

In-Situ $^{13}\text{C}/^{12}\text{C}$ Ratio Analysis in Water Carbonates using FTIR

Application Note

Environmental

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Introduction

Natural waters' carbon isotopes content is an important parameter in many environmental studies, as it hints to the water's origin and history. Atmospheric water contain a certain amount of dissolved carbon dioxide, in the form of oxygen, hydrogen and carbon through their various species (CO_2 , HCO_3^- & CO_3^{2-}), which are commonly used for isotopic characterization of natural water [1]. Carbon possesses two naturally occurring stable isotope, ^{12}C and ^{13}C with the abundance of 98.9% and 1.1% respectively ($^{13}\text{C}/^{12}\text{C} \sim 0.011$) and one radioactive isotope (1 atom per 10^{12} atoms of the carbon in the atmosphere) ^{14}C .

^{13}C delta values (δ) are calculated using the following equation:

$$(1) \quad \delta \text{ (in \%)} = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \cdot 1000$$

Where "R" represents the ratio between the heavy isotope (^{13}C) and the light isotope (^{12}C) in the sample and in the standard.

This study investigated the use of FTIR spectroscopy for the analysis of environmental carbon isotopes, using the standard MS method as a comparison. The FTIR analysis of CO₂ yields a peak between wavenumber 2,240 to 2,385 cm⁻¹ which contains the two isotopes: ¹²CO₂ and ¹³CO₂.

Instrumentation

Mass Spectrometer

A BALZERS model QMG421 quadrupole mass spectrometer has been used as a reference unit for the determination of stable isotopic content. The analysis of the CO₂ yields a peak at mass 44 amu that originates from ¹²C¹⁶O₂⁺ ion and a peak at mass 45 amu, which originates from ¹³C¹⁶O₂⁺ ion.

FTIR

The FTIR instrument used in this study is Agilent Technology's Cary 630 with a transmission sampling accessory (Figure 1).



Figure 1. Cary 630 FTIR with Transmission-Module .

The Agilent Cary 630 is a compact, robust, easy to use, high performance FTIR spectrometer. In addition to the sensitive and stable interferometer engine, the Agilent Cary 630 FTIR offers a series of customized sample interfaces which are rapidly interchangeable, while at the same time is engineered for optimum performance and ease of use. The innovative sampling technology is designed specifically for the Agilent Cary 630 spectrometer, affording both sensitivity and versatility to handle the widest array of samples. The transmission module provides the classic IR sample interface, and allows for the measurement of solids, liquids or gases.

The Cary 630 used in this study had a KBr beam splitter and a deuterated triglycine sulfate (DTGS) detector.

Materials

Standards samples were prepared using calcite (a-b), sodium carbonate and pure CO₂ gas. Calcite from two sources was used as a standard (a) or as internal standards (b):

(a) IAEA-CO-8, Calcite reference material IAEA-CO-8 is a natural carbonatite originating from Schelingen at the Kaiserstuhl, Germany.

(b) Fine CaCO₃ powder from local limestone of the Weradim formation (Judea group, Israel).

Sodium carbonate, Na₂CO₃ AR grade (supplied by Merck), was used as an internal standard.

CO₂ gas, CP grade, was taken from a gas bottle (supplied by Oxygen and Argon Works LTD.) and was used as an internal standard.

All powders were dissolved with ultra-pure distilled water (UPDI) from a Dow Water & Process Solutions ion exchange system. The water resistance was 18.2 Mohm/cm at 25 °C, with TOC values lower than 5 ppb.

Experimental

MS measurements

A BALZERS model QMG421 quadrupole Mass Spectrometer was used as a reference unit for the determination of stable isotopic content. The analysis of CO₂ yields a peak at mass 44 amu which originates from ¹²C¹⁶O₂⁺ ion and a peak at mass 45 amu which originates from ¹³C¹⁶O₂⁺ ion.

