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Advancing Carboxylic Acid Quantification: A Novel Derivatisation Procedure for UHPLC-OT-MS with Applications to Asteroid Samples

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Recent sample return missions targeting asteroids Ryugu (Hayabusa2) and Bennu (OSIRIS-REx) have provided ample materials for the characterisation and quantification of soluble organic matter (SOM) in some of the most primitive objects in the solar system. While Bennu sample analyses have shown that monocarboxylic acids are present in relatively similar abundances as in the carbonaceous meteorites Murchison, Tarda, and Orgueil [1], hot water extractions of Ryugu samples have highlighted an apparent discrepancy in the abundance of carboxylic acids with chain lengths longer than that of formic or acetic acid [2]. This discrepancy has been interpreted as a result of increased aqueous alteration on Ryugu, but can potentially be attributed to analytical challenges, including low concentrations of certain carboxylic acids and matrix effects that limit sensitivity and reproducibility. In addressing these limitations, a new derivatisation procedure for ultra-high-performance liquid chromatography orbitrap mass spectrometry (UHPLC-OT-MS) aimed at improving detection of trace-level carboxylic acids in complex matrices has been developed. This protocol leverages enhanced ionisation efficiency and matrix cleanup techniques to reduce background interference and improve peak resolution, and expands the dynamic range for mono- and di-carboxylic acids, enabling the quantification of these molecules at low nanomolar concentrations. Preliminary testing using analogue matrices simulating asteroid conditions demonstrated the ability to consistently resolve low-abundance carboxylic acids offering new insights into organic synthesis, preservation, and degradation processes in extraterrestrial environments. The new protocol has significant implications for future analysis of returned asteroid samples, such as those from the aforementioned sample return missions. By closing the gap between meteorite and asteroid carboxylic acid profiles, this method can help refine theories on organic evolution in the early solar system, as well as improving our understanding of the chemical precursors to life. This work highlights the importance of combining advanced derivatisation strategies with high-resolution mass spectrometry to push the boundaries of analytical geochemistry.

[1] Glavin, D.P., Dworkin, J.P., Alexander, C.M.O. *et al.* Abundant ammonia and nitrogen-rich soluble organic matter in samples from asteroid (101955) Bennu. *Nat Astron* (2025).

[2] Potiszil, C. et al., Organic Matter in the Asteroid Ryugu: What We Know So Far. *Life* **13**, 1448 (2023).