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## New methods for the compound specific analysis of underivatized amino acids

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The isotopic analysis of amino acids has become an important area of application in a range of geoscientific, palaeo-ecological and biochemical disciplines including in particular palaeodietary reconstruction and environmental forensics (Dunn et al., 2011; Raghaven et al., 2010; Lynch et al., 2011; Godin and McCullagh, 2011). Commercialisation of an interface between liquid chromatography and isotope ratio mass spectrometry in 2004 has enabled the analysis of non-volatile, soluble compounds without the need for derivatization (via GC-C-IRMS), providing exciting new analytical possibilities (Krummen et al., 2004).

One of the major problems facing LC-IRMS for  $\delta^{13}$ C analysis is the development of efficient and robust methods. Chromatographic restrictions on mobile phase composition and flow rates, combined with the need for baseline resolution, are analytically challenging but imperative for accurate isotopic analysis. Since the introduction of LC-IRMS a number of research groups have been working on separation methods in particular but, although suitable for resolving the majority of amino acids, current protocols are extremely time consuming, with recently published methods taking over 4 hours per sample (Smith et al., 2009). The low sample throughput of these methods is directly affecting research efficiency. For example, we are currently trying to better understand what palaeodietary information is represented by individual amino acid  $\delta^{13}$ C values from bone collagen and hair keratin, and this work has been significantly hampered by a lack of sample throughput.

Recognizing the need for larger sample sets to better understanding biogenic information represented by amino acid  $\delta^{13}$ C for palaeodietary reconstruction, high throughput approaches to amino acid LC-IRMS have been investigated and developed. This poster will present unpublished research, developing an analytical protocol which cuts analysis time for amino acids dramatically. This approach is based on mixed-mode chromatography, building on research in the literature, and is applicable to the analysis of amino acids from a wide range of sources. The figure below shows the LC-IRMS chromatogram for a set of standard proteinogenic amino acids using the new protocol and the poster will provide analytical details and demonstration of its application.

## References

Anthony H. Lynch, James S. O. McCullagh, and Robert E. M. Hedges. Liquid chromatography/isotope ratio mass spectrometry measurement of  $\delta$ 13C of amino acids in plant proteins. Rapid Communications in Mass Spectrometry. 2011, **25**, 2981–2988.

Dunn PJH, Honch NV and Evershed RP. Comparison of liquid chromatography-isotope ratio mass

spectrometry (LC/IRMS) and gas chromatography–combustion–isotope ratio mass spectrometry (GC/C/IRMS) for the determination of collagen amino acid d13C values for palaeodietary and palaeoecological reconstruction. Rapid Communications in Mass Spectrometry. 2011, **25**, 2995–3011

Jean-Philippe Godin and James S. O. McCullagh. Current applications and challenges for liquid chromatography coupled to isotope ratio mass spectrometry (LC/IRMS). Rapid Communications in Mass Spectrometry. 2011, **25**, 3019–3028

Krummen M, Hilkert AW, Juchelka D, Duhr A, Schluter HJ, and Pesch R. A new concept for isotope ratio monitoring liquid chromatography/mass spectrometry. *Rapid Communications in Mass Spectrometry*. 2004, **18**, 2260-2266

Raghavan, M., McCullagh J.S.O and Hedges R.E.M. Amino acid  $\delta$ 13C analysis of hair keratin using liquid chromatography/isotope ratio mass spectrometry: Palaeodietary implications from intra-individual comparisons with bone collagen. *Rapid Communications in Mass Spectrometry.* (2010) **24**: 541-548.

Smith CI, Fuller BT, Choy K, Richards MP. A three-phase liquid chromatographic method for d13C analysis of amino acids from biological protein hydrolysates using liquid chromatography-isotope ratio mass spectrometry. *Anal. Biochem.* 2009, 390, 165.