

Overview

High energy CID MALDI MS/MS spectra of fatty alcohol alkoxyolate copolymers show different fragmentation patterns for alkali adduct ions. The spectra show additional fragmentation information for the Li adduct ion compared to the fragment spectra of the sodium and potassium adduct ions.

Low energy CID MALDI MS/MS spectra show less fragmentation patterns for the Li adduct. The additional fragmentation information can only be obtained from high energy CID experiments exclusively.

The choice of a suitable adduct ion and the CID technique used can be crucial for extracting information from MS/MS experiments.

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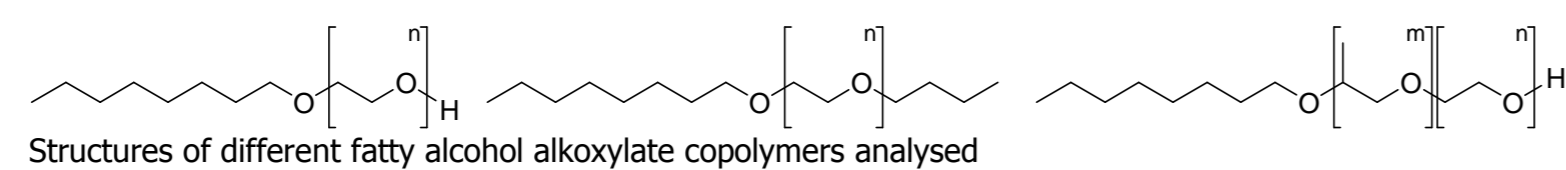
Comparative study of fatty alcohol alkoxyolate copolymers fragmentation patterns by MALDI-MS/MS using low energy and high energy CID

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Introduction

The class of fatty alcohol alkoxyolates describes surfactants that are synthesised by reaction of fatty alcohols with alkoxides like ethylene oxide, propylene oxide and others. Fatty alcohol alkoxyolates are used as nonionic surfactants in home and industrial cleaning and washing agents. They have important properties like foam suppression, foam control and wetting effects in these products. Furthermore alkoxyolates are also relevant in a broad range of chemical industry applications (e.g. in coating and polymerisation additives or agrochemicals), where these serve as dispersal agents and emulsifiers.



Here we present a comparative analysis of fatty alcohol alkoxyolate copolymers using MALDI-MS/MS with low energy trap and high energy collision cell technique.

Methods

Samples were provided by Cognis (Düsseldorf, Germany) and diluted in THF to a concentration of 4 mg/ml. Cationizing salts were used at concentrations of 0.1 mol/l in MeOH/water (volume ratio 1:1). MALDI measurements were performed with Dithranol, 10 mg/ml in THF. The target spot was pre-coated with 1.3 µl of the salt solution. Sample and matrix solutions were premixed in a volume ratio of 1:1 and applied onto the MALDI target.

High energy CID MS/MS experiments were performed using a MALDI-reflectron-TOF mass spectrometer (AXIMA Performance™, Shimadzu Biotech, Manchester, UK). The accelerating voltage used was 20 kV. Helium was used as collision gas.

Low energy CID MS/MS experiments were performed using a MALDI-Trap-TOF hybrid mass spectrometer (AXIMA Resonance™, Shimadzu Biotech, Manchester, UK). Argon was used as collision gas.

Solvents were obtained from Roth (Karlsruhe, Germany). Dithranol and the used salts were purchased from Sigma-Aldrich (Steinheim, Germany).

Discussion and Conclusions

High energy CID MALDI MS/MS spectra of fatty alcohol alkoxyolate copolymers show different fragmentation patterns for alkali adduct ions. The spectra show additional fragmentation information for the Li adduct ion compared to the fragment spectra of the sodium and potassium adduct ions (Fig. 2, 4, 6). While the fragmentation of sodium and potassium adducts results in vinyl- or carbonyl-endgroups lithium adducts additionally show ethoxy- or propoxy- group reduced hydroxyl group fragments (red CID spectra in Fig. 2, 4).

Low energy CID MALDI MS/MS spectra show less fragmentation patterns (hydroxyl group fragments) for the Li adduct (Fig. 1, 3, 5) in comparison to the high energy CID MALDI MS/MS spectra shown. The additional fragmentation information can only be obtained from high energy CID experiments exclusively. The low energy CID MALDI MS/MS spectrum of the n-butyl endcapped polymer shows fragmentation by starting with an octyl- and also with a butyl- group cleavage (Fig. 3).

