Soft Ionization (Li Ion/ QTOF)

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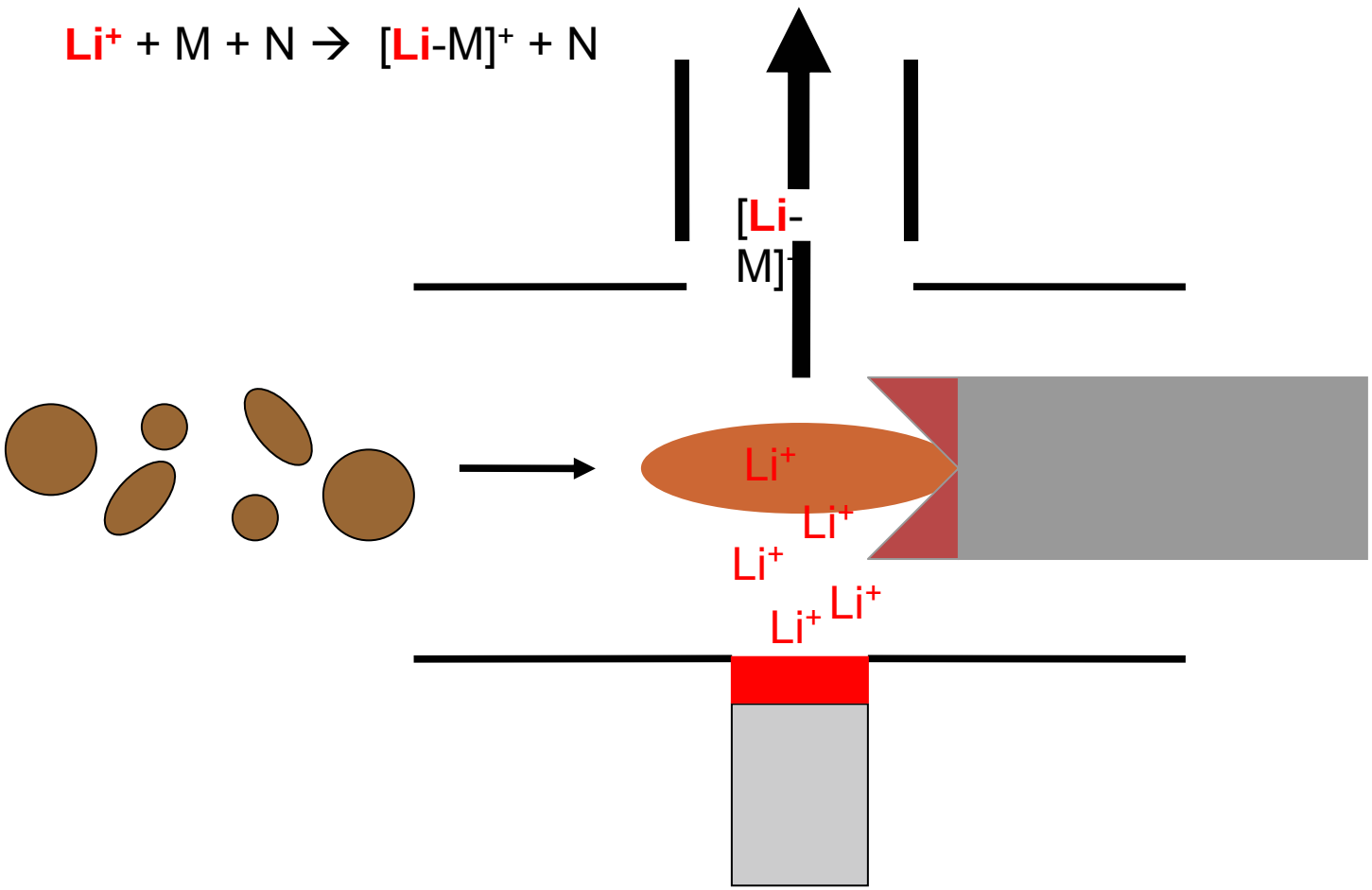
Motivation

- molecular information on organic aerosol
- little or no fragmentation
- high sensitivity
- compatible to standard AMS

Ionization

$A^+ + M + N \rightarrow [A\text{-}M]^+ + N$

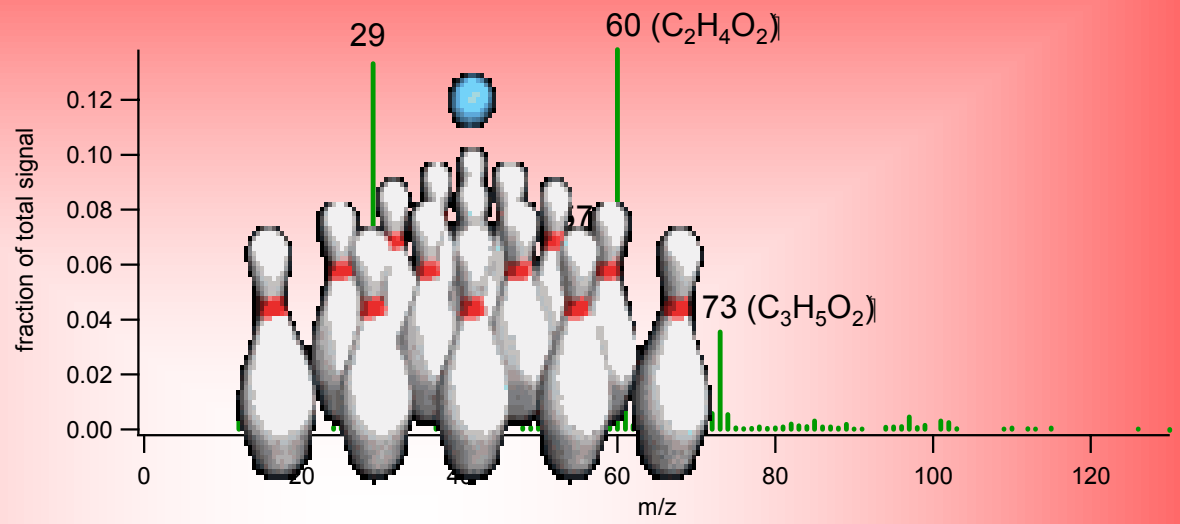
$Li^+ + M + N \rightarrow [Li\text{-}M]^+ + N$



