

Influence of sodium adducts on metastable decay of short oligonucleotides

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The influence of sodium adducts on fragmentation pattern of metastable oligonucleotide anions is studied using a reflectron type MALDI-TOF instrument. In this study the instrument is used as a tandem mass spectrometer. The precursor anion produced in desorption / ionization process is mass-selected by gate and flown over the flight tube. Subsequently, the ions are reflected and reaccelerated and their mass spectrum, showing the products of decay processes during flight time (Post Source Decay - PSD), is obtained.

The fragmentation channels of PSD was studied on following oligonucleotides: 5'TTACTT, 5' TTCATT, 5'TTAGTT 5'TTGATT, 5'TTCGTT, 5'TTGCTT and 5'TTTTTT. The oligonucleotides were partly sodiated containing 0 to 4 sodium atoms. For non-sodiated oligonucleotides the predominant fragmentation channels are the formation of Y_3 (w_3) and X_3^* (a_4-B_4) ions [1,2], i.e. a 3' phosphate ester cleavage at the third position and a 3' phosphate ester cleavage at the fourth position accompanied by a base loss from the same sugar, respectively. Also the loss of a single base from the third and fourth position is observed.

The fragmentation channels are suppressed when precursor is sodiated. This suppression increases with multiplicity of sodiation. Here we discuss the possible fragmentation mechanism in context to previous work.

[1] E. Nordhoff, M. et al. J. Mass Spectrom. 30 (1995), p. 99.

[2] S.A. McLuckey et al., J. Am. Soc. Mass Spectrom. 3 (1992)

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