Bench II method. Samples are put into vials and phosphoric acid is added. The resulting sample-acid chemical reaction releases CO_2 gas, which is then introduced into the Delta Ray IRIS via the Variable Volume.

Three international standards of carbonate materials (NBS-18, NBS-19 and IAEA-CO-1) were analyzed. NBS-18 and NBS-19 were used as standards for calibration, and IAEA-CO-1 was treated as unknown. The Principle of Identical Treatment was applied in sample and standard preparation, in measurement procedure, as well as in the evaluation of the results.

Step by Step Sample Preparation

a) 400 – 500 µg per sample was used for analysis.
b) Residual air was removed from the vials by an automated autosampler-assisted flushing procedure. Flushing procedure is carried out at a flow of 30 mL/min for 3 minutes.
c) Samples were manually acidified using 3 droplets of 104% phosphoric acid (H_3PO_4).
d) Reaction time was 60 minutes at a constant temperature of 80°C.
e) Start of measurement

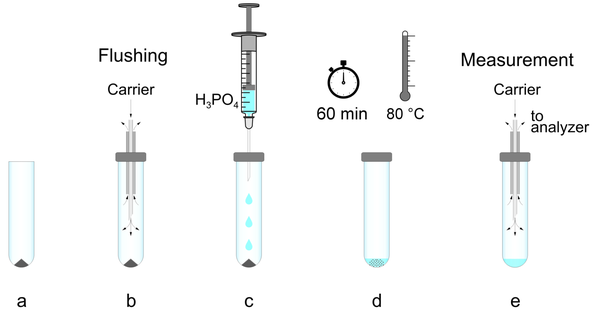

Fig 3. Sample Preparation.

Measurement Procedure

Sampling and measurement procedure were driven automatically from Qtegra ISDS Software with the Labbook shown in Figure 4. The built-in method "Transfer Sample" executes sample collection from the autosampler, CO_2 concentration determination prior to measurement, and optimization of the measurement conditions. Each sample measurement was followed by a measurement of a working standard gas to correct for instrument drift. Prior to each sample transfer, the Variable Volume and plumbing was flushed twice with Carrier by means of an Action Script ("Preclean D").

	Label	Flush time [sec.]	Measurement time [sec.]	Concentration[ppm]	Dilution flow [ml/min]	Smart Ref. Source	Action	Sample Processing	Type	Rack	Vial
1	AS cleaning	0	600		40	☐	None	None	UNKNOWN	1	60
2	Ref. 1	60	180	380		☐	None	None	STD	Standard	1
3	NBS 18	40	180	380	0	☑	Preclean D	Transfer Sample	UNKNOWN	1	1
4	Ref. 1	60	180	380		☐	None	None	STD	Standard	1
5	NBS 19	40	180	380	0	☑	Preclean D	Transfer Sample	UNKNOWN	1	2
6	Ref. 1	60	180	380		☐	None	None	STD	Standard	1
7	IAEA-CO-1	40	180	380	0	☑	Preclean D	Transfer Sample	UNKNOWN	1	3
8	Ref. 1	60	180	380		☐	None	None	STD	Standard	1
9	IAEA-CO-1	40	180	380	0	☑	Preclean D	Transfer Sample	UNKNOWN	1	4
10	Ref. 1	60	180	380		☐	None	None	STD	Standard	1
11	IAEA-CO-1	40	180	380	0	☑	Preclean D	Transfer Sample	UNKNOWN	1	5
12	Ref. 1	60	180	380		☐	None	None	STD	Standard	1

Fig 4. Qtegra Labbook Layout.

RESULTS

The obtained isotope ratios for NBS-18 and NBS-19 were averaged and used to generate two-point calibration curves for the $^{13}C/^{12}C$ and $^{18}O/^{16}O$ ratios. The calibration functions were then applied to the measured isotope ratios of the samples. The resulting numbers are in perfect agreement with the values certified by IAEA. Fig 5 shows the obtained $\delta^{13}C$ and $\delta^{18}O$ values for all IAEA-CO-1 standards and mean, median, minimum and maximum, as well as the second and third quartile. For comparison, the certified values plus their uncertainty are also indicated.

Table 1: Expected and measured Isotope Ratios of NBS 18 and NBS 19, as well as derived Calibration functions.

$^{13}C/^{12}C$	$R_{expected}$	$R_{measured}$	Calibration function
NBS-18	0.0111241	0.0111998	$R_{expected} = 0.998347 \times R_{measured} + 2.07438 \times 10^{-5}$
NBS-19	0.0112020	0.0111218	

$^{18}O/^{16}O$	$R_{expected}$	$R_{measured}$	Calibration function
NBS-18	0.00201920	0.0020334	$R_{expected} = 1.02488 \times R_{measured} - 6.47652 \times 10^{-5}$
NBS-19	0.00206261	0.0020757	

Table 2: Resulting $\delta^{13}C$ and $\delta^{18}O$ values for ten IAEA-CO-1 standard samples.

IAEA-CO-1	Measured	1 SD	Certified*
$\delta^{13}C$(‰ VPDB)	2.46	0.03	2.49 ± 0.03
$\delta^{18}O$ (‰ VPDB-CO_2)	-2.42	0.06	-2.4 ± 0.1

* Recommendation only for $\delta^{18}O$

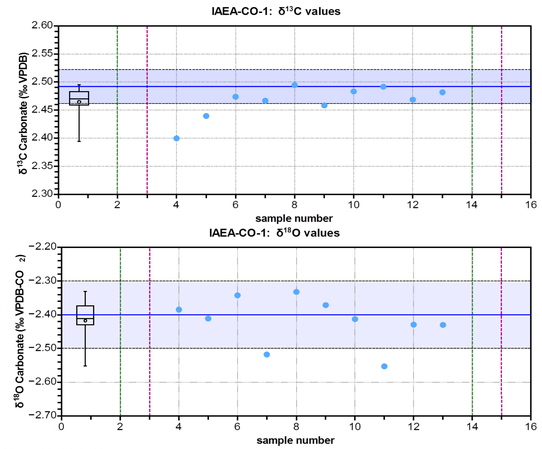

Fig 5. $\delta^{13}C$ and $\delta^{18}O$ values of ten IAEA-CO-1 standard samples.
The green and pink vertical lines indicate the position of NBS 18 and NBS 19 standards used for scale calibration. The blue line and shading refers to the value and uncertainty certified ($\delta^{13}C$) or recommended ($\delta^{18}O$) by the IAEA[1].

CONCLUSIONS

The Thermo Scientific™ Delta Ray™ IRIS with URI Connect allows determination of $\delta^{13}C$ and $\delta^{18}O$ values from carbonates with a precision comparable to IRMS.
In addition, the Delta Ray IRIS allows the researcher also to obtain these data directly in the field.
The workflow for analysis of carbonates and other samples is fully automated.

REFERENCES

1. IAEA Reference Material Online Catalog:
https://nucleus.iaea.org/rpst/referenceproducts/ReferenceMaterials/index.htm

*danijela.smajgl@thermofisher.com