

Development of H, C, N, O stable isotope reference materials at Indiana University

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The development of continuous flow GC-pyrolysis-IRMS for determination of organic compound-specific D/H ratios by John M. Hayes' group at Indiana University more than 10 years ago prompted the need for pure organic stable isotope reference compounds for calibration. Before the introduction of modern continuous flow EA-IRMS methods, the only way to measure stable isotope ratios of organic compounds was to process multi-milligram aliquots off-line using sealed combustion ampoules, vacuum lines for cryogenic preparation of pure analyte gases (CO₂, N₂, H₂), and subsequent manual dual-inlet mass spectrometry. Although time-consuming and cumbersome, these traditional techniques still offer more accurate isotopic characterization of organic materials than modern continuous flow methods, because off-line work can often strictly adhere to the "principle of identical treatment" of organic unknown samples and primary international stable isotope standards, such as VSMOW and SLAP. In the case of hydrogen, only compounds with no exchangeable hydrogen qualify as D/H reference materials. Water produced by combustion is reduced over 800°C uranium metal turnings and the resulting H₂ gas is collected with a Toepler mercury pump. VSMOW and SLAP are reduced, collected, and measured in exactly the same way. Other traditional off-line techniques yield C, N, O isotope ratios. Since the initial development of a small matrix of n-alkanes and fatty acid methyl esters in 1999 as lab-internal D/H and ¹³C/¹²C reference materials, the collection of Indiana University reference materials has grown by popular demand over the years to include a wide variety of compounds for GC and EA continuous flow applications (<http://mypage.iu.edu/~aschimme/hc.html>). Latest additions are chlorinated hydrocarbons, nictines, acetanilides and ureas, some with multiple levels of D, ¹³C and ¹⁵N enrichment. Developments of new reference compounds usually start as collaborative projects with users. Acquisition of pure starting materials is followed first by verification of purity, because off-line combustion of milligram amounts of substance yields bulk isotope ratios that can be biased if contamination is included. Next, multiple aliquots of each compound are processed and measured off-line. Only compounds with sufficiently tight analytical statistics are accepted as reference materials. Suggestions by the scientific community for development of additional reference materials are welcome.