The sampling reactor was filled with 20 mL of sample solution, via the septa. It was then frozen at 77K (using liquid nitrogen) and the air was pumped via a vacuum line. Concentrated hydrochloric acid was injected (1 mL) via the septa, and was frozen again (air residue was pumped out). Following this step, the frozen sample was melted by heating to room temperature. The resultant reaction between carbonates in the sample and acid released CO₂ gas to the reactor. Finally, the gas sample was injected into the MS for analysis at 5 × 10⁻⁶ mbar, via a special leak valve. The background measurement was carried out at high vacuum of 7 × 10⁻⁸ mbar.

FTIR measurements

A similar sample preparation procedure was used for the FTIR measurements, as shown in Figure 2. The first step was to eliminate the ~400ppm atmospheric CO₂ by setting it as background.

To do this, the FTIR gas cell was emptied, and then opened to atmospheric air, closed, and measured as background. A glass sampling bulb with a magnet was then filled with 80 mL

sample solution, and attached to an empty FTIR gas cell. Concentrated hydrochloric acid was added (4 mL) and the solution was stirred for 1-2 minutes (The valve between the cell and the reactor was closed). The released carbon dioxide was transported from the sampling bulb to the cell (by opening a connecting valve) – the CO₂ degassing from the solution lasted ~ 2-3 minutes. The cell was reattached from the reactor (all the cell valves were closed). The FTIR was operated using 2 cm⁻¹ resolution, 100 scans (for background and sample measurements).

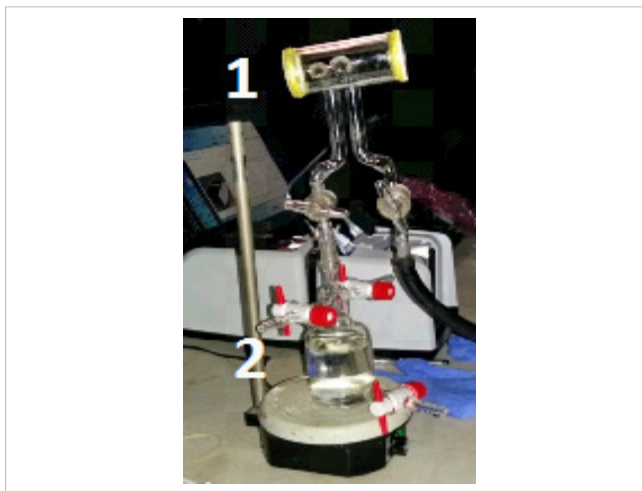


Figure 2. Sampling system for gas analysis in the FTIR (1. Gas cell; 2. Sampling reactor)

Results

A typical IR spectrum of CO₂ is shown in Figure 3. The easily recognized doublet consists of the P-branch (2345 cm⁻¹) and the R-branch (2365 cm⁻¹) representing the ¹²CO₂ absorption. The small peak at 2275 cm⁻¹ represents the P-branch of the ¹³CO₂ absorption. The R-branch of ¹³CO₂ is masked underneath the ¹²CO₂ P-branch, which introduces difficulty when calculating the ¹³C/¹²C ratio using peak area. While the peak area ratio calculation is usually more accurate and commonly used, it could not be used in this case due to the masking of the ¹³CO₂ R-branch.

Alternatively, the height ratio of the most representative ¹³CO₂ and ¹²CO₂ peaks was chosen for the calculations. In order to determine a calibration factor, it was needed to establish which wavenumber is most representative. For this purpose, five potential wavenumber points were tagged with numbers 1-5 for further evaluation.