As a general rule, the energy transferred in a low energy CID event of a lithium adduct should be sufficient enough to break one bond by cleavage of one monomer unit without subsequent rearrangement to a vinyl- or carbonyl-endgroup. High energy CID MALDI MS/MS events result in less selective fragmentations (Fig. 2, 4).

MALDI-MS/MS was successfully used for the endgroup identification of alkoxyolated fatty alcohols. In connection with these results alkali adduct ions of such copolymers show differences in fragmentation patterns related to high energy and low energy CID. Low energy CID MALDI MS/MS experiments and the use of lithium salts as cationisation reagents can be meaningful for a simplified characterisation of these copolymer products.

Results: ethoxylated fatty alcohol, not endcapped

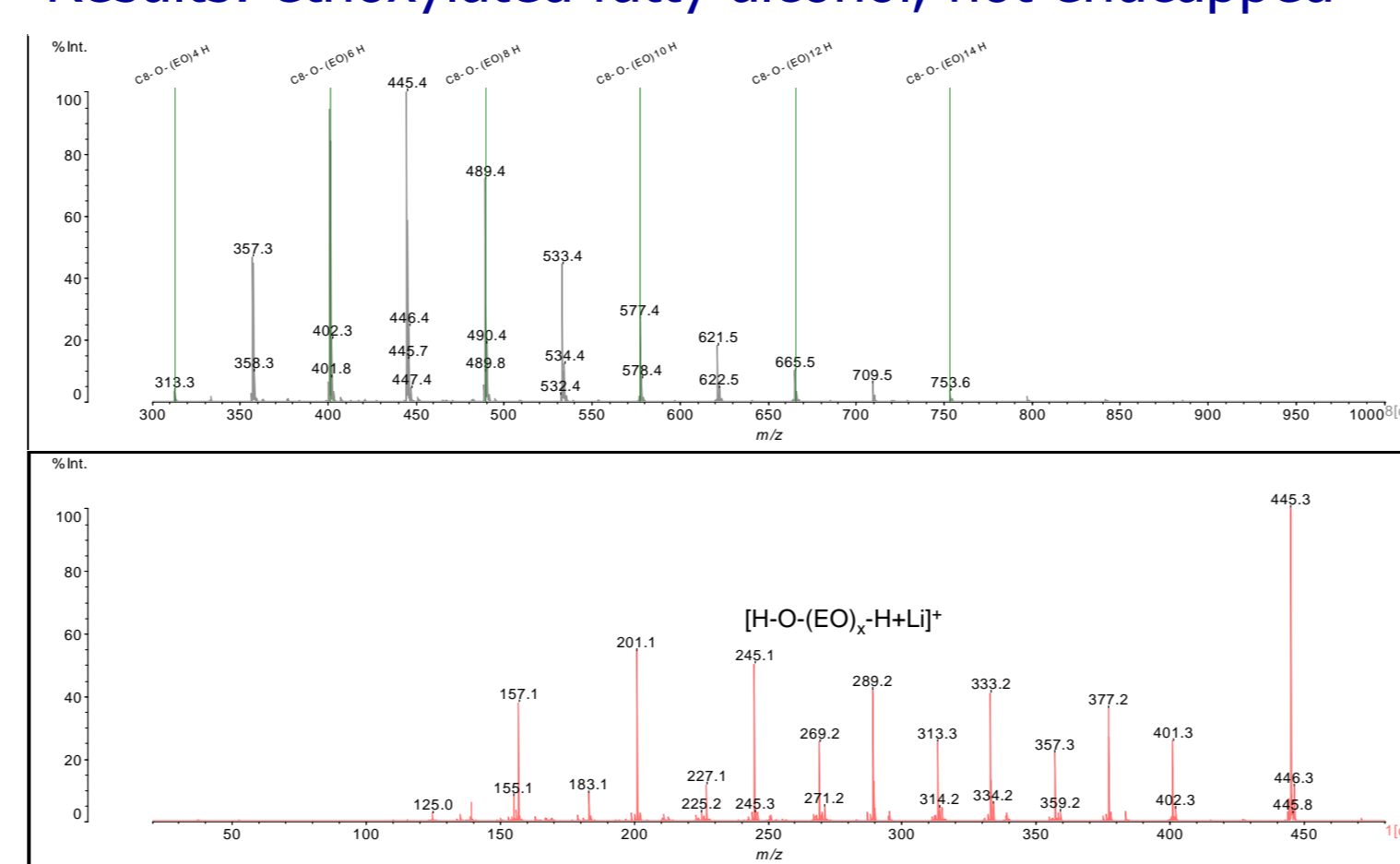


Fig. 1: MALDI-Trap-TOF spectrum [M+Li]⁺ and MALDI low energy CID MS/MS spectrum of precursor ion [M+Li]⁺ m/z 489

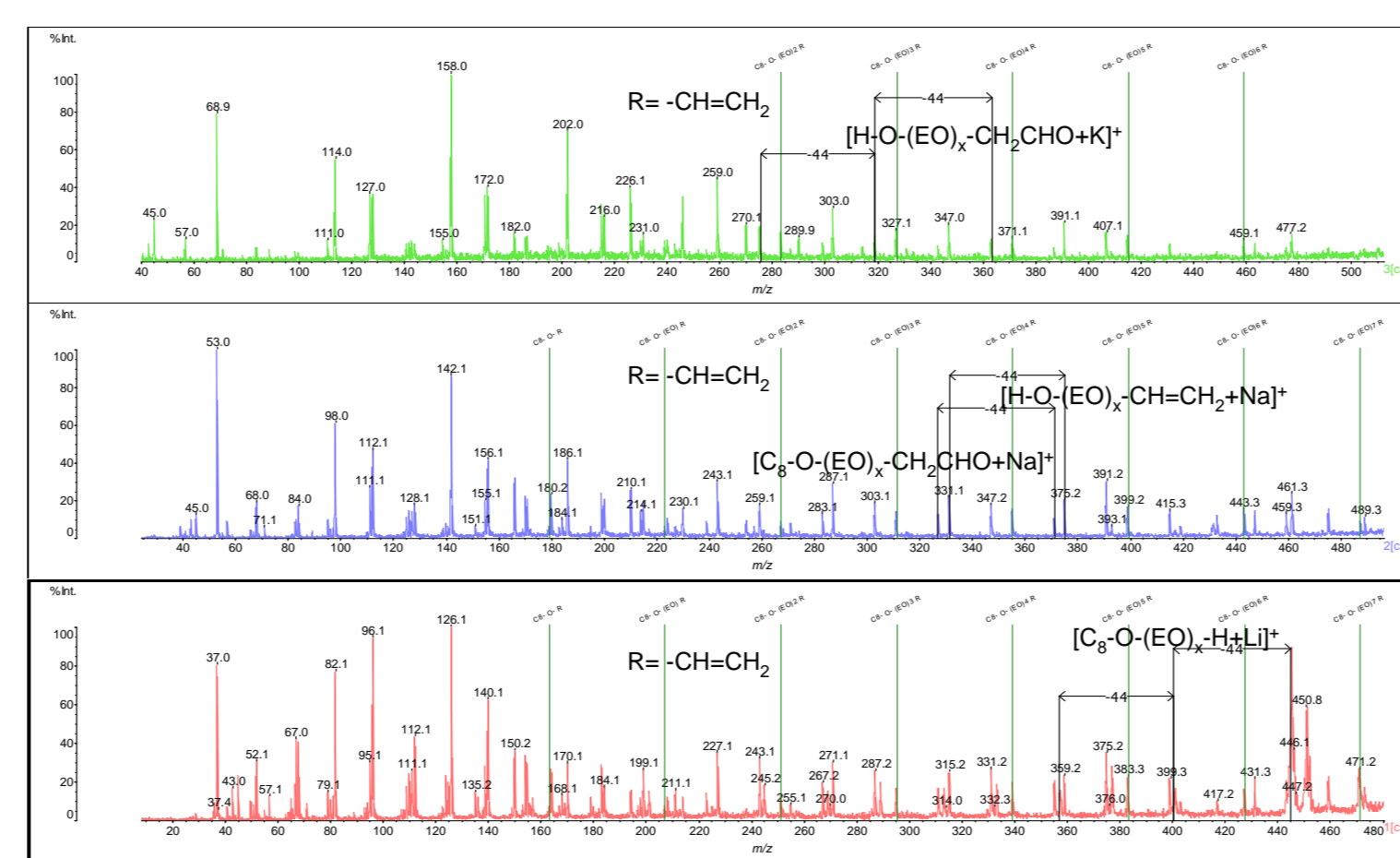


Fig. 2: MALDI high energy CID MS/MS spectra of precursor ions [M+Li]⁺ m/z 489, [M+Na]⁺ m/z 505 and [M+K]⁺ m/z 521

