



$\delta^{13}\text{C}$ of DIC and carbonate samples: comparison of traditional mass spectrometry methods with an infrared spectrometry method

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Keywords

Delta Ray Connect, IRIS,
Carbonates, Dissolved Inorganic
Carbon (DIC), IRMS

Goal

To compare measurements from an infrared spectrometry method for $\delta^{13}\text{C}$ conducted with a Thermo Scientific™ Delta Ray™ IRIS with URI Connect™ with those from traditional mass spectrometry methods.

Introduction

Isotope ratio mass spectrometry (IRMS) is a widely used technique for measurements of stable isotopic compositions. It is employed in different applications for environmental and geochemical studies. One example is paleo-environmental reconstruction based on carbonate measurements. In the past, high throughput and high precision of the measurements could only be achieved with a Thermo Scientific™ Kiel Carbonate Device connected to the IRMS via the dual viscous flow inlet system or as a second option with the Thermo Scientific™ GasBench II™ with the Carbonate Option. Now, in addition to IRMS systems, Thermo Fisher Scientific™ offers a laser-based and field deployable instrument: the Thermo Scientific™ Delta Ray™ Isotope

Ratio Infrared Spectrometer (IRIS) with the Universal Reference Interface (URI) Connect™ (Figure 1). Because of its size and robustness, the Delta Ray IRIS with URI Connect can be moved and installed much easier than mass spectrometers and it offers a possibility of direct measurements in the field. Here we present a sample preparation and sample processing method for determination of the isotopic composition of carbon ($\delta^{13}\text{C}$) in dissolved inorganic carbon (DIC) and carbonate material with the Delta Ray IRIS with URI Connect and provide a comparison with traditional mass spectrometry methods.

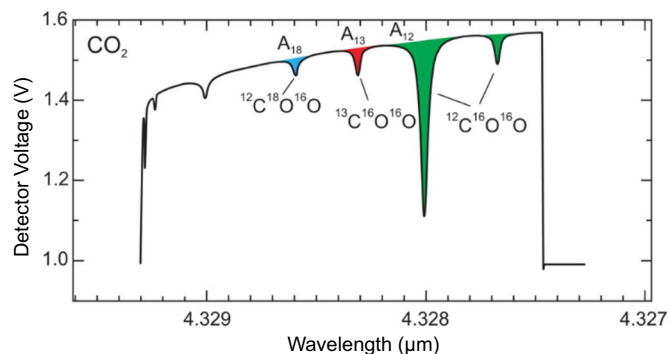


Figure 2. Mid-infrared spectral region at a wavelength of 4.3 μm and characteristic absorption lines for CO_2 isotopologues

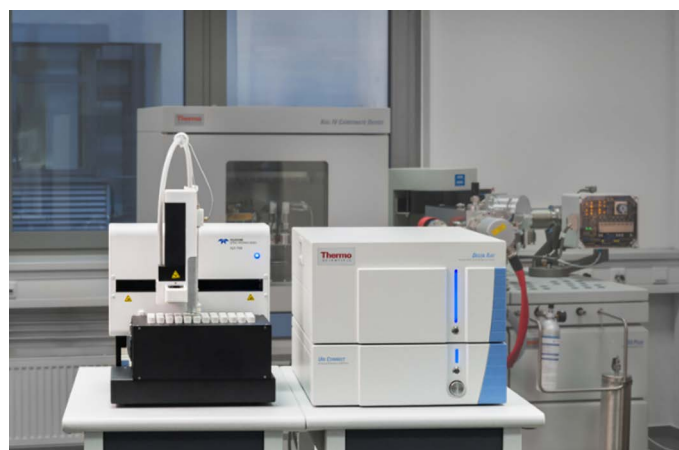


Figure 1. Delta Ray IRIS with URI Connect and Teledyne™ Cetac™ ASX-7100 Autosampler with heated sample rack, and in the background, Kiel IV Carbonate Device with Thermo Scientific™ MAT 253™ Mass Spectrometer

Mid-infrared isotope ratio spectroscopy

The Delta Ray IRIS with URI Connect is based on direct absorption spectroscopy and uses a mid-infrared laser that operates at 4.3 μm . The laser light is generated by two tunable near-infrared diode lasers that are combined in nonlinear crystal. The laser scans over the spectral region containing four CO_2 absorption lines, and isotope ratios are calculated from the spectrum fit. Calculation of different CO_2 isotopologues and determination of stable isotope ratios from the spectrum is possible due to absorption lines that are shifted relative to each other (Figure 2).