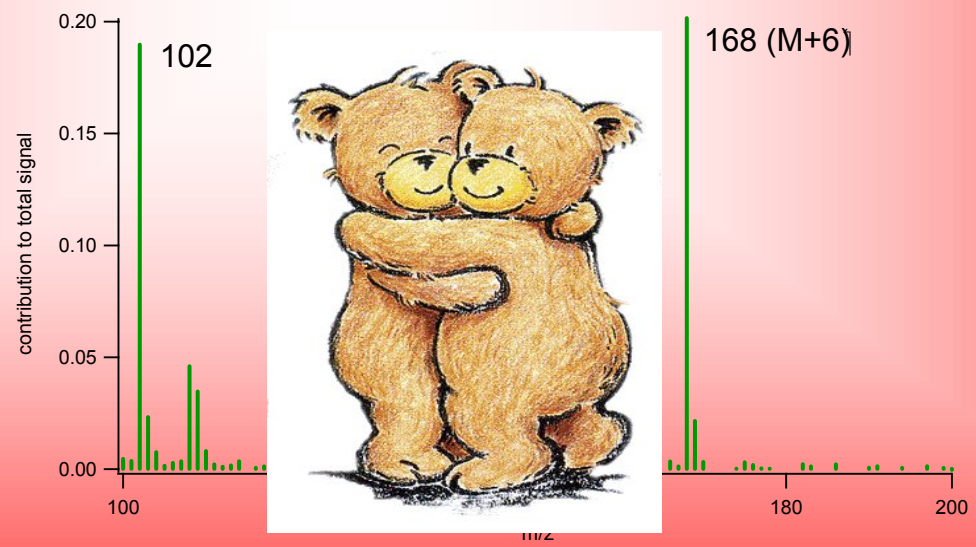
Source provides Li ion current of ~10 μA -> $6*10^{13}$ ions per second

Why Lithium ion attachment?

