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Assessing the uncertainties of δ^{13}C- and δ^{15}N-values determined by EA-IRMS for palaeodietary studies

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For palaeodietary studies the variation of the stable isotope ratios of carbon and nitrogen (given in the δ-notation as deviation [in ‰] of the respective isotope ratio of the sample from that of the corresponding international standard, VPDB and AIR, respectively) in bone collagen is widely used. Usually these parameters are determined with a continuous flow elemental analyzer–isotope ratio mass spectrometer (EA-IRMS) system. In such determinations it is advantageous and recommended to use for the normalization of the δ-values at least two reference materials with δ-values bracketing the expected δ-value range of the samples (see e.g. Paul et al.). Further, it is accepted practice in several laboratories to report the δ^{13}C- and δ^{15}N-values of palaeodiet samples as mean values of replicate determinations. Following this strategy implies a detailed investigation of various uncertainty contributions and their propagation.

At the beginning of a program on palaeodiet at our laboratory we established a suitable measurement protocol for stable isotope ratio measurements for palaeodiet reconstructions. The measurements were performed with a C*E Instruments NC2500* elemental analyzer coupled to a *Micromass Optima* isotope ratio mass spectrometer. In one sample batch multiple replicates of a laboratory standard (Merck alanine calibrated against international δ^{13}C and δ^{15}N reference materials) for monitoring the performance of the EA-IRMS system, and several replicates of various certified reference materials were measured together with the "unknown" collagen samples. The respective δ-values of the samples were normalized via linear regression calculated from the actually measured and the known δ-values of at least three reference materials present in the sample batch. In a few cases only two standard materials were included in the sample batch and thus a two point normalization was applied. A measure for the precision of the EA-IRMS measurements was derived from the standard deviation of the alanine replicates, either calculated from the variation of the replicates present in a single batch measurement, or estimated from their long-term variation.

Various components contributing to the overall uncertainties were explored for the final evaluation of the results. For the error propagation also the off-diagonal elements of the respective variance-covariance matrices were taken into account (e.g. Brandt). This procedure permits not only to calculate the combined uncertainty of the normalized δ-values, but also to estimate the contributions of the various sources of uncertainties to the final uncertainty value.

We present an in-depth investigation of the propagation of various uncertainty components and discuss the effect of considering covariances in the uncertainty analysis of δ^{13}C and δ^{15}N determinations for palaeodietary investigations.

References:

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Brandt S., Datenanalyse. Mit statistischen Methoden und Computerprogrammen, 4. Auflage, Spektrum akademischer Verlag, Heidelberg, Berlin, 1999.