



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

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For many decades different instrumental methods, involving generations of the Thermo Fisher Scientific isotope ratio mass spectrometers with Kiel Carbonate device, and the continuous flow Gas Bench II 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) Analyzer 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. Delta Ray IRIS 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 $4.3 \mu\text{m}$. 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. The system can measure up to 100 samples per day, with a $\delta^{13}\text{C}$ precision better than 0.15‰ .

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

We analyzed carbonate material of several different calcifying organisms and seawater samples collected from coral culturing tank at GEOMAR. The preparation of the samples for analysis on the Delta Ray IRIS is similar to the previously mentioned Gas Bench II method. Both carbonate and water samples were acidified using a few droplets of 104% H_3PO_4 and left for equilibration to finish. Carbonates were measured at 80°C while water samples were measured at room temperature. Sample processing was identical. The CO_2 gas generated by reaction was flushed into the Variable Volume inside the URI Connect through the Nafion based built-in water trap. As part of the workflow, reference gas was regularly measured at the same concentration as the sample to allow automatic drift and linearity correction. Sampling and measurement procedure were driven automatically from Qtegra Software. With each batch of samples, NBS 18 and IAEA-603 were measured and used as reference material for calibration. The obtained isotope ratios for NBS 18 and IAEA-603 were averaged and used to generate two-point calibration curves for the $^{13}\text{C}/^{12}\text{C}$ ratio. The calibration function was then applied to measured isotope ratios of the samples.

Results gained with above described method are in a good agreement with data obtained using traditional IRMS methods, performed in two independent laboratories in Kiel, Germany and Graz, Austria.