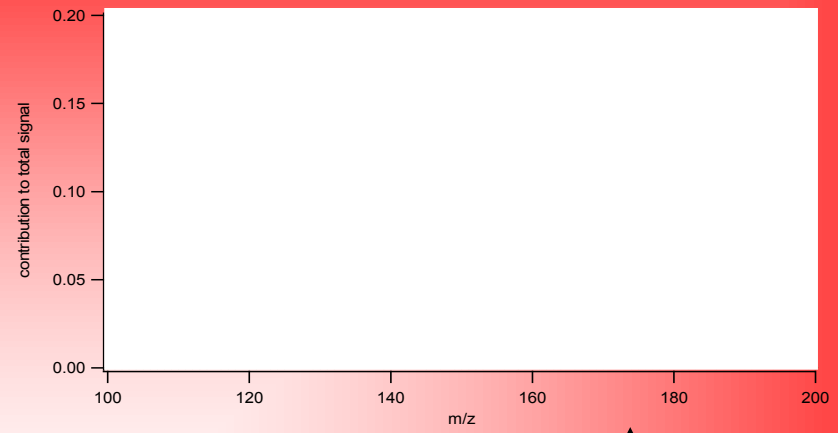
electron impact

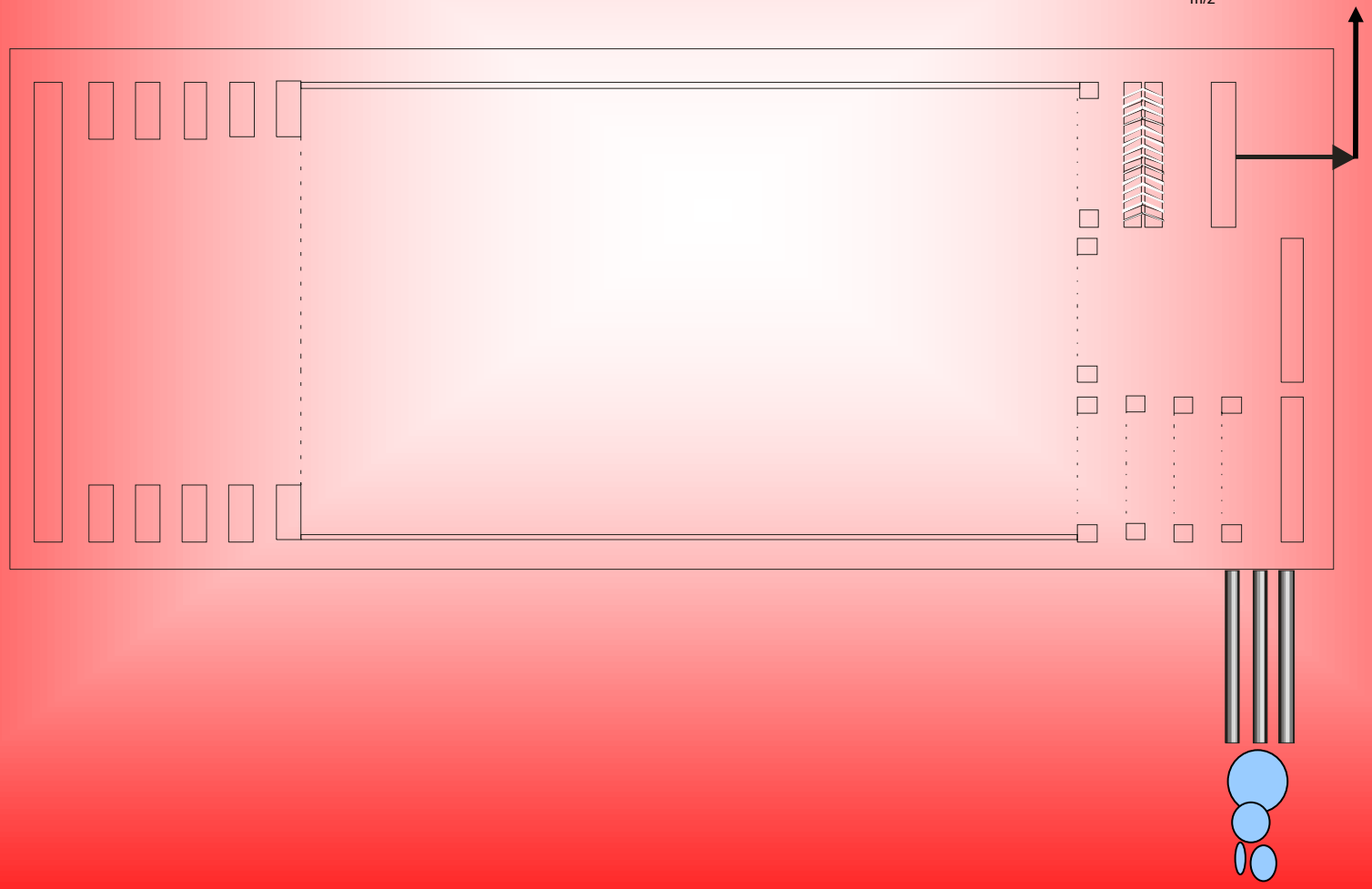


Li^+ ion attachment



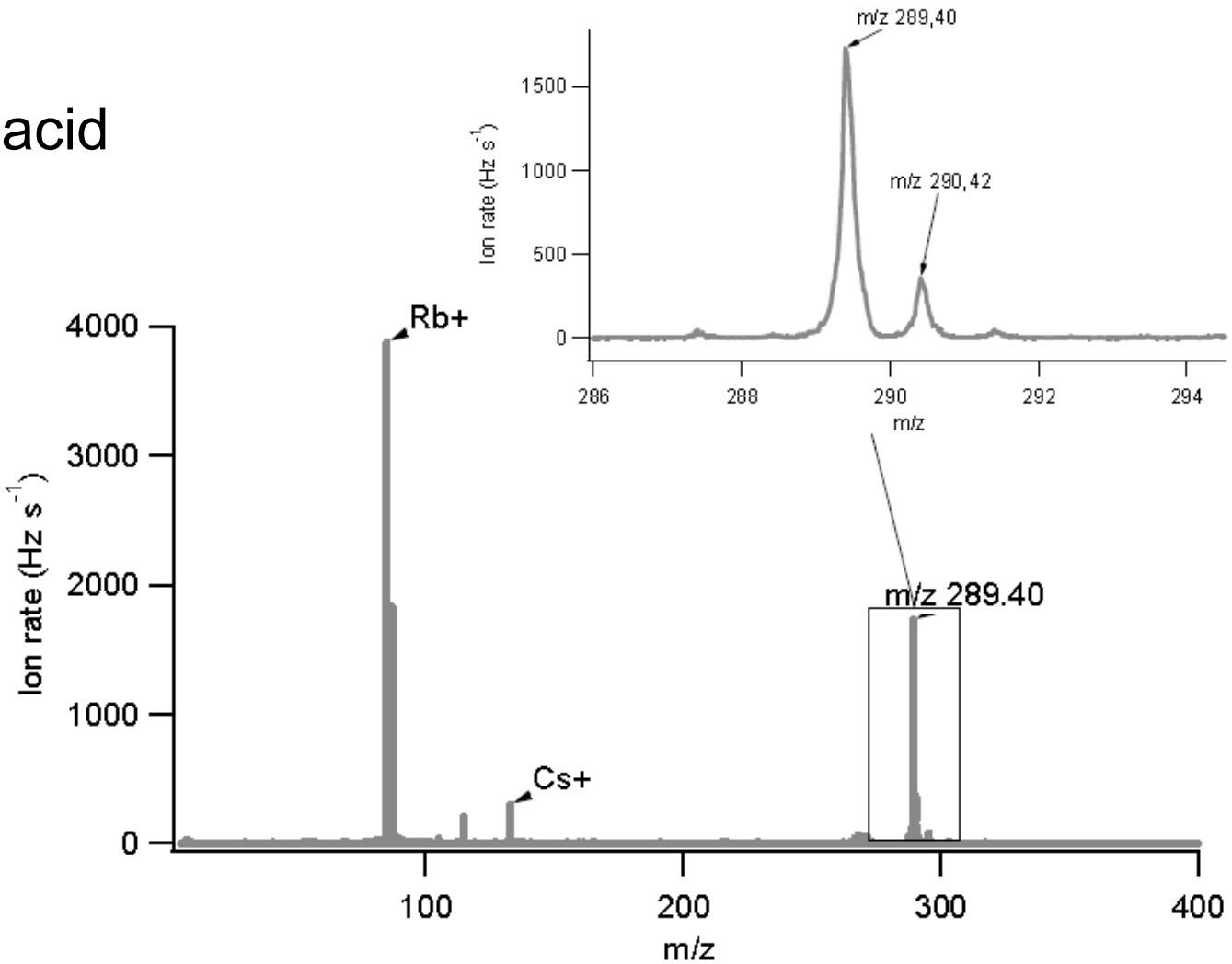
Ion blanking with quad



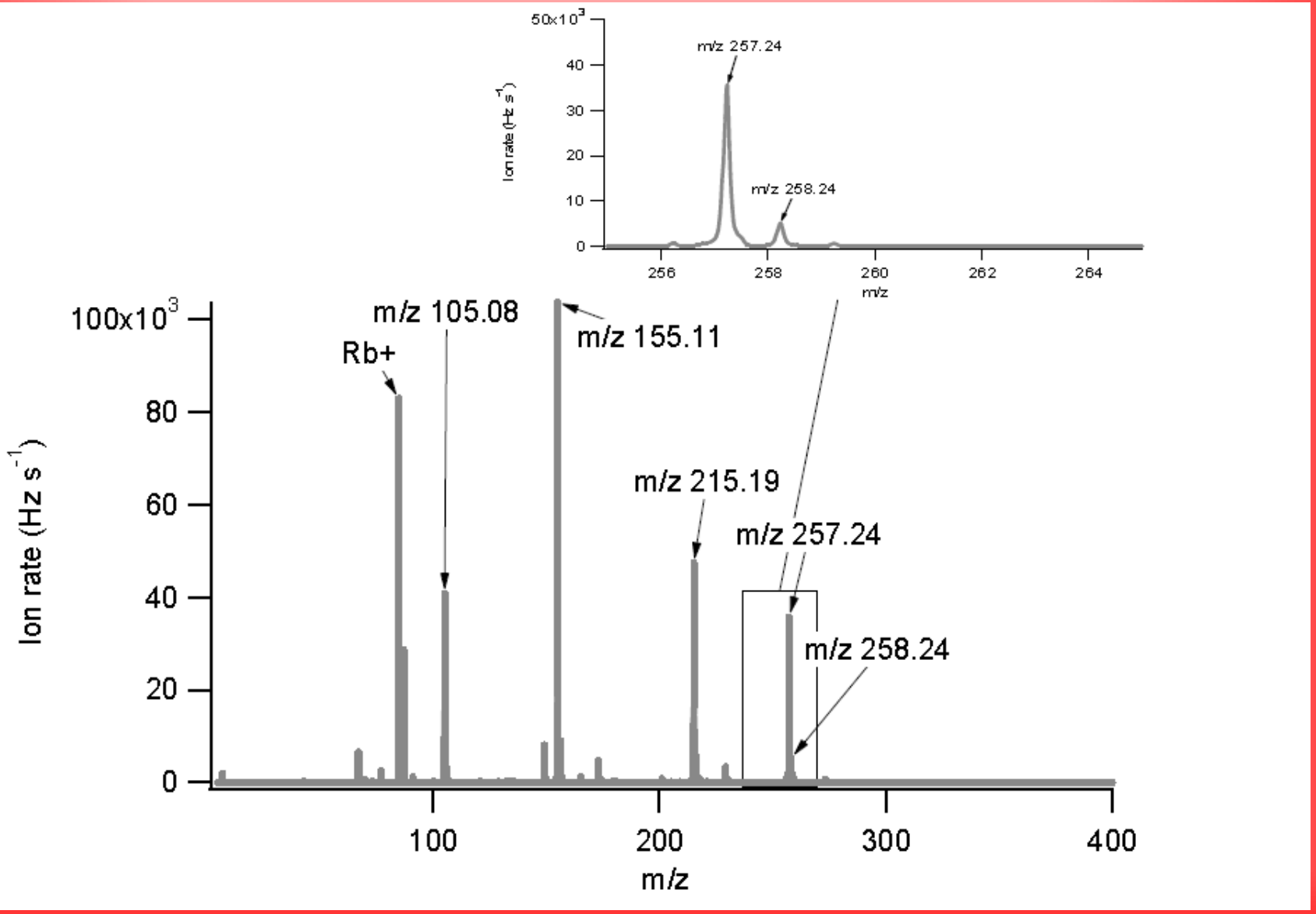


Fragmentation due to Li^+ ionization

Oleic acid



Phthalsaeuredipropylester



Fragmentation (quantification)

$$F = \frac{\sum I_{Frag} + I_{Quasimolekülion}}{I_{Quasimolekülion}}$$

$$I_{Norm} = \frac{A_{Quasimolekülion} \cdot F}{\#Pt}$$

Substanz	$A_{Quasimolekülion}$	Fragmentfaktor F	Partikelzahl #Pt	I_{Norm}
Phthalsäuredibutylester	96,692	2,09	5222	0,03871
Phthalsäuredipropylester	7,043	2,07	800	0,01826
Diethanolamin	26,386	5,60	9832	0,01502
Pinsäure	0,472	2,78	110	0,01189
Ölsäure	528,941	1,00	53915	0,00981
Glycerin	39,930	1,00	4568	0,00874
Phthalsäurediethylester	n/a	n/a	6	n/a
4-Hydroxybenzoesäure	n/a	n/a	832	n/a

