



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

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The isotopic composition of calcifying organisms is a key tool for reconstruction past seawater temperature and water chemistry. Therefore stable carbon and oxygen isotopes ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) in carbonates have been widely used for reconstruction of paleoenvironments.

Precise and accurate determination of isotopic composition of carbon (^{13}C) and oxygen (^{18}O) from carbonate sample with proper referencing and data evaluation algorithm presents a challenge for scientists. Mass spectrometry was the only widely used technique for this kind of analysis, but recent advances make laser based spectroscopy a viable alternative. The Thermo Scientific Delta Ray Isotope Ratio Infrared Spectrometer (IRIS) analyzer with the Universal Reference Interface (URI) Connect is one of those alternatives and with TELEDYNE Cetac ASX-7100 autosampler extends the traditional offerings with a system of high precision and throughput of samples.

To establish precision and accuracy of measurements and also to develop optimal sample preparation method for measurements with Delta Ray IRIS and URI Connect, IAEA reference materials were used. Preparation is similar to a Gas Bench II method. Carbonate material is added into the vials, flushed with CO_2 free synthetic air and acidified with few droplets of 104% H_3PO_4 . Sample amount used for analysis can be as low as 200 μg . Samples are measured after acidification and equilibration time of one hour at 70°C. The CO_2 gas generated by reaction is flushed into the variable volume inside the URI Connect through the Nafion based built-in water trap. For this step, carrier gas (CO_2 free air) is used to flush the gas from the vial into the variable volume with a maximum volume of 100 ml. A small amount of the sample is then used for automatic concentration determination present in the variable volume. The Thermo Scientific Qtegra Software 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 and linearity correction.

With described sample preparation and measurement method, samples are measured with standard deviation less than 0.1‰ $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, respectively and accuracy of <0.01‰. The system can measure up to 100 samples per day. Equivalent of about 80 μg of pure CO_2 gas is needed to complete an analysis. Due to its small weight and robustness, sample analysis can be performed in the field.

Applying new technology of Isotope Ratio Infrared Spectrometers in environmental and paleoenvironmental research can extend the knowledge of complex seawater history and CO_2 cycle.