



New Organic Stable Isotope Reference Materials for Distribution through the USGS and the IAEA

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The widespread adoption of relative stable isotope-ratio measurements in organic matter by diverse scientific disciplines is at odds with the dearth of international organic stable isotopic reference materials (RMs). Only two of the few carbon (C) and nitrogen (N) organic RMs, namely L-glutamic acids USGS40 and USGS41 [1], both available from the U.S. Geological Survey (USGS) and the International Atomic Energy Agency (IAEA), provide an isotopically contrasting pair of organic RMs to enable essential 2-point calibrations for δ -scale normalization [2, 3]. The supply of hydrogen (H) organic RMs is even more limited. Numerous stable isotope laboratories have resorted to questionable practices, for example by using 'CO₂, N₂, and H₂ reference gas pulses' for isotopic calibrations, which violates the principle of identical treatment of sample and standard (i.e. organic unknowns should be calibrated directly against chemically similar organic RMs) [4], or by using only 1 anchor instead of 2 for scale calibration. The absence of international organic RMs frequently serves as an excuse for indefensible calibrations. In 2011, the U.S. National Science Foundation (NSF) funded an initiative of 10 laboratories from 7 countries to jointly develop much needed new organic RMs for future distribution by the USGS and the IAEA.

The selection of targeted RMs attempts to cover various common compound classes of broad technical and scientific interest. We had to accept compromises to approach the ideal of high chemical stability, lack of toxicity, and low price of raw materials. Hazardous gases and flammable liquids were avoided in order to facilitate international shipping of future RMs. With the exception of polyethylene and vacuum pump oil, all organic RMs are individual, chemically-pure substances, which can be used for compound-specific isotopic measurements in conjunction with liquid and gas chromatographic interfaces. The compounds listed below are under isotopic calibration by the 10 laboratories. Successfully calibrated organic RMs could become available as early as 2015.

- n-Hexadecane (C₁₆ n-alkane), three H, C-isotopic varieties;
- Glycine (amino acid), three H, C, N-isotopic varieties;
- L-valine (amino acid), three H, C, N-isotopic varieties;
- Methyl n-heptadecanoate (methyl ester of C₁₇ n-alkanoic fatty acid);
- Methyl icosanoate (methyl ester of C₂₀ n-alkanoic fatty acid), three H, C-isotopic varieties;
- Caffeine, three H, C, N-isotopic varieties;
- Hydrocarbon vacuum pump oils, two H-isotopic varieties;
- Polyethylene powder, and possibly a 2H and 13C-enriched polyethylene string.

[1] Qi H., Coplen T.B., Geilmann H., Brand W.A., Böhlke J.K. (2003) Two new organic reference materials for $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ measurements and a new value for the $\delta^{13}\text{C}$ of NBS 22 oil. *Rapid Communications in Mass Spectrometry* 17, 2483-2487. [2] Coplen T.B. (1996) New guidelines for reporting stable hydrogen, carbon, and oxygen isotope-ratio data. *Geochimica et Cosmochimica Acta* 60, 3359-3360. [3] Coplen T.B., Brand W.A., Gehre M., Gröning M., Meijer H.A.J., Toman B., Verkouteren R.M. (2006) New guidelines for $\delta^{13}\text{C}$ measurements. *Analytical Chemistry* 78 (7), 2439-2441. [4] Werner R.A., Brand W.A. (2001) Referencing strategies and techniques in stable isotope ratio analysis. *Rapid Communications in Mass Spectrometry* 15, 501-519.