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Cluster Ion Formation of Saccharose in Positive-Ion Direct Analysis in Real Time Mass Spectrometry

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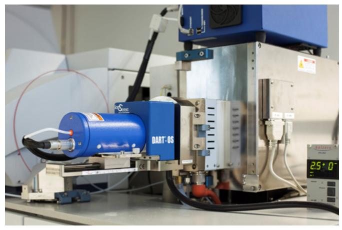
Intention

- The analysis of mono-, di, and trisaccharides by positive-ion direct analysis in real time mass spectrometry (DART-MS) [1] revealed that all of these sugars yielded $[M+NH_4]^+$ ions while some additionally formed abundant $[M_n+NH_4]^+$ cluster ions [2].
- Cluster ion formation of highly polar or ionic analytes is common in DART-MS, can extend to very high mass [3], and may be exploited for mass calibration [4].
- Saccharose, the most common sugar, is among the $[M_n+NH_4]^+$ ion forming species, and thus, may potentially be used as mass calibrant.
- However, the factors influencing the extent of saccharose cluster ion formation such as temperature of the DART gas and sample load as well as instrumental factors like trapping conditions of ions prior to mass analysis have to be well defined.
- Therefore, this study deals with the optimization of experimental conditions and identifies critical parameters for saccharose cluster ion formation in positive-ion DART-MS.

Experimental

- A Bruker Apex-Qe Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) was used.
- Ions were collected for 0.3-1.0 s prior to ICR mass analysis in the RF-only accumulation hexapole. Ions of the range *m/z* 200-2500 were excited and detected using standard setting from previous DART work [4].
- The DART-SVP ionization source (IonSense, Saugus, MA), was mounted onto the ESI interface of the Bruker MTP ion source via the Vapur Interface. Transmission mode DART was employed by using the Open Source kit.
- External mass calibration in positive-ion DART mode was established on an ionic liquid (IL) [4].
- For DART-MS, sample solutions were applied to the Open Source cards. The temperature of the DART source was set to 200-450°C.

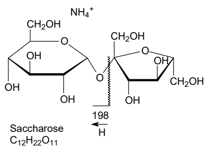


DART-SVP source with OpenSource and Vapur Interface (IonSense) mounted to the atmospheric pressure interface at the source housing of the Bruker ApexQe (Bruker Daltonik) FT-ICR mass spectrometer.

Saccharose Ions

Calculated accurate masses of saccharose cluster ions

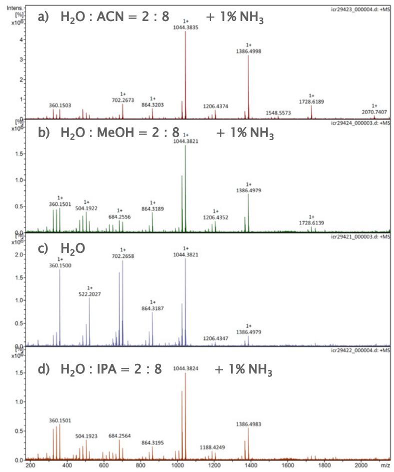
Saccharose Ions	*m/z*	Type of Ion
$[C_6H_{10}O_5+NH_4]^+$	180.086649	$[M-C_6H_{12}O_6+NH_4]^+$
$[C_6H_{12}O_6+NH_4]^+$	198.097214	$[M-C_6H_{10}O_5+NH_4]^+$
$[C_{12}H_{22}O_{11}+NH_4]^+$	360.150037	$[M+NH_4]^+$
$[C_{24}H_{44}O_{22}+NH_4]^+$	702.266249	$[2M+NH_4]^+$
$[C_{36}H_{66}O_{33}+NH_4]^+$	1044.382460	$[3M+NH_4]^+$
$[C_{48}H_{88}O_{44}+NH_4]^+$	1386.498672	$[4M+NH_4]^+$
$[C_{60}H_{110}O_{55}+NH_4]^+$	1728.614883	$[5M+NH_4]^+$
$[C_{72}H_{132}O_{66}+NH_4]^+$	2070.731095	$[6M+NH_4]^+$
$[C_{84}H_{154}O_{77}+NH_4]^+$	2412.847306	$[7M+NH_4]^+$
$[C_{98}H_{176}O_{88}+NH_4]^+$	2778.963518	$[8M+NH_4]^+$



Sucrose cluster ions start with the NH_4^+ adduct of sucrose. The series expands at least up to the $[6M+NH_4]^+$ ion, but even $[8M+NH_4]^+$ ions can occur. Some fragment ions are also formed.