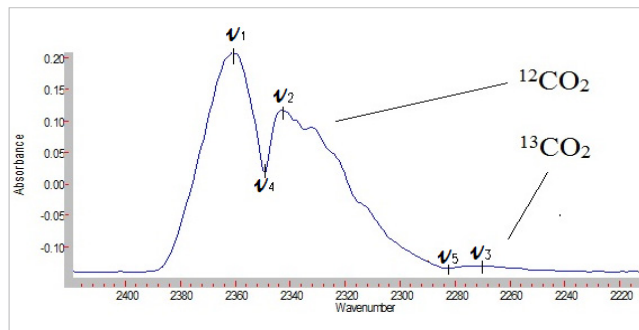


Figure 3. FTIR Spectrum of CO₂ gas representing isotopes of ¹³C and ¹²C ($\nu_1=2361$ cm⁻¹, $\nu_2=2343$ cm⁻¹, $\nu_3=2273$ cm⁻¹, $\nu_4=2350$ cm⁻¹, $\nu_5=2285$ cm⁻¹)

In order to calculate the FTIR samples calibration factor, data from MS was used as standard. The MS calculations of ¹³CO₂ / ¹²CO₂ ratio were done by dividing the signal in mass 45 amu to the signal in mass 44 amu. The results of the ratio values from the MS (MS ratio) are given in Table 1 for three different sources of carbon: Na₂CO₃, CaCO₃ Weradim, CO₂ (Gas) and CaCO₃ IAEA (standard), the results of the ¹³CO₂ / ¹²CO₂ ratio were in the range of 0.0115-0.0121.

Table 1. ¹³C ratios from the MS of the 3 carbon sources and IAEA standard.

	Na ₂ CO ₃	CaCO ₃ Weradim	CO ₂ (Gas)	CaCO ₃ IAEA (Standard)
MS ratio	0.0121	0.0119	0.0115	0.0117

In order to choose the best peak ratio from the five wavenumbers, it was necessary to estimate which ratio provided the best calibration factor. The calibration factor (f) was calculated by dividing each absorption value at certain wavenumber in the sample (carbon source) and in the standard (IAEA) – this is noted as α^{FTIR} . This was then divided by α^{MS} – the ratio of the signals 45/44 amu in the sample and the standard from the MS data. The result that gave the best value of $f_i/f_j = 1$ was used for the calculation of the calibration factor. Thus, the measurements at $\nu_2=2343$ cm⁻¹ and $\nu_3=2273$ cm⁻¹ were used for the ¹³C/¹²C determination [$\nu_{(2/3)}$].

Once the best peak ratio was determined (meaning the closest $f_i/f_j=1$), calculation of the average calibration factor was done as shown in Table 2. In order to establish the standard calibrated values, the calcite value was aligned to the IAEA-CO-8 standard [2]. In order to correlate the FTIR values to those determined by the MS method, the MS standard ratio (0.0117) was used for calibration factor (f) calculation (Table 2). In the next stage, δ values were calculated both for the MS and for the FTIR. MS δ calculation consisted of the ratio between the signals in mass 45 and 44 amu in both the sample and the standard (α^{MS}). For FTIR, the ratio was calculated between peaks 2 to 3 (Figure 3), both in the sample and in the standard (α^{FTIR}) and then multiplied by the calibration factor (f).

Table 2. Calculation of calibration factor (f) and δ from the 3 carbon sources.

Name of sample	CO ₂ Gas	Na ₂ CO ₃	CaCO ₃ Weradim	CaCO ₃ IAEA (standard)
FTIR ratio	29.11	30.69	30.08	30.14
MS ratio	0.0115	0.0121	0.0119	0.0117
α^{FTIR}	0.9658	1.0182	0.998	
α^{MS}	0.9829	1.0342	1.0171	
f	1.0177	1.0157	1.0191	
FTIR in ‰	-17.28	36.05	15.46	
MS in ‰	-17.09	34.19	17.09	
Error in ‰	0.1904	1.8663	1.6325	

Average Calibration factor $f = 1.0175$

Discussion

While determining the abundance of ¹³C isotopes in CO₂ using MS is common practice, it also demands special sampling procedures and the transportation of the sample to the laboratory for analysis. Both actions may produce an inherent difference from the measured in-situ values [3]. While in-situ field applications of MS techniques are complex and expensive, there are several IR-spectroscopy-based devices under ongoing development.

