

## $\delta^{13}\text{C}$ Analysis of Bulk Organic Matter via EA-IRMS

### 1. Introduction

The determination of the  $^{13}\text{C}/^{12}\text{C}$  ratio on bulk compounds (SARA fractions, kerogen, whole oil, etc.) historically has been used as an indicator of depositional environment, oil-oil, and oil- source rock correlations (Sofer, 1984). In order to provide timely, accurate and precise carbon isotope analyses, the latest continuous-flow technology is utilized to link an elemental analyzer to a modern isotope ratio mass spectrometer. All stable isotope methods employed by the Energy Geochemistry Laboratory follow the best practices and procedures as detailed in peer-reviewed literature.

### 2. Interfaces with Other Methods

- a. EGL Method 04: Fractionation of Oil or Bitumen by Column Chromatography and Gravimetric Determination of Saturated, Aromatic, Resin, and Asphaltene Compounds
- b. EGL Method 25: Method for Sample Login, Control, and Disposition

### 3. Materials and Equipment

**Instruments:** Thermo Fisher Flash 2000 EA<sup>1</sup>  
Thermo Fisher ConFlo IV  
Thermo Fisher MAT253 IRMS

**Materials:** UHP helium  
UHP oxygen  
For a listing of EA required materials refer to:  
Organic Elemental Analysis Flash 2000 Elemental Analyzer  
Operating Manual, May 2012, pg. 34

### 4. Procedure

---

<sup>1</sup> Any use of trade names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

A sample (0.2 to 0.6 mg in a folded tin boat) is introduced into a Thermo Fisher Flash 2000 EA (see pictures 1 and 2) through a zero blank autosampler. Flow rate is typically 80 ml/min. The sample is flash combusted at 1030 °C in a stream of oxygen. The resulting eluent passes over hot copper at 600 °C to remove excess oxygen and convert NO<sub>x</sub> to N<sub>2</sub>. The sample is then passed through a magnesium perchlorate trap to remove water and finally through a CarboSieve G™ column (@90°C, 1 meter in length by 5mm OD) for CO<sub>2</sub> separation. The final analyte CO<sub>2</sub> is passively drawn via open split into the source of a Thermo Finnigan-MAT253 isotope ratio mass spectrometer for subsequent carbon isotope analysis (Carter and Barwick , 2011).

## 5. Calibration and Quality Control Samples

Carbon isotope values from the instrument undergo off-line isotope corrections for drift (as many batch runs take many hours to complete), for isotopic linearity due to any systematic error in the auto-sampler, chromatographic and oxidation processes (<sup>13</sup>C vs amount), and finally are normalized on the vPDB (PeeDee Belemnite) scale using two well-calibrated, working laboratory standards (after Paul et al., 2007). On average, for every 24 samples run in replicate (n = 2, 48 total determinations), ~8 or more analyses of standards are performed to ensure proper analytical calibration. The final carbon isotope values represent the average of multiple replicate analyses (generally, n=2) with a standard deviation of generally less than 0.2 per mil. The accuracy of stable isotope measurements historically is not specified, neither by commercial laboratories nor instrument manufacturers. That said, as we utilize two-point calibrations, our estimated accuracy is generally better than 2 times our precision, or ± 0.4 ‰. All final δ<sup>13</sup>C values are reported relative to the international standard, Pee Dee Belemnite Carbonate (PDB).

## 6. Limits, Precautions, and Interferences

Sample size is dependent on carbon content; because these samples are essentially all hydrocarbons, sample and standard size is approximately 0.2 to 0.6 mg. High temperature furnaces present a potential burn hazard.

## 7. Acceptance of Data

Data are deemed acceptable if CO<sub>2</sub> peak response (area/height) and working isotopic standards are within acceptable parameters (e.g, accuracy and precision). Replicate analyses are usually better than 0.2 ‰ standard deviation.

## 8. Data Handling and Transfer

Data is compiled for the EGL database as follows: Sample ID,  $\delta^{13}\text{C}_{(\text{PDB})}$ , std, n; where Sample ID is the sample job ID, Parameters are what has been analyzed,  $\delta^{13}\text{C}_{(\text{PDB})}$  is the average carbon isotope value for the sample component, std is the standard deviation of replicate analyses and n is the number of replicate analyses. An example of a final results data table is shown below.

Sample ID	Parameters	Date Run	Number of Runs	Std Dev	Result
asparagine-5694	C13 Solid Organic	6/30/2014	4	0.06	-24.56
E131001-001	C13 Aromatic	6/30/2014	2	0.06	-26.85
E131001-002	C13 Aromatic	6/30/2014	2	0.08	-26.93
E131001-003	C13 Aromatic	6/30/2014	2	0.03	-29.42
E131001-004	C13 Aromatic	6/30/2014	2	0.02	-29.29
E131001-005	C13 Aromatic	6/30/2014	2	0.04	-29.42
E131001-006	C13 Aromatic	6/30/2014	2	0.01	-29.4

Finally, data are submitted to the USGS Geochemical Database for general dissemination as per Energy Geochemistry Laboratory QA protocols.

## 9. References

Sofer, Z. (1984) Stable Carbon Isotope Compositions of Crude Oil: Application to Source Depositional Environments and Petroleum Alteration. The American Association of Petroleum Geologists Bulletin, 68/1, p. 31-49.

Carter, J.F. and Barwick, V.J. (Eds), Good practice guide for isotope ratio mass spectrometry, FIRMS (2011). ISBN 978-0-948926-31-0.

Paul, D., Skrzypek, G. and Forizs, I., (2007) Normalization of measured stable isotopic compositions to isotope reference scales – a review. *Rapid Communications in Mass Spectrometry*, v. 21, p. 3006-3014.

## **10. Attachments**

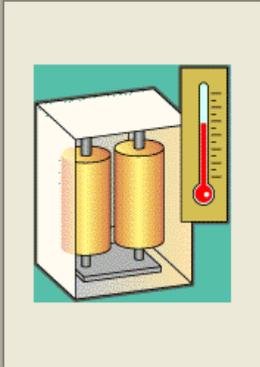
Attachment 1: Flash Method Temperature Screen  
Attachment 2: Flash Method Flow/Timing Screen

## **11. History of Changes**

R0: Initial Issue

**Flash Method**

Temperature | Flow / Timing | Detector



**Furnaces**

Left Furnace:  1020 °C

Right Furnace:  600 °C

**Oven**

Oven:  90 °C

**Other**

Set Instrument to Stand-By:

Get Send Help

Get the method settings from the EA