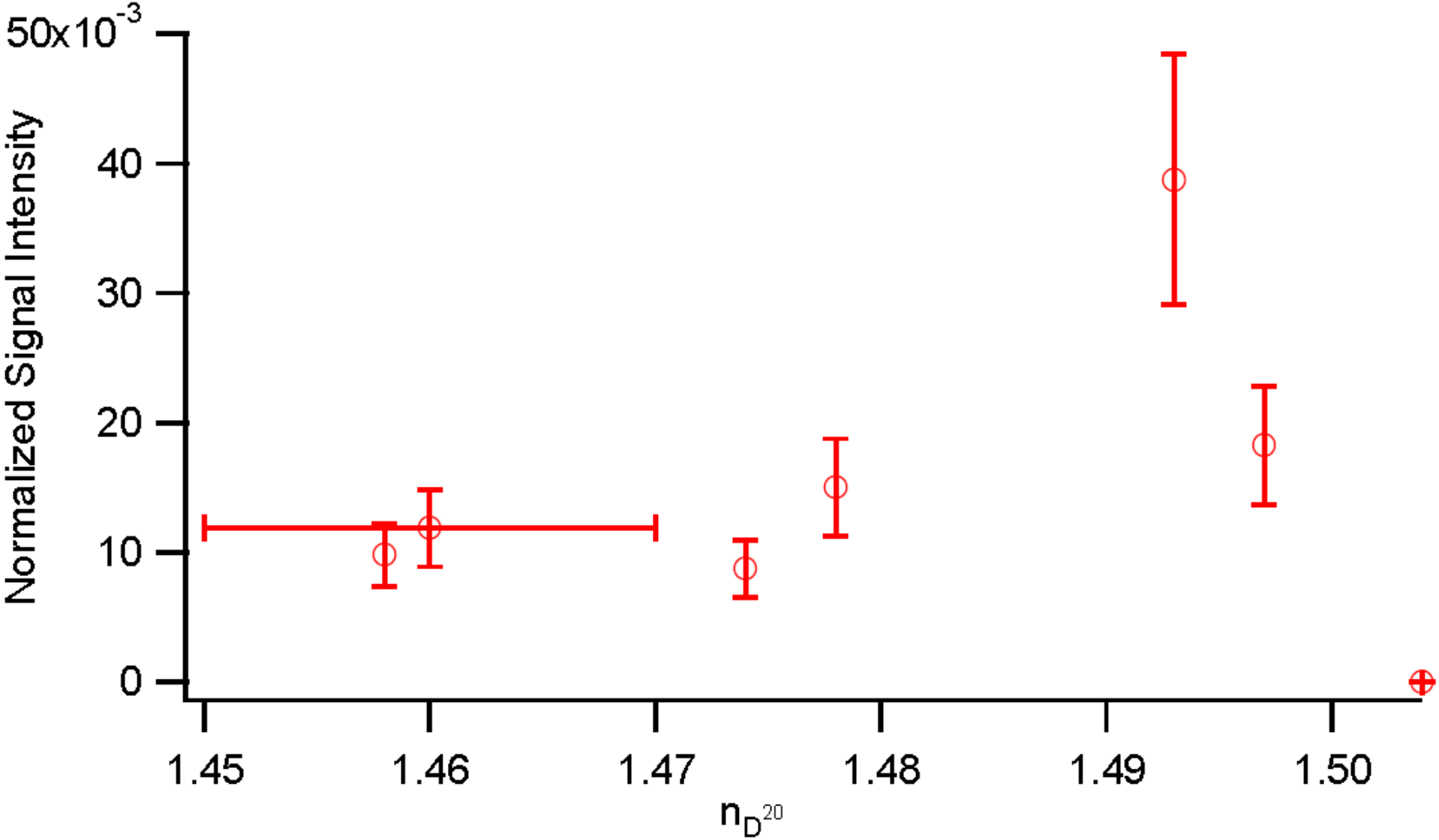
Tabelle 4-6: Gemessene Ionisationseffizienzen

