

**Determination of  $^{13}\text{C}/^{12}\text{C}$  isotopic ratios of biogenic organometal(loid) compounds in complex matrices**

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Methylated metal(loid) compounds are formed in the environment by abiotic as well as enzymatically catalyzed transfer of a methyl group. Due to the increased mobility and toxicity in comparison to the inorganic precursors, the investigation of the formation process is of high relevance. Though the natural abundance carbon isotope ratio can give important insights towards their origin as well as the biochemical methyl transfer process, these species have not been investigated by carbon isotope ratio mass spectrometry (IRMS) so far. This is due to the analytical challenge to precisely determine the natural isotope distribution of trace amounts of metal(loid)-bound carbon in complex organic matrices.

To overcome this problem, we tested the concept of selective derivatization of non-volatile organometal(loid)s by hydride generation (HG) followed by purge and trap (P&T) enrichment, heart-cut gas chromatography (hcGC) and subsequent analysis by GC-IRMS. Parameter optimization of HG-P&T-hcGC was conducted using online coupling to element-sensitive ICP-MS (inductively coupled plasma mass spectrometry) detection. The purity of the HG-P&T-hcGC fraction was verified by GC-MS. For the model substance trimethylarsine oxide (TMA<sub>3</sub>O), an excellent agreement of the  $\delta^{13}\text{C}$ -value analyzed by HG-P&T-hcGC-GC-IRMS was achieved in comparison to the bulk  $\delta^{13}\text{C}$ -value, which shows that no significant isotope fractionation occurred during the hydride generation and subsequent separation.

The optimized method showed good reproducibility and a satisfying absolute detection limit of 4.5  $\mu\text{g}$  TMA<sub>3</sub>O (1.2  $\mu\text{g}_{\text{carbon}}$ ). This method was applied to the analysis of TMA<sub>3</sub>O in compost. The low  $\delta^{13}\text{C}$ -value of this compound ( $-48.38 \pm 0.41\text{‰}$ ) indicates that biomethylation leads to significant carbon fractionation. HG-P&T-hcGC-GC-IRMS is a promising tool for investigation of the biomethylation process in the environment.