Results: ethoxylated fatty alcohol, n-butyl endcapped

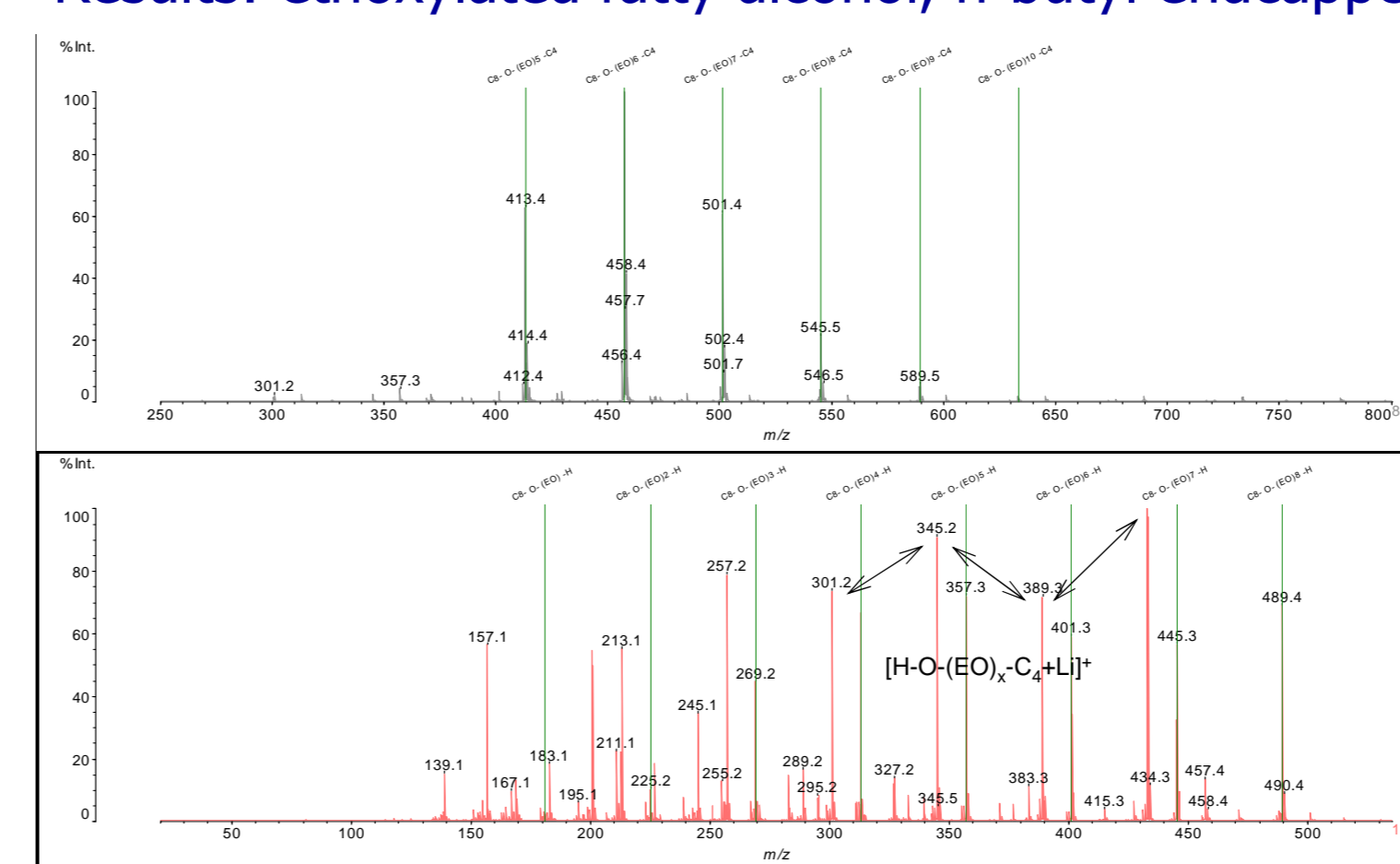


Fig. 3: MALDI-Trap-TOF spectrum [M+Li]⁺ and MALDI low energy CID MS/MS spectrum of precursor ion [M+Li]⁺ m/z 545

