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Determination of Carbon δ^{13} C isotopic composition from DIC samples

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Keywords

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Goal

To demonstrate the method for Dissolved Inorganic Carbon (DIC) analysis by using the Thermo Scientific Delta Ray Isotope Ratio Infrared Spectrometer with URI Connect.

Introduction

Dissolved Inorganic Carbon (DIC) is a common term for dissolved CO_2 , H_2CO_3 , HCO^{3-} and CO_3^{2-} in water and their relative contribution varies with different environmental conditions.

By measuring DIC and other hydrological and geophysical environmental parameters at a study site, redistribution of carbon among different Earth reservoirs can be investigated. Various applications, including paleoclimatic temperature changes, investigation of the origin of water, mineral digenesis, microbial activity in various media and many more require information on the isotopic composition of DIC to draw scientific conclusions.

For many decades different instrumental methods involving different models of the Thermo Scientific[™] Isotope Ratio Mass Spectrometer portfolio with Thermo Scientific[™]Kiel[™] IV Carbonate Device, or the continuous flow Thermo Scientific[™] GasBench II System with the carbonate-option in conjunction with a CTC GC PAL or Combi PAL Autosampler, offered the scientifically required high precision and high throughput capabilities for these samples and applications.



The Thermo Scientific[™] Delta Ray[™] Isotope Ratio Infrared Spectrometer (IRIS) with the Universal Reference Interface (URI) Connect and the Teledyne CETAC ASX-7100 Autosampler (Figure 1) now extends the traditional offerings with a system that can be used in the laboratory or in the field and offers high precision and throughput capabilities. It employs optical spectroscopy for continuous measurement of isotope ratio values and concentration of carbon dioxide in ambient air, and also for analysis of discrete samples from vials, syringes, bags, or other user-provided sample containers.



Figure 1. Thermo Scientific Delta Ray Isotope Ratio Infrared Spectrometer with URI Connect.

The preparation of the samples for analysis on the Delta Ray IRIS is similar to the method previously mentioned for the Gas Bench II System. Samples are put into vials, flushed with carrier, and phosphoric acid is added. The resulting sample-acid reaction releases CO_2 gas, which is then introduced into the Delta Ray IRIS via the Variable Volume. With this workflow, more than 100 samples in vial can be analyzed per day with a δ^{13} C precision better than 0.1‰.

URI connect with Teledyne CETAC ASX-7100 Autosampler

For the analysis performed using the Teledyne CETAC[™] ASX-7100 Autosampler, a dual probe is required (Figure 1). Samples are placed in 12 mL Labco Exetainer vials and then preflushed with carrier using the autosampler. The CO₂ gas released by the acid is flushed into the Variable Volume inside the URI Connect through the Nafi on based built-in water trap. For this step, carrier gas (usually CO₂ free air) is used to flush the gas from the vial in the autosampler into the Variable Volume with a maximum volume of 100 ml. A small amount of the sample is then used for automated determination of the CO₂ concentration present in the Variable Volume. The Thermo Scientific[™] Qtegra[™] Intelligent Scientific Data Solution[™] (ISDS) Software then automatically adjusts any additional dilution of the sample to achieve the desired concentration (usually 400 ppm) in the analyzer.

As part of the workflow, reference gas measurements are regularly measured at the same concentration as the sample to allow for automatic drift correction.



Figure 2. Dual probe of the Teledyne CETAC ASX-7100 Autosampler allowing carrier gas to enter at the bottom and to flush the vial headspace through the top feed into the Variable Volume of the URI Connect.

Experimental setup

Measurements were done with three Delta Ray IRIS operating in parallel. To confirm high accuracy and precision of the Delta Ray IRIS, three IAEA international standard materials were used (LSVEC, NBS 18 and NBS 19). LSVEC and NBS 19 were used as reference materials and NBS 18 was treated as the unknown. The Principle of Identical Treatment (IT) was applied in sample and standard preparation and measurement procedure as well as in the evaluation of the results.

The NBS 18 sample material was measured in 20 replicates on each instrument while the reference material NBS 19 and LSVEC were measured in 2-3 replicates usually at the start, in the middle and at the end of the sequence.

Sample preparation

Samples of 200 to 300 μ g were introduced into precleaned borosilicate vials, then caped and flushed with carrier gas for 3 minutes each. After flushing, samples were manually acidified using 300 μ L of 43% phosphoric acid (H₃PO₄) and left to react overnight at room temperature.



