FDM based OA-ICOS for high accuracy 13C quantification in gaseous CO2

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Abstract: The wide-range applications of isotope analysis make isotope measurement approaches under attentive focus. Off-axis integrated cavity output spectroscopy technology (OA-ICOS) is the most advanced isotope analysis method; however, further studies are still needed to avoid signal noise and improve accuracy. Zero-phase low pass filtering multivariate Fourier Decomposition Method (FDM) was applied for data analysis in the present study, which has its unique advantage to fix up rapid but seasonal changes for nonlinear and non-stationary time series data. In the present study, δ13C content in gaseous CO2 sample were measured by OA-ICOS at ambient temperature. The experimental data treated by FDM showed less signal fluctuant and clearer value change tendency than what showed in raw data, whereas the data density kept same with that of raw data. In the meantime, the experimental results suggested that it is flexible to decide the variance explanation rate by simply change the order of an FDM filter. This approach meets up with the requirements of different practical application scenarios of isotope analysis, which enhances the feasibility for OA-ICOS application in real-time environmental monitoring field.

1. Introduction
Isotope analysis has been widely used for environmental issues, because of its stable and clear explanation for both cross-sectional study and longitudinal study. Stable 13C can be exploited as intrinsic biochemical markers for marine live track over large geographical distances [1]. Detrital zircon U-Pb system presents great performance in processes of subduction erosion and underplating [2].

Because of its diverse applications, approaches for isotope measurement have been studied in the last several decades [3]. One new technology called Off-Axis Integrated Cavity Output Spectroscopy technology (OA-ICOS) is now one of the most advanced isotope analysis approaches, which is based on directing the laser beam off axis with respect to the cavity which provides low drift, high precision and minimal downtime [4].

Comparing with the commonly used method called Isotope-ratio mass spectrometry (IRMS), ICOS owns following advantages. OA-ICOS shows higher accuracy in isotope analysis and with significantly shorter maintenance time compared with IRMS, which shorten the measurement duration [5]–[7]. The pretreatment of ICOS involves no conversion of sample which results for easier data collection and lower cost [6]. Also, it is suitable for remote sensing due to its simple structure and can be applied for continuous flow configuration [7], [8].

However, due to the fact that the detection of OA-ICOS depends on laser and cavity, the laser intensity noise, detector noise and optical noise by cavity length dithering cannot be avoid [9], [10].
There are two major approaches to reduce such noises. One is to improve the design of ICOS which eliminates the noise during measurement [11]. The other is appropriate data pretreatment before analysis which reduce the noise mathematically.

For structure improvement, a three mirror setup which allows a third reinjection before the absorption cavity makes the signal-to-noise ratio be 10 times larger than original OA-ICOS [9], [12]. Such setup enhances the intensity and sensitivity of ICOS significantly. Compact cage-based absorption cell used in near-infrared OA-ICOS can realize a ~9.28 m effective optical path length while has only 6 cm cavity length, so that the optical noise can be reduced [13].

For data treatment, Membrane -ICOS method sets a delay time between sample extraction time and time that it reaches the module, which improves the measurement accuracy [14]. Allan variance curve plots the $\delta$13C – time relation where the time interval is determined by the Allan deviation. Allan deviation represents the information explanation rate in one certain time interval, which stabilize the data by eliminating the less important signal [15]. However, one major shortage of this approach is the information loss between two time interval points, which is eliminated during the above process.

In this study, Fourier Decomposition Method (FDM) was learned for the capability of signal stabilization in short time period. FDM shows its practicability for dealing with noise in output signal for a spectroscopy when applied to optical frequency comb spectroscopy [16]. But no research for now applied FDM in an OA-ICOS. In data analysis field, zero-phase low pass filtering multivariate FDM presents its unique advantage to fix up rapid but seasonal changes for nonlinear and non-stationary time series data [17], so that FDM can be one possible approach to avoid information loss such as in Allan deviation method.

To verify the practicability, zero-phase low pass filtering multivariate FDM was applied to the calibrated $\delta^{13}$C data collected from OA-ICOS. By bringing FDM into conventional data treatment method, OA-ICOS is possible to be applied for real-time environmental monitoring for learning contaminant sources, hydrology ecosystem, environmental microbiology, etc.