URI (Universal Reference Interface) Connect

With an option of continuous air measurements, URI Connect offers the possibility to measure discrete samples. It is composed of three functional units: MITCH™, Variable Volume (sample inlet), and Dryer (Figure 3). The Variable Volume (VV) collects the sample gas, which comes from a sample port. The system automatically determines the concentration of the sample in the VV and adjusts the dilution during measurement. Dilution is done by the reference section with the MITCH valve block (gas Mixing and swITCHing device). This enables the instrument to perform the measurements at constant concentration. The referencing for isotope values is done by introduction of pure CO_2 gases diluted using a carrier gas. The change of concentration allows the determination of linearity (change of delta value with concentration), which can be used for subsequent correction of data. The concentration of the reference gas is balanced against that of the sample to improve accuracy.

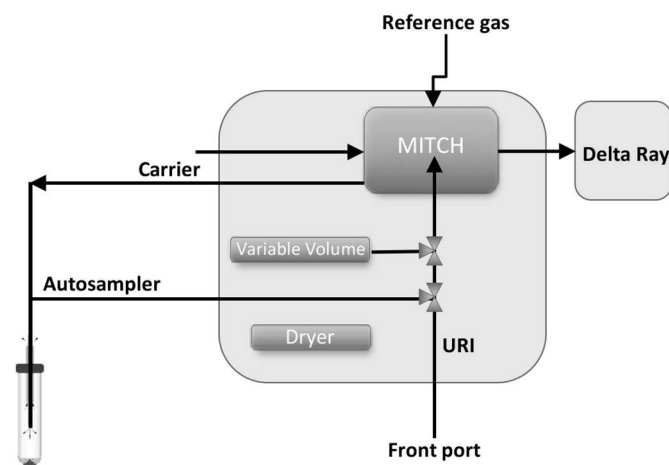


Figure 3. Schematic view of the URI Connect

Experimental

$\delta^{13}\text{C}$ of carbonate samples method

Delta Ray IRIS with URI Connect

Borosilicate vials were washed and dried overnight at 70 °C. After adding 400–500 μg of sample, vials were sealed with new septa and residual air was removed from the vials by an automated autosampler-assisted flushing procedure. The flushing procedure is carried out at a flow of 30 mL/min for 3 min. Further, samples were manually acidified using three droplets of 104% phosphoric acid (anhydrous phosphoric acid; 104% of $\text{H}_3\text{PO}_4 = 0.25 \text{ mol H}_2\text{O/L H}_3\text{PO}_4$) and placed into a heated tray at a constant temperature of 80 °C. After one hour at 80 °C, the measurement was started. The Principle of Identical Treatment was applied in sample and standard preparation, in the 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 normalized carbon isotope ratios of the samples were reported in per mill (‰) relative to VPDB.

Kiel IV Carbonate Device coupled to a MAT 253 Mass Spectrometer (Figure 4)

Phosphoric acid was added dropwise at full reaction temperature into the evacuated septum-free vial. The samples reacted at 70 °C with the oversaturated phosphoric acid (>1.92 kg/L phosphoric acid) to produce CO_2 sample gas. The developed CO_2 gas was subsequently separated from moisture and other gases remaining in the samples by leading the gas over two cooling traps (fluid nitrogen). Subsequently, the CO_2 gas was injected under vacuum into the mass spectrometer.



Figure 4. Kiel IV Carbonate Device coupled to MAT 253 Mass Spectrometer

$\delta^{13}\text{C}$ of DIC (water samples) method

Delta Ray IRIS with URI Connect

Vials were preloaded with 1 droplet of 104% phosphoric acid, capped and flushed with zero air (synthetic air without CO_2). Then, 0.8 mL per sample was injected into the vials using a disposable needle syringe. Reaction time was approximately 15 hours (overnight) at a constant room temperature. The Principle of Identical Treatment was applied in the sample and standard preparation, in the 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, IAEA-603, and LSVEC were used to perform a three-point calibration. Assigned $\delta^{13}\text{C}$ values of the samples were reported in per mill (‰) vs. VPDB scale.

