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$\delta^{13}C$ of DIC and carbonate samples - Comparison of traditional mass spectrometry methods with infrared spectrometry method

Danijela Smajgl, Magda Mandic, Thermo Fisher Scientific, Bremen, Germany; Dirk Nürnberg, Sebastian Fessler, GEOMAR Helmholtz Centre for Ocean Research Kiel, Kiel, Germany; Albrecht Leis, JR-AquaConSol GmbH, Graz, Austria

INTRODUCTION

For many decades different instrumental methods, involving generations of the Thermo Scientific™ MAT 253™ Isotope Ratio Mass Spectrometers with Thermo Scientific™ Kiel™ Carbonate Device, and the continuous flow Thermo Scientific™ Gas Bench II™ System with the carbonate-option, offered the scientifically required high precision and high throughput of samples for these applications. The Thermo Scientific™ Delta Ray™ Isotope Ratio Infrared Spectrometer (IRIS) with the Universal Reference Interface (URI™) Connect and TELEDYNE™ Cetac ASX-7100 autosampler, now extends the traditional offerings with a system that can be used in the laboratory or field and offers high precision and throughput of samples (Figure 1).

Here we present sample preparation and sample processing method for determination of isotopic composition of carbon ($\delta^{13}C$) in dissolved inorganic carbon (DIC) and carbonate material with Delta Ray IRIS with URI Connect, and comparison with traditional mass spectrometry methods.

MATERIALS AND METHODS

Isotope ratio infrared spectrometry

Delta Ray Connect uses isotope ratio infrared spectroscopy (IRIS) to determine isotope ratios. The laser light is generated by a difference frequency generation (DFG) mid-infrared laser which operates at 4.3 µm. Calculation of different carbon dioxide isotopologues and determination of stable isotope ratios from spectrum is possible due to absorption lines which are shifted relative to each other (Figure 2). The system can measure up to 100 samples per day, with a $\delta^{13}C$ precision better than 0.15‰.

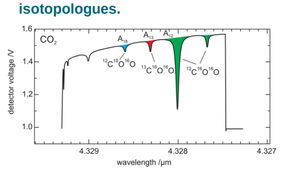
Experimental setup

The URI Connect contains a Variable Volume (VV) of up to 100 mL in size. The sample gas 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 volume of VV is decreased, resulting a continuous gas flow of diluted sample CO_2 into the measurement cell.

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 automatically adjusts the dilution of the CO_2 to achieve the desired concentration in analyzer cell. As part of the workflow, reference gases are regularly measured at the same concentration as the sample to allow for automatic drift correction.

Figure 1. Delta Ray IRIS with URI Connect and Cetac ASX-7100 with heated sample rack, and in the background, Kiel IV Carbonate Device with MAT 253 IRMS.

Figure 2. Mid-infrared spectral region at a wavelength of 4.3 µm. The laser scans over the absorption lines at 500 Hz. The stable isotope ratios of carbon dioxide can be calculated from the respective peak areas of the different isotopologues.

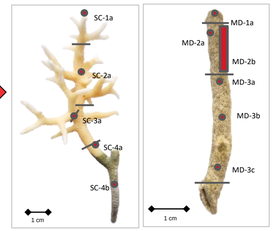


$\delta^{13}C$ OF CARBONATE SAMPLES

Different calcifying organisms collected from coral culturing tank at GEOMAR (snail shells, red algae, corals…).

Figure 3. Coral culturing tank at GEOMAR, Kiel.

Figure 4. Corals used for isotopic analysis. *Seriatopora caliendrum* left and *Montipora digitate* right.



Delta Ray IRIS with URI Connect: Method for isotopic analysis

Standards: Principle of Identical Treatment was applied in sample and standard preparation, in measurement procedure, as well as in the evaluation of the results.

The international reference materials NBS 18 and IAEA-603 were used to perform a two-point calibration. The normalised carbon isotope ratios of the samples were reported in per mill (‰) relative to VPDB.

$$R_{expected} = m * R_{measured} + b$$

m = slope
b = offset

Table 1. Isotopic composition of international standard materials given by IAEA.