Figure 3. Sample preparation description a) Load the sample in the cleaned vial (prior using, vial should be rinsed 3 times with de-ionized water and dried overnight at 70 °C) b) Flush the vials with carrier for 3 minutes with autosampler c) Add 3 μ L of acid to the vial d) Overnight reaction of the acid and sample at stable room temperature e) Start the measurement.

Setting up samples in the tray and measurement

Samples and reference materials were interspersed in the autosampler tray to check whether large differences in delta values of the different carbonate samples affect the measurement of the next sample, e.g. to test for any memory effect.

Sampling and measurement procedure were generated automatically by Qtegra ISDS Software. The labbook used for the analysis is shown in Figure 4. The build-in method "Transfer Sample" was chosen for sample measurement. This method executes sample collection from the autosampler, sample concentration determination prior to measurement, and optimization of the measurement conditions, all fully automated.

Each sample measurement was followed by a measurement of a working standard gas (Ref. 1) to correct for instrument drift. In order to gain maximum precision, both samples and working standards were measured for 180 seconds.

Prior to each sample transfer, the Variable Volume and plumbing was flushed with twice with Carrier by means of an Action Script ("Preclean D").

Analysis of the results

For each instrument, the molecular ratios of NBS 19 and LSVEC were used to perform a two-point calibration of the type:

 $R_expected = m * R_measured + b$, with m being the slope an b the offset. These equations were then applied to the measured isotope ratios of NBS 18.

Figure 5 shows measurement results of one instrument for all samples and references.

2 ²²	Label ⊽‡	Flush time [sec.] 🗸 🕫	Measurement time [sec.] 🖓 🗗	Port ⊽+¤	Concentration [ppm] ▽+	Action 🖓 🕫	Smart Ref Source ▽+	Sample Processing ⊽ 中	Type ⊽+¤	Rack ⊽+⊐	Vial ⊽+¤
1	AS cleaning	0	600	Sample A	380	None		None	UNKNOWN	1	60
2	Ref. 1	60	180	Reference 1	380	None		None	STD	Standard	1
3	NBS 18	40	180	Sample A	380	Preclean D	~	Transfer Sample	UNKNOWN	1	3
4	Ref. 1	60	180	Reference 1	380	None		None	STD	Standard	1
5	NBS 18	40	180	Sample A	380	Preclean D	v	Transfer Sample	UNKNOWN	1	4
6	Ref. 1	60	180	Reference 1	380	None		None	STD	Standard	1
7	NBS 18	40	180	Sample A	380	Preclean D	~	Transfer Sample	UNKNOWN	1	5
8	Ref. 1	60	180	Reference 1	380	None		None	STD	Standard	1
9	NBS 18	40	180	Sample A	380	Preclean D	V	Transfer Sample	UNKNOWN	1	6
10	Ref. 1	60	180	Reference 1	380	None		None	STD	Standard	1
11	NBS 18	40	180	Sample A	380	Preclean D	V	Transfer Sample	UNKNOWN	1	7
12	Ref. 1	60	180	Reference 1	380	None		None	STD	Standard	1
13	NBS 18	40	180	Sample A	380	Preclean D	~	Transfer Sample	UNKNOWN	1	8
14	Ref. 1	60	180	Reference 1	380	None		None	STD	Standard	1
15	NBS 18	40	180	Sample A	380	Preclean D	~	Transfer Sample	UNKNOWN	1	9
16	Ref. 1	60	180	Reference 1	380	None		None	STD	Standard	1
17	NBS 18	40	180	Sample A	380	Preclean D	~	Transfer Sample	UNKNOWN	1	10
18	Ref. 1	60	180	Reference 1	380	None		None	STD	Standard	1
19	NBS 18	40	180	Sample A	380	Preclean D	V	Transfer Sample	UNKNOWN	1	11
20	Ref. 1	60	180	Reference 1	380	None		None	STD	Standard	1
21	NBS 18	40	180	Sample A	380	Preclean D	~	Transfer Sample	UNKNOWN	1	12
22	Ref. 1	60	180	Reference 1	380	None		None	STD	Standard	1
23	NBS 19	40	180	Sample A	380	Preclean D	~	Transfer Sample	UNKNOWN	1	13
24	Ref. 1	60	180	Reference 1	380	None		None	STD	Standard	1
25	LSVEC	40	180	Sample A	380	Preclean D	✓	Transfer Sample	UNKNOWN	1	14
26	Ref. 1	60	180	Reference 1	380	None		None	STD	Standard	1
27	NBS 18	40	180	Sample A	380	Preclean D	V	Transfer Sample	UNKNOWN	1	15
28	Ref. 1	60	180	Reference 1	380	None		None	STD	Standard	1
29	NBS 18	40	180	Sample A	380	Preclean D		Transfer Sample	UNKNOWN	1	16