2. Materials and methods

2.1 Materials and Instruments

LGR’s OA-ICOS (LGR CCI2A-912) was used in the experiment to measure the $\delta^{13}$C in the CO$_2$ sample. The CO$_2$ sample was collected from the soda maker (SodaStream 1101098010). The container of sample was aluminum bags of 0.5 L volume. Deionized water is used for liquor confecting.

2.2 Experiment Setup

The experiments were conducted in hydro-laboratory at Fach Hochschule Luebeck, Germany, where it is a basement with constant temperature of 25 °C and pressure 1.02 atm during experiments and measurements.

For each measurement, 0.5 L CO$_2$ sample from soda maker was contained in an aluminum bag (IV in Figure.1) to keep the constant pressure, which avoid fractionation bias from pressure drop [18]. One CO$_2$ dilution system (see in Figure.1) which using 20% NaOH solution was introduced in the experiment to ensure the CO2 concentration below the up-limit of the OA-ICOS device, which is 50,000 ppm [19]. The dilute ratio was controlled at about 10:1 (air: CO$_2$).

The whole system was first running without aluminum bag IV to refresh the air in the system by indoor air, in which the isotope values in ambient air were measured for further calibration. Then the bag was connected to the system. The sample gas moving process was shown as follow: The ambient air got into the system from tube 1, where the CO$_2$ was removed through 20% NaOH solution. Then the gas moved through the safety bottle II and mixing bottle III, in which it mixed up with CO$_2$ sample gas from aluminum bag. The screen showed the change of $\delta^{13}$C value for the mixed gas in bottle III.

When the $\delta^{13}$C value keeps constant (vary in range of 0.3 per mil) for about 5 minutes, one measurement was finished. Between each measurement, the system was refreshed to avoid the influence from sample gas that the last measurement remained.
Figure 1. Set-up for measurement. I represents 20% NaOH solution; II represents safety bottle aim to avoid liquid leaking into the analyzer; III mix up air and CO$_2$ sample (max. concentration 45000pm) at a ratio of 10:1 (air : CO$_2$); IV is an aluminum bag filled up with 0.5 L CO$_2$ sample; V represents OA-ICOS device.

2.3 Data processing
Before applying FDM to the $\delta^{13}$C data, calibrations should be done to compensate the measurement error. Routine calibration, which calibrated for concentration-dependent error when certain volume of CO$_2$ gas was used in the experiment, were carried out by the correcting formula from Hagedorn (2019), which works well for highly varying CO$_2$ concentration like in this case [20]. Another major calibration was for the offset introduced by the Off-Axis Integrated Cavity Output Spectroscopy due to the ambient CO$_2$ concentration change in different time period. Matplotlib package is used for figure plotting [21].

Then the zero-phase low pass filtering multivariate FDM was applied to the calibrated data to remove signal noise and give clear relation between $\delta^{13}$C and time interval. The FDM used is supported by Scipy package [22].

3. Results and discussion

3.1 Raw data from OA-ICOS
The changes in $\delta^{13}$C value with time is shown in Figure 2. The measurements of $\delta^{13}$C change are repeated 3 times and present similar results. There is one obvious change tendency between $\delta^{13}$C and time: $\delta^{13}$C first decreases from about -20‰ to -24‰ in the 100 sec, then the value keeps increasing to around -13‰, after about 12 min, the $\delta^{13}$C value decreases a little bit. Such tendency comes into being mainly because of the diffusive fractionation.

This fractionation occurs when diffusive velocities are different between isotopes[18]. The fractionation factor given by Graham’s Law can be shown as Eq. (1):

$$\alpha_{m^*-m} = \frac{v^*}{v} = \sqrt{\frac{kT}{2\pi m^*}} = \sqrt{\frac{m}{m^*}}$$  \hspace{1cm} (1)