Standards	$\delta^{13}C$ VPDB ‰
NBS 18	-5.014 ± 0.035
IAEA-603	2.46 ± 0.01

Step by Step Sample Preparation

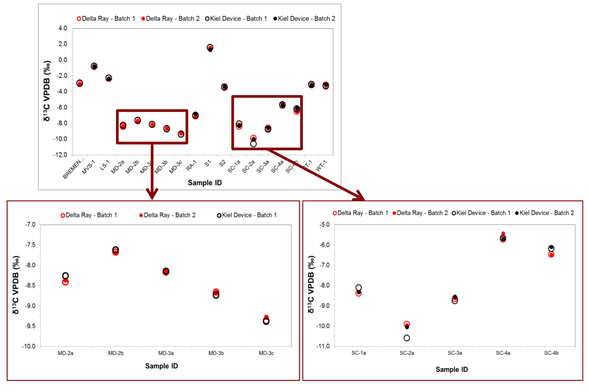
1. ~ 300 µg per sample was used for analysis
2. Residual air was removed from the vials by an automated autosampler-assisted flushing procedure
3. Samples were manually acidified using 3 droplets of 104% phosphoric acid (H_3PO_4)
4. Reaction time was 60 minutes at a constant temperature of 80ºC
5. Start of the measurement

RESULTS

- Repeatability (3 aliquots of one sample) was better than 0.05‰ (MIN = 0.008‰; MAX = 0.165‰)
- Reproducibility of data (comparison of Batch 1 and Batch 2) was better than 0.06‰

IRIS / IRMS: In addition to IRIS measurements using Delta Ray Connect we performed traditional IRMS-based measurements with an automated KIEL IV Carbonate Device coupled to a Thermo Scientific MAT 253 Mass Spectrometer. When comparing IRMS and IRIS method, average of absolute difference is 0.1‰ with minimal difference of 0.01‰ and maximal difference of 0.39‰.

Figure 5. $\delta^{13}C$ values of 19 carbonates samples measured using Delta Ray IRIS with URI Connect (marked in red) and Kiel IV Carbonate Device coupled to a MAT 253 Mass Spectrometer (marked in black).



$\delta^{13}C$ OF DIC (SEAWATER SAMPLES)

Water samples were collected directly from aquarium and filtered through Surfactant-Free Cellulose Acetate membrane syringe filters, with pore diameter of 0.2 µm. Samples were then stored at temperature of 4ºC in 50 ml sealed glass vials.

Delta Ray IRIS with URI Connect: Method for isotopic analysis

Standards: Principle of Identical Treatment was applied in sample and standard preparation, in measurement procedure, as well as in the evaluation of the results. Three international standards of carbonate materials (NBS 18, IAEA-603 and LSVEC) were analyzed along with laboratory standards $NaHCO_3$ (s), $NaHCO_3$ (aq), Na_2CO_3 (s) and Na_2CO_3 (aq). NBS 18, IAEA-603 and LSVEC were used as standards for calibration, while laboratory standards were used for quality control.

NBS 18 and IAEA-603 were used to perform a two-point calibration. Assigned $\delta^{13}C$ values of the samples were reported in per mill (‰) vs. VPDB scale.

$$R_{expected} = m * R_{measured} + b$$

m = slope
b = offset

Table 2. Isotopic composition of international standard materials given by IAEA.

Standards	$\delta^{13}C$ VPDB ‰
NBS 18	-5.014 ± 0.035
IAEA-603	2.46 ± 0.01
LSVEC	-46.6 ± 0.2

Step by Step Sample Preparation

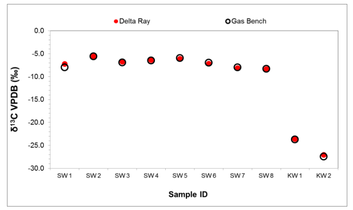
1. 0.8 ml per sample was used for analysis
2. Residual air was removed from the vials by an automated autosampler-assisted flushing procedure
3. Samples were manually acidified using 1 droplet of 100% phosphoric acid (H_3PO_4)
4. Reaction time was approximately 15 hours (overnight) at a constant room temperature
5. Start of the measurement

RESULTS

Repeatability (3 aliquots of one sample) was better than 0.05‰ (MIN = 0.01‰; MAX = 0.13‰).

IRIS / IRMS: In addition to measurements using Delta Ray IRIS with URI Connect, we performed classical IRMS measurements with a GasBench II System coupled to a Delta XP Mass Spectrometer. When comparing IRMS and IRIS method, average of absolute difference is 0.2‰ with minimal difference of 0.03‰ and maximal difference of 0.73‰.

Figure 6. $\delta^{13}C_{DIC}$ values of 10 water samples measured using Delta Ray IRIS with URI Connect (marked in red) and GasBench II System (marked in black).



CONCLUSIONS

- We present preliminary results of comparing traditional IRMS and newly developed IRIS methods for $\delta^{13}C$ measurements.
- Both methods show high accuracy and precision when measuring $\delta^{13}C$ of carbonates and DIC of seawater samples.
- In addition to traditional IRMS methods for laboratory analysis of stable isotopes of carbonates and DIC, IRIS offers a very interesting new option of performing high precision isotopic measurements in the laboratory as well as in the field.

REFERENCES

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2. Spötl, C. 2005: A robust and fast method of sampling and analysis of $\delta^{13}C$ of dissolved inorganic carbon in ground waters. Isotopes in Environmental and Health Studies Vol. 41, No. 3, September 2005, 217–221

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