This study aimed to develop and evaluate a FTIR-spectroscopy-based methodology for environmental isotope analysis. The methodology presented in this study requires a simple portable FTIR device and a pump to transfer the water sample, which was measured directly. Data processing was done by a simple calibration factor, to correct the FTIR results with the atomic weight values (based on MS data). Other studies e.g. Mohn et al. 2008, used a PLS-based calibration strategy [4], classical least squares method [5], or non-linear least squares using the program MALT [6].

The CO₂ which is released from the carbonate reaction with the acid, is in relatively high concentration (almost 60 times

higher than its concentration in air) which ensures an accurate and sensitive analysis. The main problem with ¹³C determination using FTIR spectroscopy is that the strong ¹²CO₂ P-branch masks the low intensity ¹³CO₂ R-branch.

Because of this, the isotope ratio calculations used the peak height values (absorbance intensity values) instead of area calculation.

The main challenge during the study was the accurate determination of the ¹³C absorbance best ν_s wavelength (Figure 3). The best ν ratio was found to be between ν_2 (2345 cm⁻¹) and ν_3 (2275 cm⁻¹), which showed the best reproducibility (Table 2). Nevertheless, it is different from that determined in the MS measurement and thus a calibration factor was needed. The difference between MS and FTIR might be caused by height calculation that does not take into consideration all of the impacts of the two isotopes disparity, as area calculation will do. Owing to that, a calibration factor was determined ($f = 1.0175$). The error between the two methods was calculated and showed a maximum deviation of $\pm 1.87\%$ (Table 2) which is an acceptable error for carbon isotope analysis.

Conclusion

A method for in-situ measurements of ¹³C/¹²C isotope ratio using a simple and affordable Agilent Cary 630 FTIR spectrophotometer was developed.

The method involves the application of a calibration factor for the FTIR measurements. This factor was calculated from three sources of carbon ($f = 1.0175$), but it is advised to calculate a singular factor for any specific carbon reservoir.

The difference between the results of the FTIR method and those measured with the MS method that is usually used for such measurements, was only 1.87% in δ values, which is acceptable in most environmental processes.

References

- (1) Mook, W. G. Environmental isotopes in the hydrological cycle. *Technical documents in hydrology*, **2000**, pp 1–291.
- (2) Riaux, C. G.; Carney, P. C.; Suchodolski, J. S.; Steiner, J. M. New IUPAC guidelines for the reporting of stable hydrogen, carbon, and oxygen isotope-ratio data. *J. Res. Natl. Inst. Stand. Technol.* **1995**, 100 (3), 285 DOI: 10.1111/j.1939-1676.2011.00858.x.
- (3) Rodriguez-Escales, P.; Folch, A.; Vidal-Gavilan, G.; van Breukelen, B. M. Modeling biogeochemical processes and isotope fractionation of enhanced in situ bionitrification in a fractured aquifer. *Chem. Geol.* **2016**, 425, 52–64 DOI: 10.1016/j.chemgeo.2016.01.019.
- (4) Mohn, J.; Zeeman, M. J.; Werner, R. a; Eugster, W.; Emmenegger, L. Continuous field measurements of delta(13) C-CO(2) and trace gases by FTIR spectroscopy. *Isotopes Environ. Health Stud.* **2008**, 44 (3), 241–251 DOI: 10.1080/10256010802309731.
- (5) Griffith, D. W. T.; Jamie, I.; Esler, M.; Wilson, S. R.; Parkes, S. D.; Waring, C.; Bryant, G. W. Real-time field measurements of stable isotopes in water and CO₂ by Fourier transform infrared spectrometry. *Isotopes Environ. Health Stud.* **2006**, 42 (1), 9–20 DOI: 10.1080/10256010500503098.
- (6) Vardag, S. N.; Hammer, S.; Sabasch, M.; Griffith, D. W. T.; Levin, I. First continuous measurements of δ¹⁸O-CO₂ in air with a Fourier transform infrared spectrometer. *Atmos. Meas. Tech.* **2015**, 8 (2), 579–592 DOI: 10.5194/amt-8-579-2015.

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