Saccharose: Sweet and Ubiquitous Mass Calibrant for Direct Analysis in Real Time–Fourier Transform Ion Cyclotron Resonance–Mass Spectrometry

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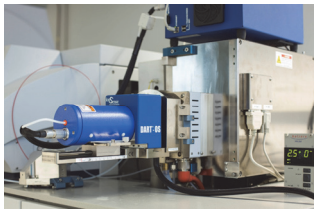
Project

- In positive-ion direct analysis in real time mass spectrometry (DART–MS) [1] mono-, di, and trisaccharides all form $[M+NH_4]^+$ ions.
- Some of them, in addition, yield abundant $[M_n+NH_4]^+$ cluster ions [2].
- Highly polar or ionic analytes commonly deliver cluster ion series that extend to high mass [3], and thus, may serve for mass calibration [4].
- Saccharose, the most common sugar, is among the $[M_n+NH_4]^+$ cluster ion forming species.
- Saccharose may therefore be employed as a mass calibration standard.
- The extent of saccharose cluster ion formation depends on the temperature of the DART gas, sample load, and instrumental parameters like trapping conditions of ions prior to mass analysis.
- This study identifies optimized experimental conditions and presents illustrative applications of saccharose cluster ion-based mass calibration for accurate mass measurements in DART–FT–ICR–MS.

Experimental

- A Bruker Apex-Qe 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* 300–2500 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.
- Initial external mass calibration in positive-ion DART mode was established on an ionic liquid (IL) [4], also as a control for data obtained from sucrose-based mass calibration.
- Sample solutions were applied to the Open Source cards. The temperature of the DART source was set to 200–450°C.

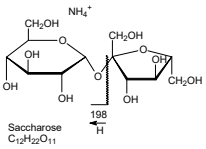


DART-SVP source with OpenSource and Vapur Interface (IonSense) mounted to the atmospheric pressure interface at the source housing of the Bruker ApexQe (Bruker Daltonik) FT-ICR mass spectrometer.

Saccharose Cluster Ions

Calculated accurate masses of saccharose cluster ions

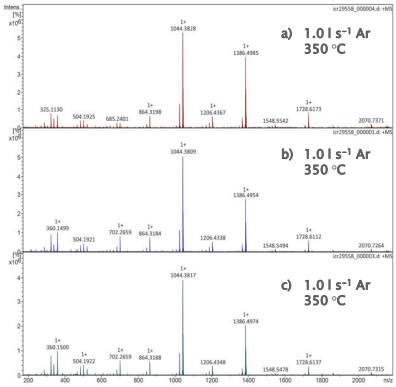
Saccharose Ions	*m/z*	Type of Ion
$[C_6H_{10}O_5+NH_4]^+$	180.086649	$[M-C_6H_{12}O_6+NH_4]^+$
$[C_6H_{12}O_6+NH_4]^+$	198.097214	$[M-C_6H_{10}O_5+NH_4]^+$
$[C_{12}H_{22}O_{11}+NH_4]^+$	360.150037	$[M+NH_4]^+$
$[C_{24}H_{44}O_{22}+NH_4]^+$	702.266249	$[2M+NH_4]^+$
$[C_{36}H_{66}O_{33}+NH_4]^+$	1044.382460	$[3M+NH_4]^+$
$[C_{48}H_{88}O_{44}+NH_4]^+$	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.

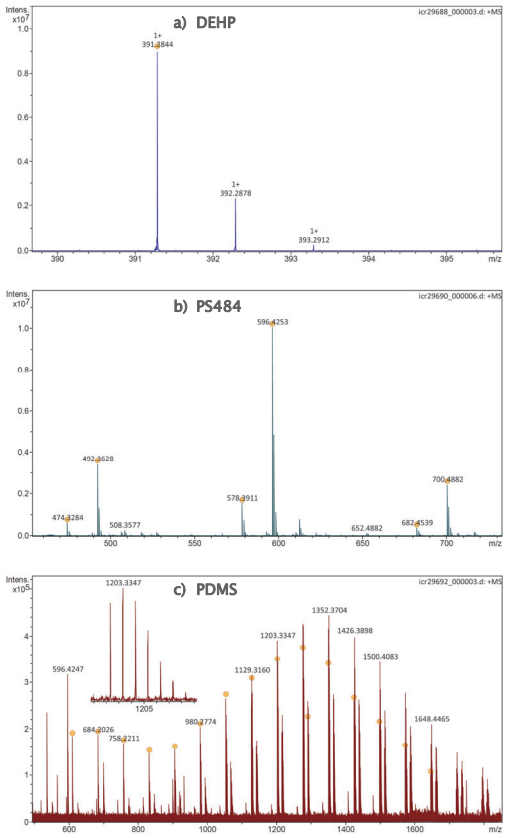
Optimum Conditions for Cluster Ions

- Saccharose at 10 mg ml^{-1} was supplied as solution in H_2O : ACN = 2 : 8 with 1% of NH_3 for enhanced ammonium adduct ion formation.
- The best sample load was 3 µl of the sucrose solution.
- Widest cluster ion distribution and lowest degree of ion dissociation were achieved at a helium temperature setting of 350 °C
- The ApexQe 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. 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.



- The reproducibility of cluster ion formation and the general appearance of the cluster ion distribution are quite high as exemplified by three consecutive runs (*above*).
- 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).