Properties that influence the ionization efficiency of Li ion attachment

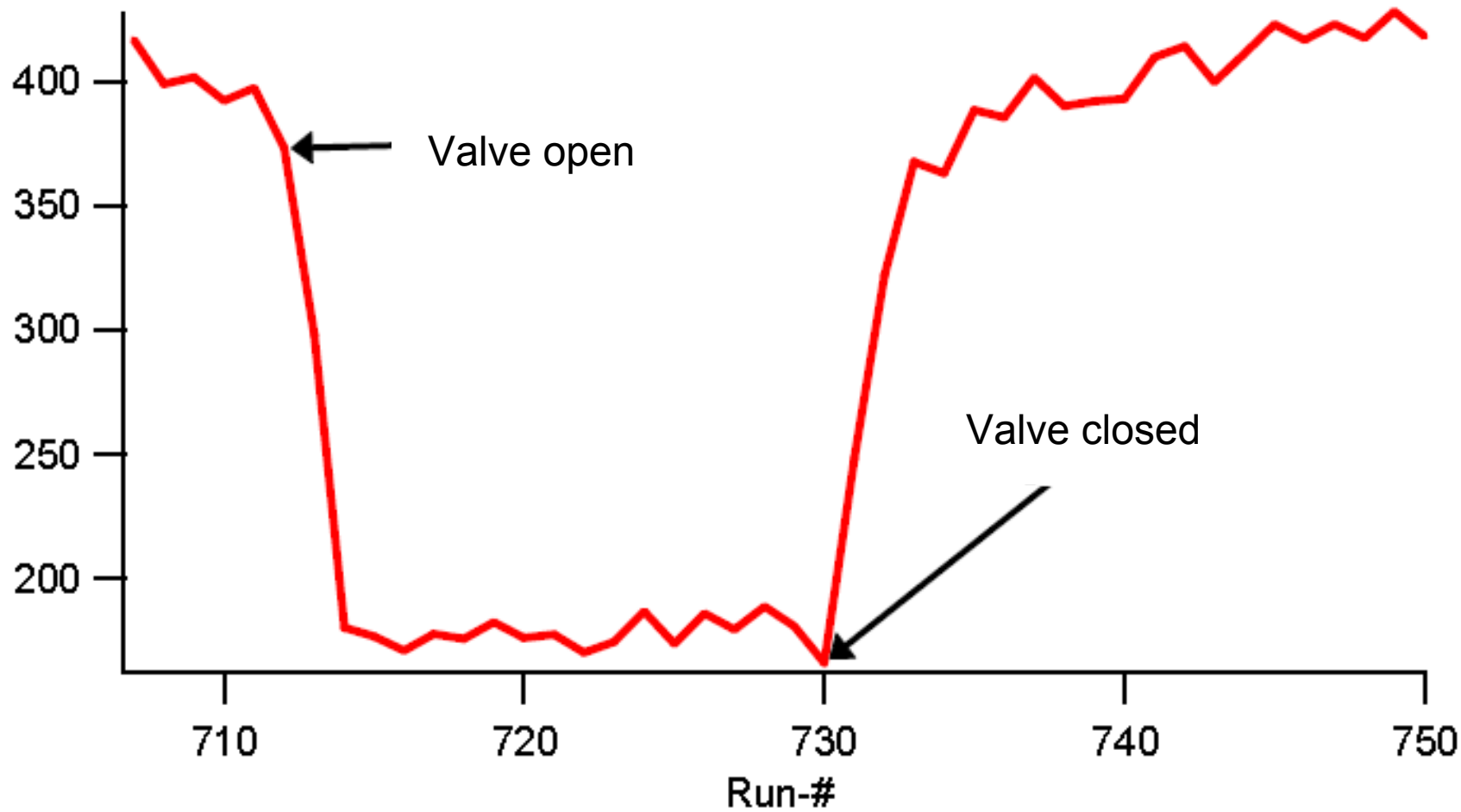
- Polarization
  - Not known for many compounds
  - Refractive index a measure for polarization
- gas phase acidity
  - Unknown for most of the compounds

normalized ionization efficiency

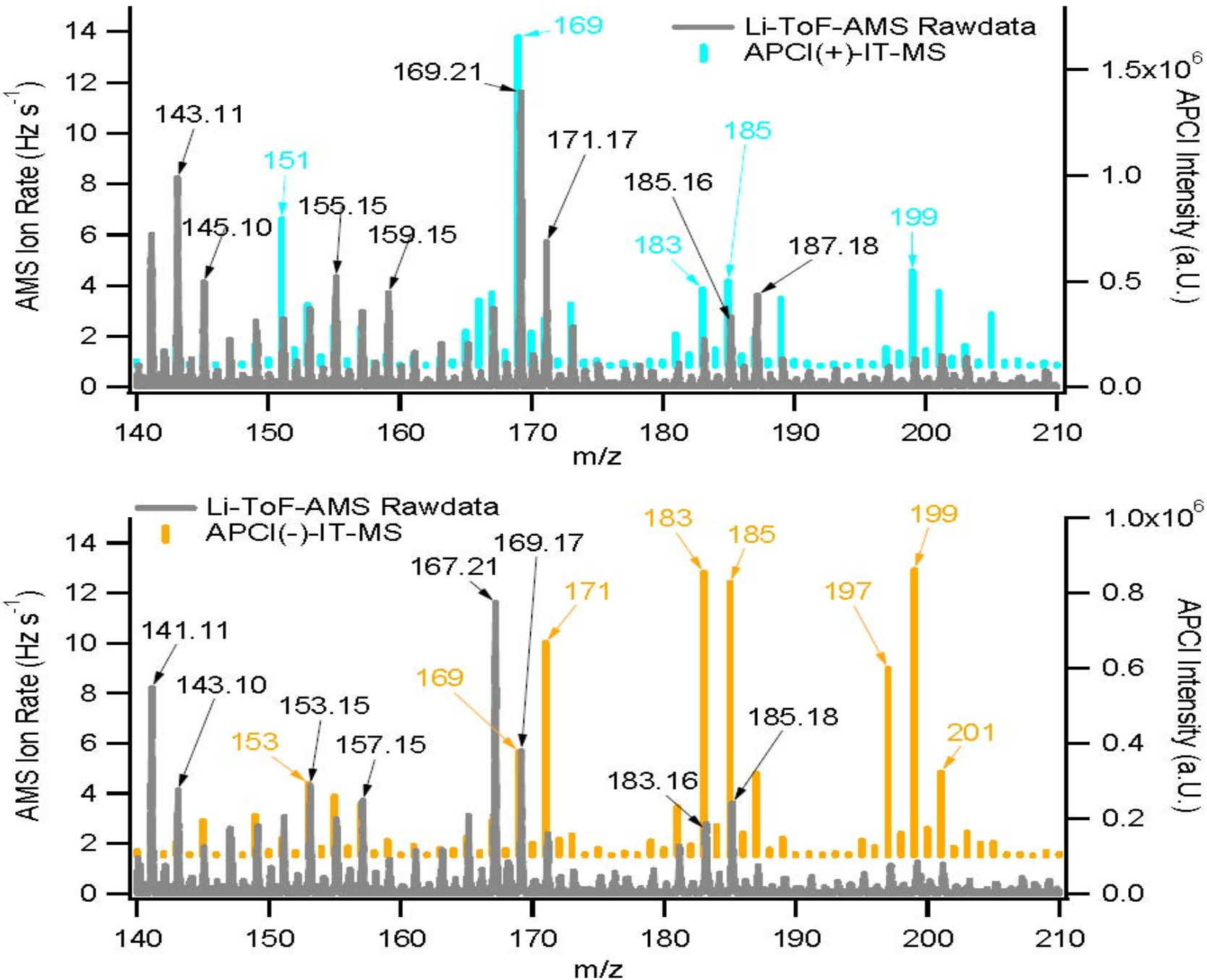
(refractive index used as measure for polarization)

