# $\delta^{13}C$ and $\delta^{15}N$ isotopic analysis of solid materials

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Overview:

Analyses of $\delta^{13}C$, wt%C, $\delta^{15}N$ and wt%N of solid matter are done using Continuous Flow-Elemental Analysis-Isotope Ratio Mass Spectrometry (CF-EA-IRMS) technology. In the ISL-AGg, a Thermo DeltaV$^{Plus\,®}$ mass spectrometer is interfaced with either an Elementar *Isotope CUBE*® or Costech *4010*® elemental analyzer via a ConfloIV® device. All materials (RMs, QA/QCs and unknowns) are packed in tin cups of varying and appropriate size, which are dropped by auto sampler onto a quartz tube combustion reactor. The temperature of this reactor is maintained at ~1000$^{o}$C and 'flash-combustion' is achieved by injecting a pulse of $O_2$(gas) exactly at the time of sample drop. The eluent gases are then swept by the helium carrier stream through a reduction reactor (~650$^{o}$C), thus reducing $NO_x$ species to $N_{2(gas)}$. GC separation of $N_2$ and $CO_2$ is achieved before the gas stream is leaked through the Conflo-IV open split into the ion source of the mass analyzer. $\delta^{13}C$ and $\delta^{15}N$ values are determined by comparing the respective sample peak areas, as [Vs], to reference gas peaks also inlet through the open split. For materials with widely varying [C:N] ratios, $\delta^{13}C$ and $\delta^{15}N$ analyses must be done separately. For samples whose C:N ratio approaches [3:1] (i.e. bone collagen) the peak jumping feature of the mass spectrometer can be used and a single sample suffices. These instruments are fully automated and computer controlled using ISODAT 3.88 software. Prior to sample analysis instrument conditions: reactor temperature(s), carrier gas flows, ion beam background(s), ion source stability and signal linearity are checked and recorded ("*Daily check*" routine).

Stable isotope ratios are expressed as delta (δ) and are measures of a 'per mill' (‰), or parts per thousand difference between the isotope ratio of a sample and that of a known (International) standard material. Values are reported relative to 'Vienna Peedee Belemnite' (VPDB) formation for Carbon (Craig, 1957) and 'Atmospheric air' for Nitrogen (Air-$N_2$).

**Internal lab standards:**

| Standard | Supplier | Prod. # | Formula |
|---|---|---|---|
| Caffeine | Sigma Aldrich | C-0750 | $C_8H_{10}N_4O_2$ |
| Gelatin | Sigma Aldrich | G-9382 | unknown |
| Glycine | MP Biomedicals | 100570 | $C_2H_5NO_2$ |
| Keratin | MP Biomedicals | 902111 | unknown |

**International standards**:

| Identifier | $\delta^{13}C$ (‰)$_{VPDB}$ | $\delta^{15}N$ (‰)$_{Air\text{-}N2}$ |
|---|---|---|
| USGS 24 | -16.0 ± 0.1 | |
| IAEA-CH-6 | -10.4 ± 0.2 | |
| IAEA-CH-7 | -31.8 ± 0.2 | |
| NBS 22 | -30.03 ± 0.2 | |
| USGS 40 | -26.39 ± 0.2 | -4.52 ± 0.2 |
| USGS 41 | 37.63 ± 0.2 | +47.57 ± 0.2 |
| USGS 25 | | -30.40 ± 0.2 |
| USGS 26 | | +53.70 ± 0.2 |
| USGS 34 | | -1.80 ± 0.2 |
| USGS 35 | | +2.70 ± 0.2 |
| IAEA N1 | | +0.43 ± 0.2 |
| IAEA N2 | | +20.32 ± 0.2 |
| IAEA $NO_3$ | | +4.69 ± 0.2 |

- Internal lab standards are used at the beginning, between (~ every 5th) and the end of each sequence to correct for instrument drift and to normalize the data to internationally accepted standards
- Six (6) replicates of different weights are placed near the beginning of each sequence to allow for element wt.% determination and 'non-linearity' correction
- Internal lab standards have been characterized against the International Standards listed above and are re-checked periodically
- USGS LIMs is used for drift correction, normalization and data management. (http://water.usgs.gov/software/LIMS/)

Accuracy and Precision:

$\delta^{13}$Corganic ± 0.2 per mil (n=10 internal lab standards)
$\delta^{15}$Norganic ± 0.2 per mil (n=10 internal lab standards)
Elemental wt%C, wt%N and C/N ratio = ± 5%

References:

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R.A. Werner and W.A. Brand, Referencing strategies and techniques in stable isotope ratio analysis, Rapid Communications in Mass Spectrometry, 2001: 15: 501-519

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