Applications of Saccharose Calibration



a) Di-sec-octylphthalate (DEHP) in acetone, DART 200 °C, *R* = 130,000 @ *m/z* 391

b) PS484 in toluene, 1 mg/ml, 4µl, DART 250 °C, *R*= 89,000 @*m/z* 596

c) silicone oil (PDMS) in $CHCl_3$ at 10 mg/ml, 3 µl, DART 300 °C, R = 45,000 @ *m/z* 1203.

These spectra were obtained using a mass calibration based on saccharose cluster ions.

In positive-ion DART, DEHP, a common impurity, forms $[M+H]^+$ ions, polystyrene yields $M^{+\cdot}$ as well as more abundant $[M+NH_4]^+$ ions, and silicone oil (PDMS) also preferably yields $[M+NH_4]^+$ ions.

The accurate mass results from four repetitive runs are tabulated below.

With the given instrumentation, a standard deviation of < 2 ppm may be achieved.

The gift of polystyrene standards by Steffen Weidner (BAM, Berlin) is gratefully acknowledged.

Accurate Mass Data by Saccharose Calibration

Compound	Ionic Formula	Calc. m/z	Exp. *m/z*	Exp. *m/z*	Exp. *m/z*	Exp. *m/z*	Avg. Exp. *m/z*	Std. Dev. [ppm]
DEHP	$[C_{24}H_{39}O_4]^+$	391.2843	391.2842	391.2844	391.2842	391.2844	391.2843	0.3
PDMS	$[C_{12}H_{40}NSi_6O_6]^+$	462.1466	462.1466	462.1467	462.1469	462.1468	462.1467	0.3
	$[C_{14}H_{46}NSi_7O_7]^+$	536.1654	536.1651	536.1655	536.1656	536.1656	536.1654	0.5
	$[C_{16}H_{52}NSi_8O_8]^+$	610.1842	610.1839	610.1842	610.1844	610.1847	610.1842	0.4
	$[C_{18}H_{58}NSi_9O_9]^+$	684.2029	684.2026	684.2032	684.2034	684.2034	684.2031	0.6
	$[C_{20}H_{64}NSi_{10}O_{10}]^+$	758.2217	758.2211	758.2222	758.2223	758.2225	758.2219	0.9
	$[C_{22}H_{70}NSi_{11}O_{11}]^+$	832.2405	832.2398	832.2411	832.2413	832.2413	832.2407	1.0
	$[C_{24}H_{76}NSi_{12}O_{12}]^+$	906.2593	906.2586	906.2600	906.2599	906.2600	906.2595	0.9
	$[C_{26}H_{82}NSi_{13}O_{13}]^+$	980.2781	980.2774	980.2789	980.2787	980.2793	980.2783	0.8
	$[C_{28}H_{88}NSi_{14}O_{14}]^+$	1054.2969	1054.2966	1054.2974	1054.2981	1054.2986	1054.2974	0.7
	$[C_{30}H_{94}NSi_{15}O_{15}]^+$	1128.3157	1128.3152	1128.3167	1128.3176	1128.3180	1128.3165	1.1
	$[C_{32}H_{100}NSi_{16}O_{16}]^+$	1202.3345	1202.3337	1202.3357	1202.3362	1202.3366	1202.3352	1.1
	$[C_{34}H_{106}NSi_{17}O_{17}]^+$	1276.3533	1276.3524	1276.3550	1276.3556	1276.3559	1276.3543	1.3
	$[C_{36}H_{112}NSi_{18}O_{18}]^+$	1350.3721	1350.3711	1350.3743	1350.3750	1350.3749	1350.3735	1.5
	$[C_{38}H_{118}NSi_{19}O_{19}]^+$	1424.3909	1424.3890	1424.3924	1424.3933	1424.3938	1424.3916	1.6
	$[C_{40}H_{124}NSi_{20}O_{20}]^+$	1498.4097	1498.4095	1498.4128	1498.4127	1498.4134	1498.4117	1.3
	$[C_{42}H_{130}NSi_{21}O_{21}]^+$	1572.4284	1572.4258	1572.4308	1572.4313	1572.4328	1572.4293	1.9
PS484	$[C_{36}H_{42}]^{+\cdot}$	474.3281	474.3283	474.3284	474.3285	474.3284	474.3284	0.2
	$[C_{36}H_{46}N]^+$	492.3625	492.3627	492.3627	492.3629	492.3627	492.3628	0.2
	$[C_{44}H_{50}]^{+\cdot}$	578.3907	578.3910	578.3910	578.3912	578.3911	578.3911	0.2
	$[C_{44}H_{54}N]^+$	596.4251	596.4252	596.4253	596.4254	596.4253	596.4253	0.1
	$[C_{52}H_{58}]^{+\cdot}$	682.4533	682.4539	682.4539	682.4541	682.4539	682.4540	0.1
	$[C_{52}H_{62}N]^+$	700.4877	700.4881	700.4882	700.4883	700.4883	700.4882	0.1

References

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Handouts

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Conclusions

- In positive-ion DART-MS saccharose yields $[M_n+NH_4]^+$ cluster ions.
- Saccharose cluster ion formation depends on the temperature of the DART gas, sample load, trapping gas pressure, and instrumental factors.
- For best cluster ion formation, experimental conditions need to be well defined.
- Cluster ions of saccharose can be exploited as a cheap and ubiquitous means for DART mass calibration.