Fragmentation in a cyclic traveling wave ion mobility cell and its effect on the arrival time distribution profile

Štěpán Dostál, Karel Lemr

Department of Analytical Chemistry, Faculty of Science, Palacký University, 779 00 Olomouc, Czech Republic

Introduction

Arrival time distribution (ATD) profiles characteristic of individual isomers have been observed, for example, for oligosaccharides,[1] peptides,[2] and oligonucleotides.[3] Previously, they were used to determine the ratio of isomeric oligosaccharides.[1] Since the profile can be influenced by the presence and content of protomers/conformers/tautomers associated with each isomer, its shape depends on experimental parameters that affect their ionization yields and fragmentation. We investigated the influence of the electrospray and ion optics settings, the height and velocity of the traveling wave in the cyclic ion mobility on the signal intensities of thermometer ions to estimate the possible influence of these parameters on ATD profiles.

Experimental

Analyzed solutions were directly infused into an electrospray ion source of a Waters SELECT SERIES Cyclic IMS mass spectrometer. The data were processed using MassLynx V4.2 software (all Waters Corp., UK). The effect of electrospray and ion optics settings was investigated by evaluating the fragmentation of benzylpyridinium derivatives (4-methyl-, 4-fluoro-, 4-methoxy-, 4-chloro-, 4-nitro-, and 4-tert-butyl-) dissolved in methanol:water (1:1, v/v). Default and tuned instrumental parameters are summarized in Table 1. Survival yield was calculated from parent ion (I_p) and fragment ion (I_f) intensities in the mass spectrum: $SY = \frac{I_p}{I_p + I_f}$

The effect of cyclic traveling wave height and velocity was studied using 4-(trifluoromethyl)benzylamine in methanol:water:acetic acid (49.5:49.5:1, v/v/v). Mobility peak areas of the parent and fragment ions were used instead of spectral intensities to determine SY.

	default	tuned
STEPWAVE body gradient (V)	20	10
STEPWAVE head gradient (V)	10	5
STEPWAVE IG TW pulse height (V)	0.4	0.2
QUADRUPOLE Trap CE (V)	6	2
QUADRUPOLE Transfer CE (V)	4	1
TRAP entrance (V)	2.0	1.0
TRAP bias (V)	2.0	1.5
TRAP post trap gradient (V)	5	1.5
TRAP post trap bias (V)	25	16
TRANSFER pre trans bias (V)	2.0	0.0
TRANSFER exit (V)	10	15
RF Stepwave (V)	200	100

Table 1: Settings of ion optics.

Results and Discussion

Tuning of ion source and ion optics significantly suppressed fragmentation. Besides the ion source parameters (as cone voltage), the tuned parameters included the voltages of the ion optics from the stepwave (in front of the ion mobility cell) to the transfer cell (behind the IM cell), see Table 1. The changes in fragmentation are evident from the SY of the thermometer ions (Figure 1). Considering the ion mobility cell, the cyclic wave velocity had little effect, the increase in wave height voltage caused a more significant decrease in SY (Figures 2 and 3). The contribution of fragmentation in front of, inside, and behind the cyclic mobility cell is shown in Figure 3.