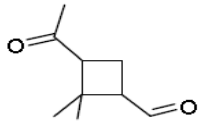
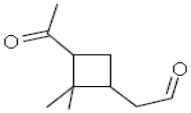
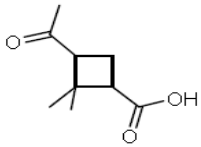
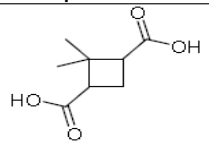
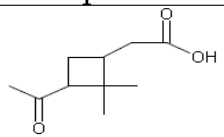
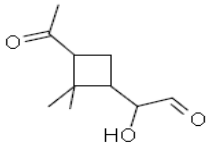
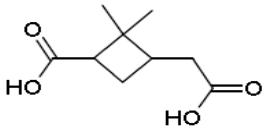
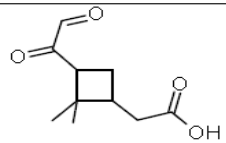
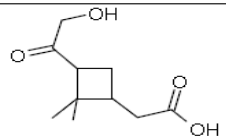


Pressure dependence of the ionization



Comparison of ACPI and Li ion atachment (□-pinene and ozone)

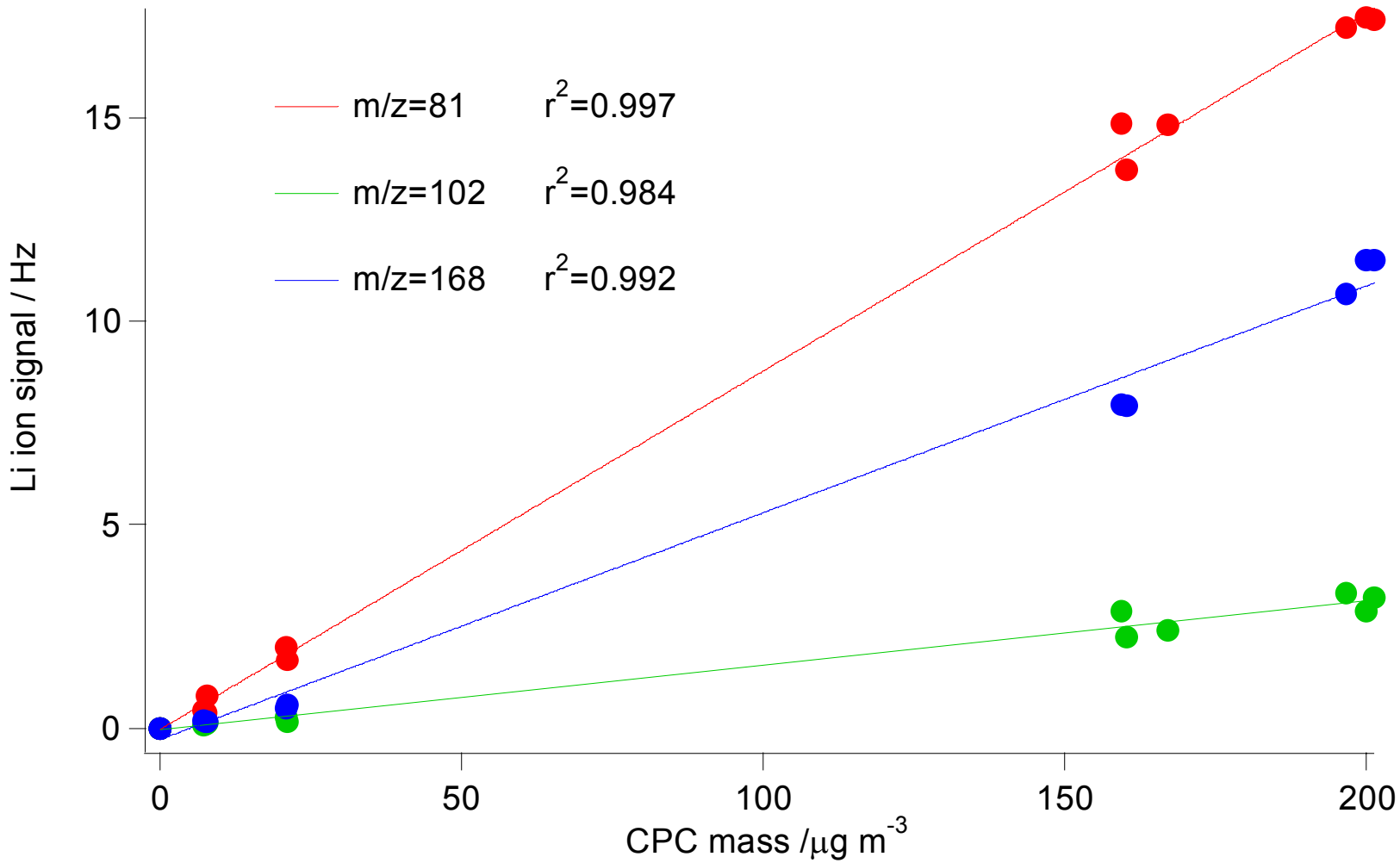


M / g mol^{-1}	m/z Li-AMS	m/z APCI(-)	m/z APCI(+)	Strukturformel / Name
154,15	161,15			 Norpinonaldehyd
168,24	175,20		169	 Pinonaldehyd
170,21	177,17	169		 Norpinonsäure
172,18	179,16	171		 Norpinsäure
184,24	191,19 (?)	183		 Pinonsäure
184,24	191,19		185	 Hydroxypinonaldehyd
186,21	193,18	185		 Pinsäure
198,22	205,15	197	199	
200,24		199		 Hydroxypinonsäure