Figure 4. Setup of the labbook in Qtegra ISDS Software (excerpt). Prior to sample measurement, carrier was flushed through a vial and the autosampler to clean all external components (autosampler needle, plumbing) from residual ambient air ("AS cleaning").



Figure 5. Measurement results for the international reference materials NBS 18, NBS 19 and LSVEC. NBS 19 and LSVEC were used as calibration standards.

Table 1. ${}^{13}C/{}^{12}C$ ratios ($R_{measured}$) of NBS 19 and LSVEC used for the calibration of the three instruments and obtained calibration functions.

	NBS 19 <i>R</i> _{measured}	LSVEC R _{measured}	Calibration Function*
Instrument 1	0.0111899	0.0106714	$R_{ ext{expected}} = 1.04680 \times R_{ ext{measured}} - 5.11578 \times 10^{-4}$
Instrument 2	0.0112002	0.0106583	$R_{ ext{expected}} = 1.00174 \times R_{ ext{measured}} - 1.75901 \times 10^{-5}$
Instrument 3	0.0111991	0.0106566	$R_{ ext{expected}} = 1.00061 \times R_{ ext{measured}} - 3.95357 \times 10^{-6}$

* Expected ¹³C/¹²C ratios are $R_{\text{expected}} = 0.0112020$ for NBS 19 and $R_{\text{expected}} = 0.0106592$ for LSVEC.

No memory effect between the samples

Figure 6 shows that the δ^{13} C values obtained for NBS 18 are independent of those of the previous samples. The green and orange vertical lines indicate the sample positions of NBS 19 and LSVEC.

This demonstrates that there is no significant memory effect when analyzing discrete samples with the Delta Ray IRIS.

The mean values of the 20 replicates of NBS 18 measured with the Delta Ray IRIS are shown in Table 2 and in Figure 6 together with mean, median, minimum and maximum values as well as second and third quartile. Certified value of NBS 18 for d13C is -5.014‰ VPDB with a standard deviation of 0.035‰.

Table 2. Mean values and standard deviation of NBS 18 measured with three independent Delta Ray IRIS Systems.

	δ ¹³ C Measured (‰ VPDB)	St. Dev. (‰ VPDB)	δ¹³C Certified (‰ VPDB)	
Instrument 1	-5.018	0.076		
Instrument 2	-5.044	0.047	-5.01 ± 0.035	
Instrument 3	-5.015	0.061		



Figure 6. δ^{13} C values of NBS 18 measured on three systems. The green and yellow lines indicate the position of NBS 19 and LSVEC samples.

The small difference $\Delta\Delta (\leq 0.3\%)$ between certified and measured value of NBS 18 is much less than the stated uncertainty of NBS 18 and demonstrates the excellent accuracy achievable with the Delta Ray IRIS.



Figure 7. Mean, median, minimum and maximum values as well as second and third quartile of the 20 replicates of NBS 18 measured on three Delta Ray IRIS Systems. The blue horizontal line and shading refer to the certified value of $-5.01 \pm 0.035\%$ VPDB.

Conclusion

The Delta Ray IRIS with URI Connect can be used for precise and accurate measurements of the δ^{13} C values from DIC. Samples containing 200-300 µg NBS 18 Calcite were measured with an accuracy better than 0.3‰ VPDB on three instruments. The precision over 20 vials was better than 0.08‰ for all instruments. The performance of the Delta Ray IRIS with URI Connect for the measurement of carbonates and DIC therefore is comparable to that of established applications like the Thermo Scientific GasBench II System. Additionally, the Delta Ray IRIS allows the researcher to obtain highly accurate and precise data also in the field.

Reference

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

Find out more at thermofisher.com/DeltaRay

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