Where $\alpha$ is fractionation factor, $v$ is molecular velocity (cm • s$^{-1}$), $k$ is Boltzmann constant which equals to n • 1.380658 • 10$^{-23}$ JK$^{-1}$, $m$ refers to molecular mass, $T$ is absolute temperature K.
$^{12}\text{C}$ has a higher velocity since the atomic mass is 12u, where the atomic mass for $^{13}\text{C}$ is 13.0034u, so that the molecule (CO$_2$) with $^{12}\text{C}$ has higher velocity. It comes to the ICOS first, which decreases the $\delta^{13}\text{C}$ value, then $^{13}\text{C}$ comes to the device to get a higher $\delta^{13}\text{C}$ value. The end condition is that all CO$_2$ in the aluminum bag runs into ICOS, the only gas source for measurement is the ambient air without CO$_2$ in it. Thus, the $\delta^{13}\text{C}$ value keeps constant. However, Figure 2 shows in the first 2 measurement, $\delta^{13}\text{C}$ value decreased a little bit after about 12 min.

\[ \text{Diff}\cdot \delta^{13}\text{C} = a\times (b - \exp(-c\times [\text{CO}_2])) \]  

where the constants $a$, $b$ and $c$ are 31.007, 0.713 and 0.000043, respectively. [CO$_2$] represents CO$_2$ concentration in ppm. Diff-$\delta^{13}\text{C}$ is the different between measured $\delta^{13}\text{C}$ and the calibrated $\delta^{13}\text{C}$ in unit of per mil.

The calibrated $\delta^{13}\text{C}$ value becomes 0 at the end of measurement. It is reasonable since the only air source has no CO2 at this time. The calibrated data show no decrease in the end, which means the CO2 concentration change is the cause of it. This found is consistent with the conclusion from Sprenger(2017) that CO2 concentration has no significant impact to stable isotope analyses with off-axis integrated cavity output spectroscopy.

Figure 2. $\delta^{13}\text{C}$ change with time, repeated 3 times

3.2 Instrument calibration and correction

The uncalibrated $\delta^{13}\text{C}$ was measured under changing CO$_2$ concentration ranging from 700 to 45000 ppm. It was then calibrated according to the correction model proposed by Hagedorn et al. [20]. The formula is shown as follow:

The calibrated $\delta^{13}\text{C}$ – time plot is shown as Figure 3. The calibrated data show that that the $\delta^{13}\text{C}$ value becomes 0 at the end of measurement. It is reasonable since the only air source has no CO2 at this time. The calibrated data show no decrease in the end, which means the CO2 concentration change is the cause of it. This found is consistent with the conclusion from Sprenger(2017) that CO2 concentration has no significant impact to stable isotope analyses with off-axis integrated cavity output spectroscopy.

Figure 3. $\delta^{13}\text{C}$ calibration
3.3 Signal noise remove
With $\delta^{13}$C change data, the overall trend in the data was focused in this study. Thus, frequency filters were applied to remove the interfering fluctuant in data. The zero-phase low pass filter was applied to the calibrated $\delta^{13}$C value. In this paper, the order of the filter was set to 5, which means the maximum number of delay elements used in the filter circuit is 5. And the sampling rate and cutoff are set to 1 and 0.05, respectively. These three hyperparameters can be change depend on how much information from raw data needs to remain, which is decided by the application scenarios. The filtered data are shown in Figure 3.

The figure infers that zero-phase low pass filter is suitable for OA-ICOS to remove the signal noise, especially when learning value change in a relatively small time interval, in which the Allen curve cannot be used. Nevertheless, the accuracy of this method cannot be calculated from the experiment, mainly because the sample used was collect from soda maker without a certified concentration. The exact value for $\delta^{13}$C at the start was not determined. To get reliable quality control, the reference material such as VPDB should be used as standard sample. The comparation with Allen curve can present the performance of FDM, which is also needed before practical application.

4. Conclusion
In the present study, $\delta^{13}$C content in gaseous CO$_2$ sample were measured by OA-ICOS at ambient temperature, and FDM was utilized for data analysis. Based on experimental results, FDM has been proved to be a remarkable simple and effective approach for eliminating the signal noise and increasing accuracy for OA-ICOS. Its flexible adjustment makes it suitable for different kinds of practical application scenarios of isotope analysis, especially in real-time environmental monitoring field. However, further researches using reference isotope material need to be done for quality control and uncertainty evaluation of the FDM method.

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