- APCI + ionizes mainly ketones and aldehydes
- ACPI - ionizes mainly acids and carboxylic groups

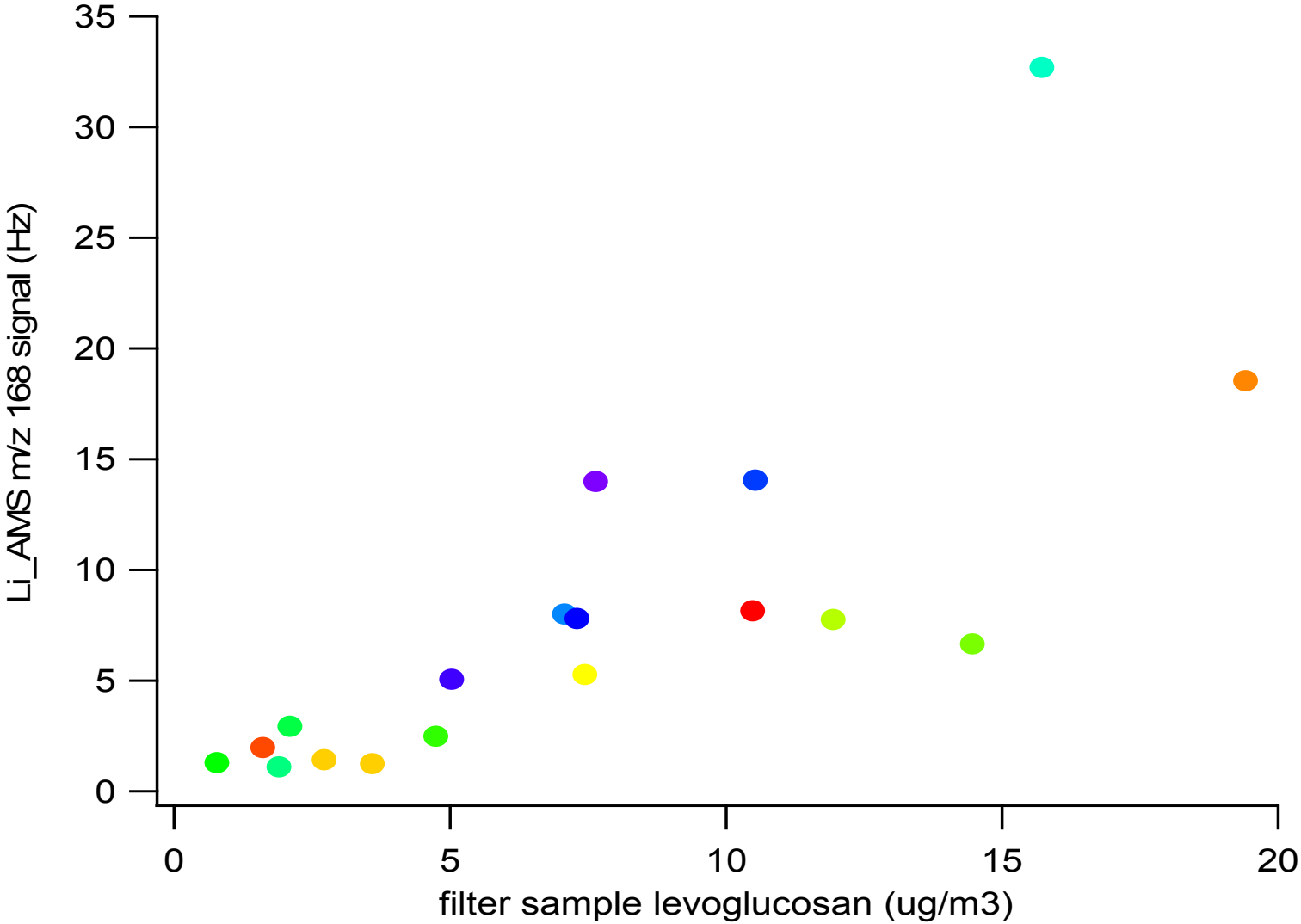
- Li ion attachment sees most of the tested components
  - Lower sensitivity

Quantification



Signal linear with mass loading (or a given compound)

Comparison to filter samples



Summary

- Li ion attachment ionization results in spectra showing less or no fragmentation
- quadrupol allows clean blanking of ions up to m/z=24
- mass resolution is the same as in EI ionization
- sensitivity is some µg m^{-3} in 10s
- signal is linear with mass loading -> allows for quantification of known compounds

- Quadrupol blanking can also be use to blank electrons in negative ion mode

Todo

- build easy to use quadrupol electronics
- measure more standards
- better understanding of ionization mechanism

Thanks to Niklas Schaper for the good characterization of the Li-ion-AMS