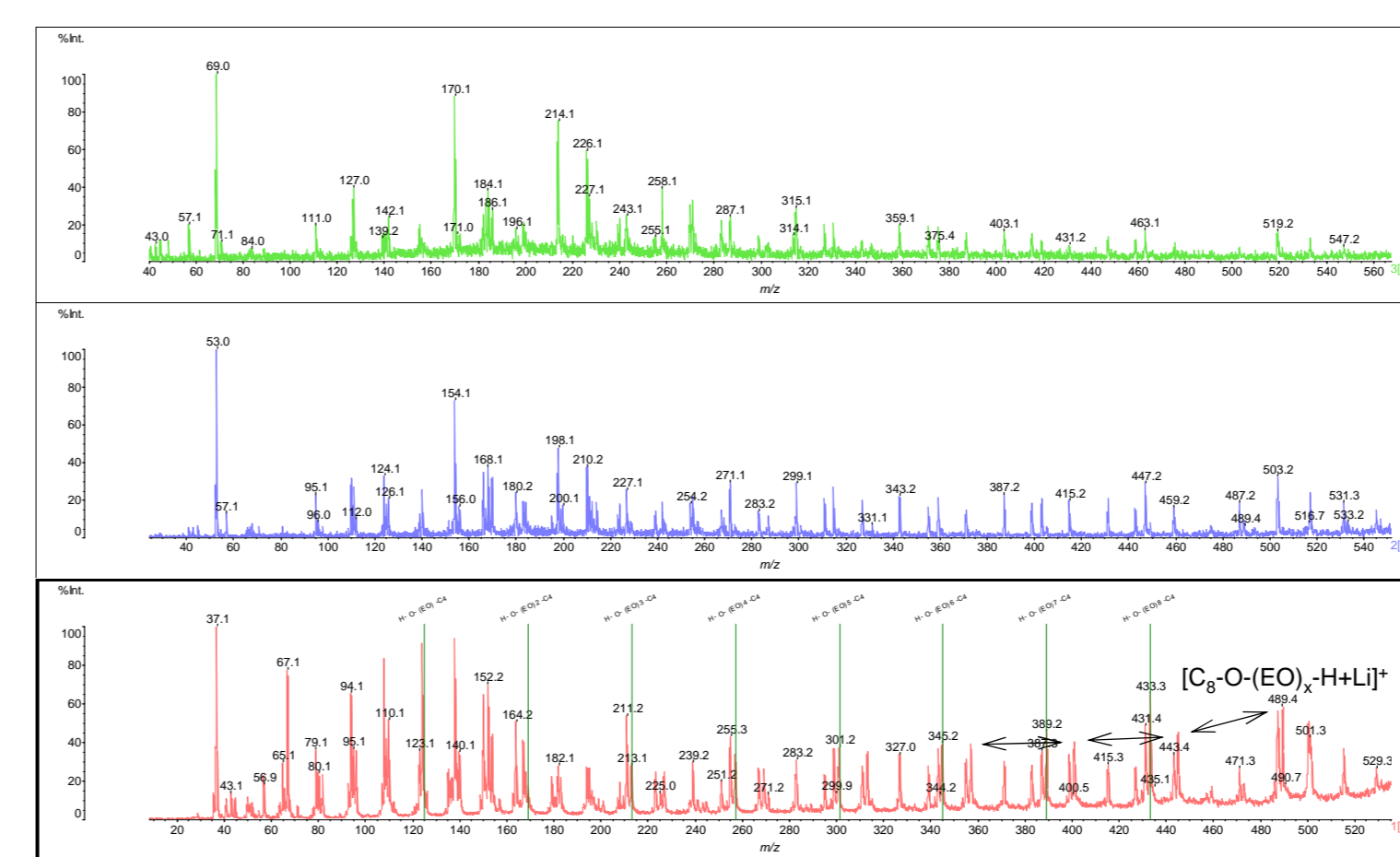


Fig. 4: MALDI high energy CID MS/MS spectra of precursor ions [M+Li]⁺ m/z 545, [M+Na]⁺ m/z 561 and [M+K]⁺ m/z 577