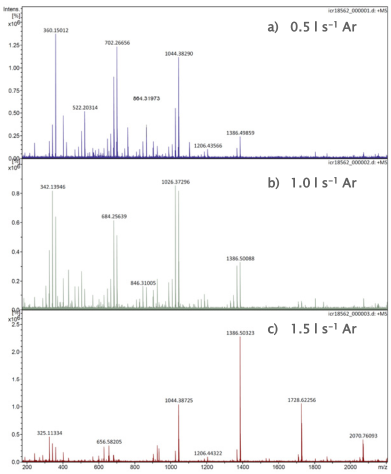
Solvent Composition

- Saccharose at 10 mg ml^{-1} was supplied as solution in a) H_2O : ACN = 2 : 8, b) H_2O : MeOH = 2 : 8, c) H_2O, and d) H_2O : IPA = 2 : 8. Apart from pure water, 1% of NH_3 was added for enhanced ammonium adduct ion formation.
- The solvent clearly influences the cluster ion distribution. It is assumed that the formation of smaller crystals upon quicker evaporation supports desorption from the metal mesh, and thus, reduces the degree of fragmentation.
- Pure water and slowly evaporating solvents cause $[nM-(H_2O)_x+NH_4]^+$ ions in addition to undecomposed cluster ions and also suppress higher-mass cluster ions.
This supports the assumption that large crystals are detrimental for cluster ion creation upon DART.



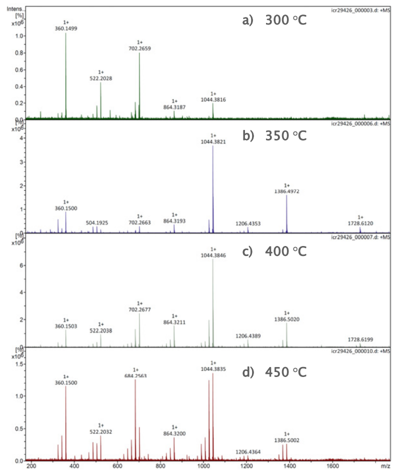
Argon Trapping Gas Pressure

- The specific instrument uses argon to cool ions during accumulation in a RF hexapole ion trap (h2).
- The argon pressure has major influence on the cluster ion distribution.
- High-mass cluster ions are most effectively trapped using comparatively high argon flow into h2.
- Optimum cluster ion distributions were achieved at an argon flow of 1.5 l s^{-1}.
- However, high argon flow causes poor vacuum in the ICR cell, e.g., up to 3.5 x 10^{-9} mbar, whereas a flow of 0.8 to 1.0 l s^{-1} serves as a good compromise keeping the ICR cell at about 2.5 x 10^{-9} mbar.



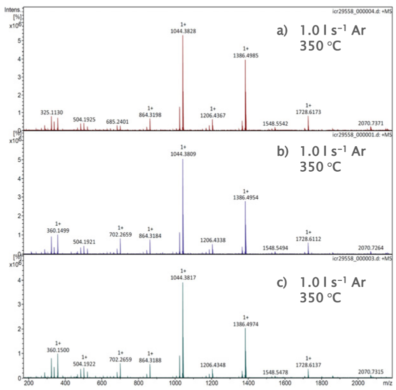
DART Gas Temperature

- Optimum cluster ion distributions require desorption/ionization to proceed faster than thermal decomposition of the sugar.
- 300 °C are the minimum helium temperature setting to deliver sucrose cluster ions.
- Low temperature of the DART gas is not effective in providing high number densities of sucrose ions and neutrals to form clusters.
- Too hot gas, i.e., 400 °C and higher, on the other side, effects cluster ion fragmentation by both loss of sucrose units and multiple losses of water from cluster ions.
- Best conditions in terms of wide cluster ion distribution and low degree of ion dissociation are achieved at a helium temperature setting of 350 °C.



Reproducibility and Other Factors

- The reproducibility of cluster ion formation and the general appearance of the cluster ion distribution are quite high as exemplified by three consecutive runs (right).
- Other instrumental factors for optimum cluster ion distribution are ion accumulation settings (12 x 0.8 s), RF voltage of the ion funnel (200 V), RF voltage of the mass-selective quadrupole (500 V), ion transfer time to ICR cell (1.8 ms), and h2 trapping RF voltage (1500 V).
- The best sample load was 3 ul of the sucrose solution.



References

1. Cody, R. B., Laramee, J. A., Durst, H. D., *Anal. Chem.* **2005**, *77*, 2297-2302.
2. Wang, Y., Liu, L., Ma, L., Liu, S., *Int. J. Mass Spectrom.* **2014**, *357*, 51-57.
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Handouts

Handouts of this posters in PDF format are available to download from www.ms-ocihd.de cf. topic Publications > Conference Contributions.

Conclusions

- The analysis of saccharose by positive-ion DART-MS results in a series of $[M_n+NH_4]^+$ cluster ions.
- The extent of saccharose cluster ion formation depends on the temperature of the DART gas, sample load, trapping gas pressure, and other instrumental factors.
- For best cluster ion formation, experimental conditions need to be well defined.
- Cluster ion formation of saccharose, the most common sugar, may potentially be used for mass calibration. Such work is under way.