Use of chromium in reductive high-temperature conversion for improved accuracy of δ^2H values of new international organic stable isotope reference materials

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Multitudinous novel analytical online techniques for measuring stable isotope ratios of light elements (HCNOS) have revolutionized and greatly expanded applications in numerous scientific sub-disciplines over the past two decades. However, ^{2}H/^{1}H ratios of hydrogen (expressed as δ^2H values) in chemically more complex organic substrates have been subject to controversial matrix effects in spite of good reproducibility in a given analytical context. This caveat applied especially to high-temperature pyrolysis (e.g., TC/EA, HTP), as well as to methods previously used with elemental chromium in a temperature range of 800-1000°C. A simple HCO-stoichiometry induced no matrix effect. However, major and irreconcilable isotopic discrepancies could arise when the conversion of organic H to H_2 was incomplete and accompanied by isotope fractionation. The presence of heteroatoms like nitrogen or chlorine in an organic sample during high-temperature pyrolysis led to the production of gaseous byproducts HCN and HCl with isotope fractionation in the product H_2. In spite of good reproducibility of δ^2H values, the isotope fractionation could amount to 25 mUr (or ‰) towards more negative δ^2H values relative to classical off-line methods that are not affected by the formation of HCN and HCl. An inexpensive and effective remedy for on-line methods is the use of chromium powder and/or granules at temperatures of 1050-1500 °C. Chromium is able to chemically scavenge all elements from organic matter except hydrogen, thus resulting in 100% yield of H_2. Practical methods for high and low flow online systems are presented. We provide an update on the ring-test calibration of new international organic stable isotope reference materials that are slated for release in 2015.