GasBench II System coupled to a Thermo Scientific™ DeltaXP Mass Spectrometer (Figure 5)

Vials were preloaded with five droplets of ~ 90% phosphoric acid, capped and the headspace was flushed with He. Further on, 1 mL of water sample was injected into the vials using a disposable needle syringe. The reaction of sample and acid started immediately. The tray holder of the CTC Combi PAL™ Autosampler was routinely loaded with DIC samples and with carbonate standards that are used because international standards for $\delta^{13}\text{C}$ of DIC are not available.



Figure 5. The GasBench II System in conjunction with a CTC Combi PAL Autosampler, coupled to Thermo Scientific™ Delta V™ Isotope Ratio Mass Spectrometer

Results and discussion

$\delta^{13}\text{C}$ of carbonate samples

Nineteen carbonate samples were measured with the Delta Ray IRIS with URI Connect and the Kiel IV Carbonate Device coupled to a MAT 253 Mass Spectrometer.

Samples present different calcifying organisms collected from coral culturing tank at GEOMAR, Kiel (snail shells, red algae, corals, etc.) (Figure 6).

Two batches with three replicates of each sample were measured using the Delta Ray IRIS with URI Connect. Repeatability (three aliquots of one sample) was better than 0.05‰ (MIN = 0.008‰; MAX = 0.165‰), while reproducibility of data (comparison of Batch 1 and Batch 2) was better than 0.06‰.

When comparing the IRMS and IRIS methods, the average of absolute difference is 0.1‰ with minimal difference of 0.01‰ and maximal difference of 0.39‰ (Figure 7).

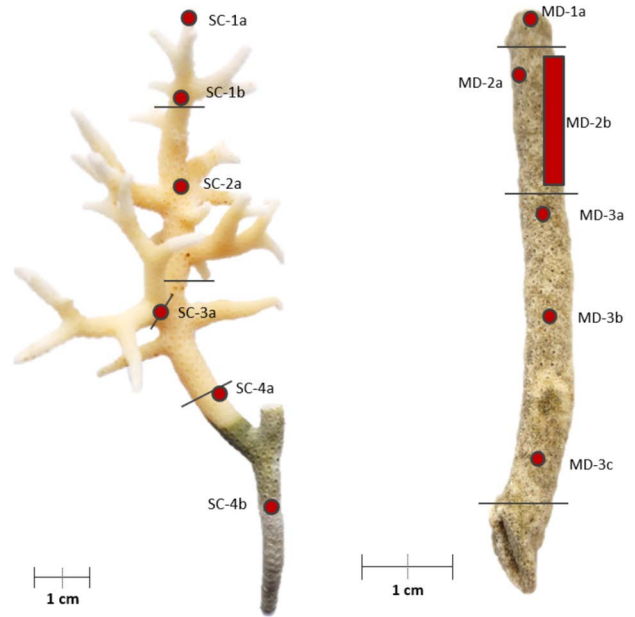


Figure 6. Example of corals used for isotopic analysis. *Seriatopora caliendrum* (left) and *Montipora digitate* (right).