Results: fatty alcohol - PO/EO - block copolymer

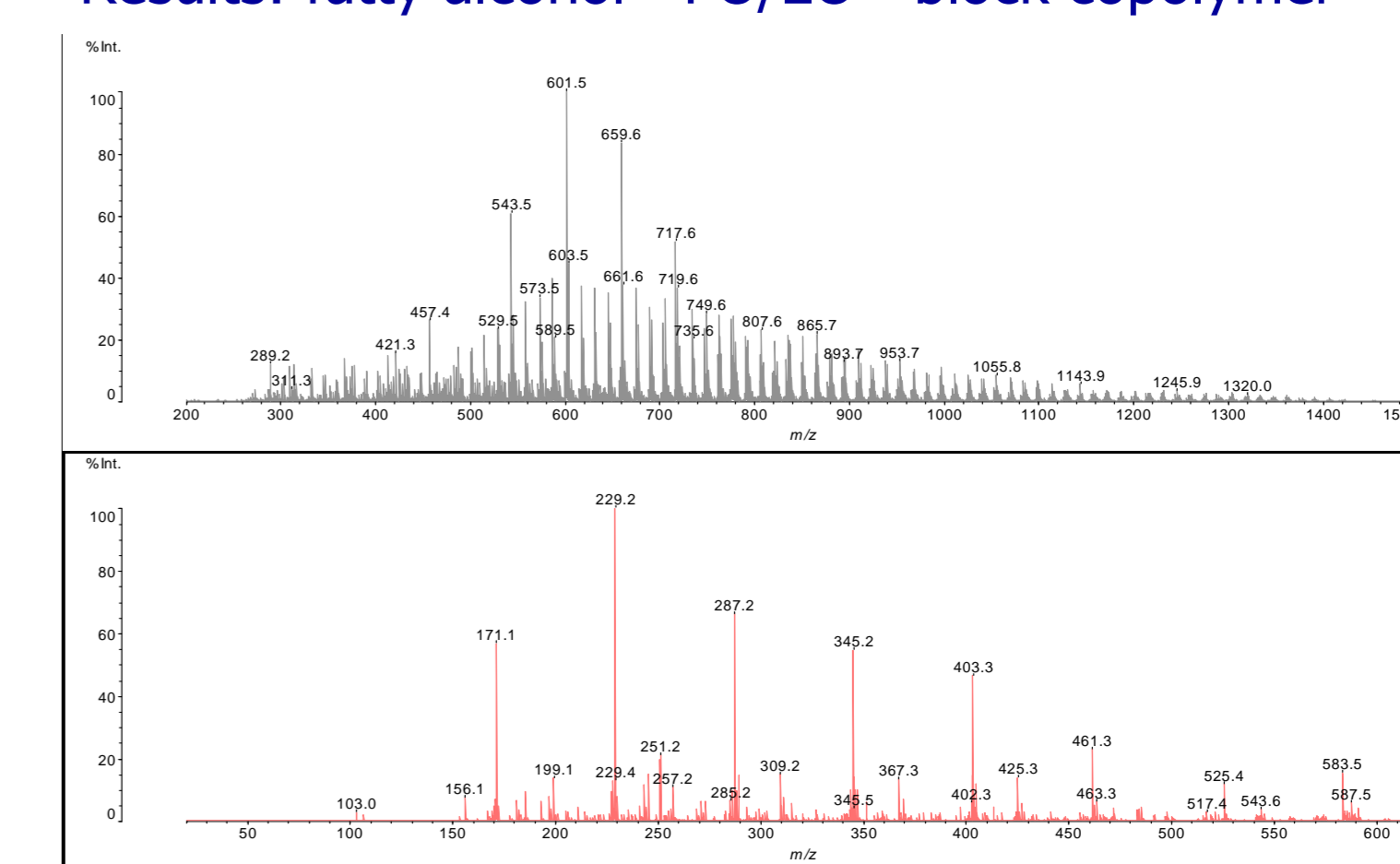


Fig. 5: MALDI-Trap-TOF spectrum [M+Li]⁺ and MALDI low energy CID MS/MS spectrum of precursor ion [M+Li]⁺ m/z 631.5

