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PREBIOTIC CHEMISTRY

Potential Pitfalls in MALDI-TOF MS Analysis of Abiotically Synthesized RNA Oligonucleotides

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Abstract Demonstration of the abiotic polymerization of ribonucleotides under conditions consistent with conditions that may have existed on the prebiotic Earth is an important goal in "RNA world" research. Recent reports of abiotic RNA polymerization with and without catalysis rely on techniques such as HPLC, gel electrophoresis, and MALDI-TOF MS to analyze the reaction products. It is essential to understand the limitations of these techniques in order to accurately interpret the results of these analyses. In particular, techniques that rely on mass for peak identification may not be able to distinguish between a single, linear RNA oligomer and stable aggregates of smaller linear and/or cyclic RNA molecules. In the case of MALDI-TOF MS, additional complications may arise from formation of salt adducts and MALDI matrix complexes. This is especially true for abiotic RNA polymerization reactions because the concentration of longer RNA chains can be quite low and RNA, as a polyelectrolyte, is highly susceptible to adduct formation and aggregation. Here we focus on MALDI-TOF MS analysis of abiotic polymerization products of imidazole-activated AMP in the presence and absence of montmorillonite clay as a catalyst. A low molecular weight oligonucleotide standard designed for use in MALDI-TOF MS and a 3′-5′ polyadenosine monophosphate reference standard were also run for comparison and calibration. Clay-catalyzed reaction products of activated GMP and UMP were also examined. The results illustrate the ambiguities associated with assignment of m/z values in MALDI mass spectra and the need for accurate calibration of mass spectra and careful sample preparation to minimize the formation of adducts and other complications arising from the MALDI process.

Keywords RNA World · Prebiotic chemistry · MALDI-TOF MS · Montmorillonite

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