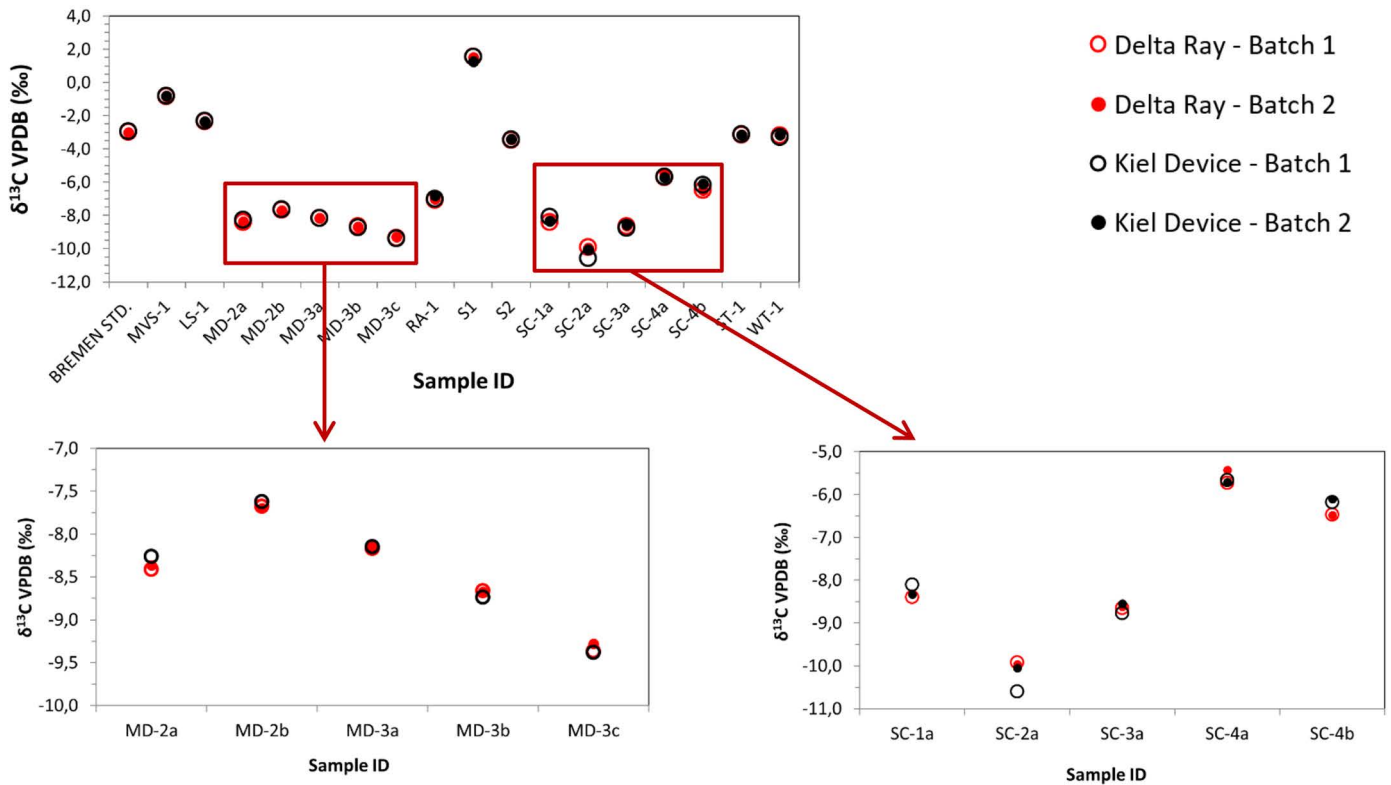


Figure 7. $\delta^{13}\text{C}$ values of 19 carbonates samples measured using a Delta Ray IRIS with URI Connect (marked in red) and Kiel IV Carbonate Device coupled to a MAT 253 Mass Spectrometer (marked in black)

$\delta^{13}\text{C}$ of DIC - water samples

Ten seawater samples were measured with the Delta Ray IRIS with URI Connect and with the GasBench II System coupled to the DeltaXP Mass Spectrometer.

Two batches with three replicates of each sample were measured using the Delta Ray IRIS with URI Connect. Repeatability (three aliquots of one sample) was better than 0.05‰ (MIN = 0.01‰; MAX = 0.13‰).

When comparing the IRMS and IRIS methods, the average of absolute difference is 0.2‰ with minimal difference of 0.03‰ and maximal difference of 0.73‰ (Figure 8).

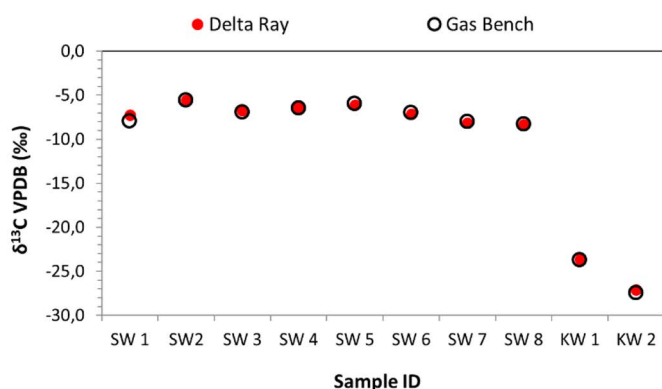


Figure 8. $\delta^{13}\text{C}_{\text{DIC}}$ values of water samples measured using the Delta Ray IRIS with URI Connect (marked in red) and the GasBench II System (marked in black)

Conclusions

We presented preliminary results of comparing traditional IRMS and newly developed IRIS methods for $\delta^{13}\text{C}$ measurements. Both methods show high accuracy and precision when measuring $\delta^{13}\text{C}$ 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 new option of performing high precision isotopic measurements in the laboratory as well as in the field.

References

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