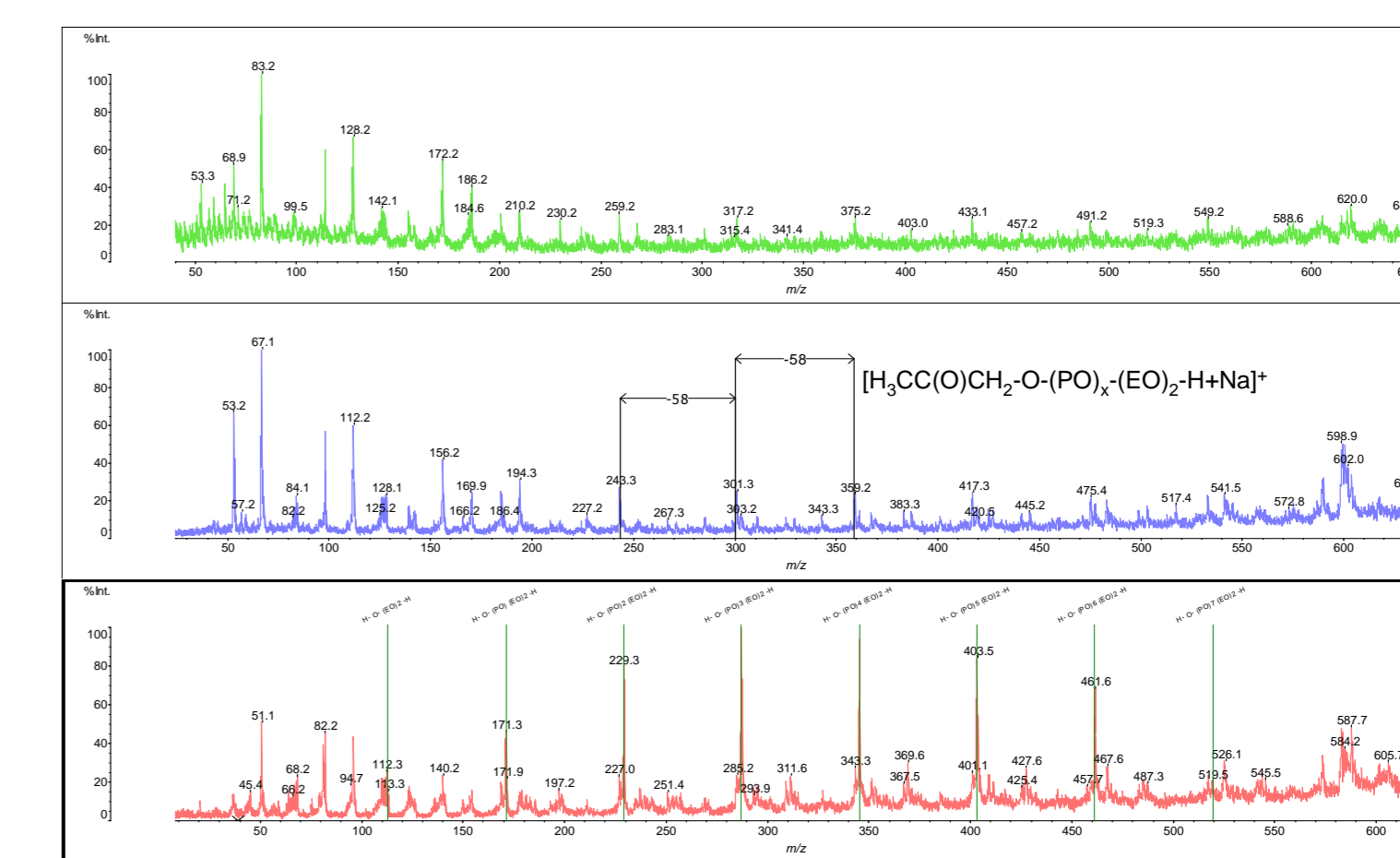


Fig. 6: MALDI high energy CID MS/MS spectra of precursor ions [M+Li]⁺ m/z 631.5, [M+Na]⁺ m/z 647.5 and [M+K]⁺ m/z 663.5