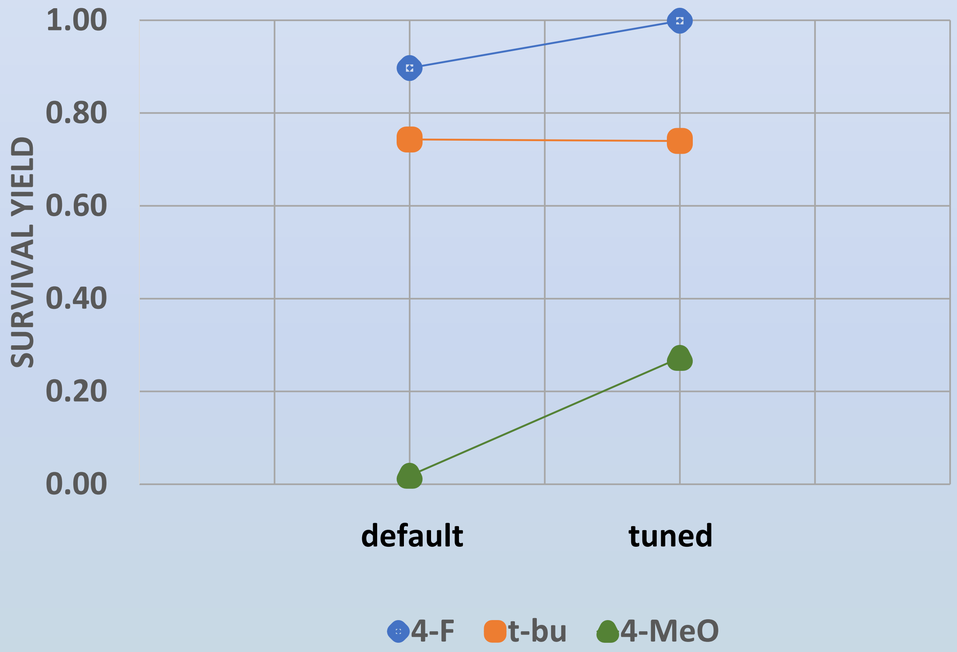

Figure 1: Survival yields of thermometer ions for default and tuned ion optics parameters. Critical energies: 4-F 1.81 eV, t-bu 1.57 eV, 4-MeO 1.30 eV [5].

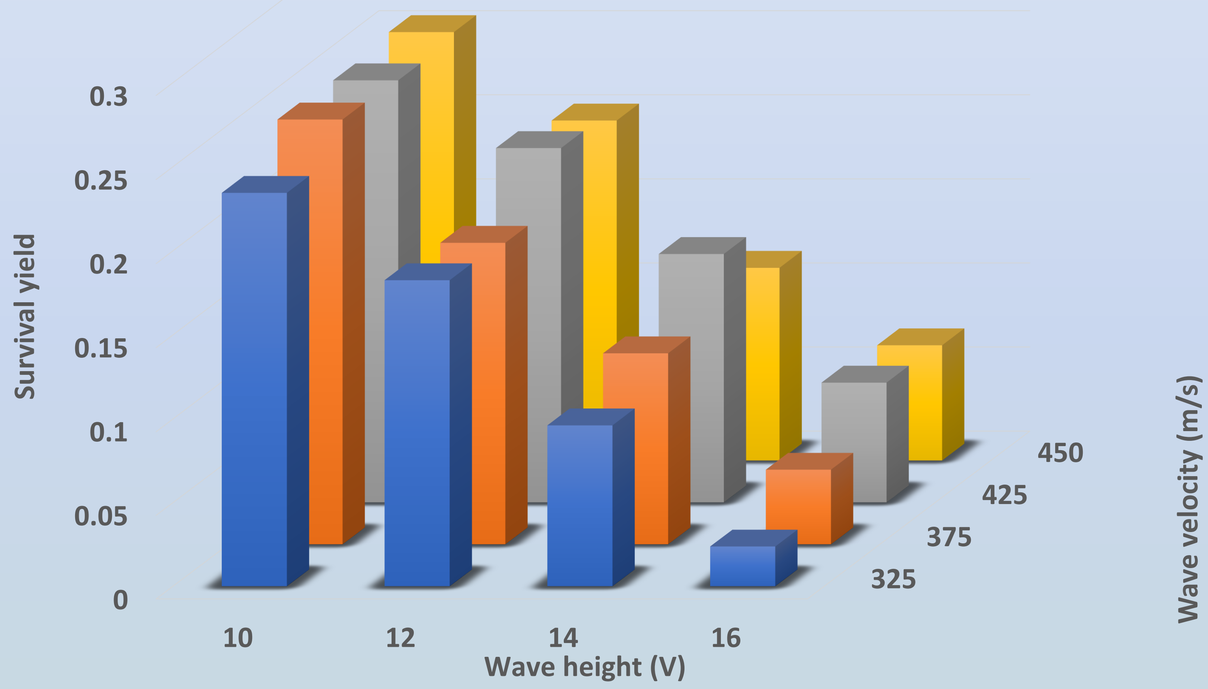

Figure 2: Effect of traveling wave height and velocity on survival yield of 4-(trifluoromethyl)benzylamine.

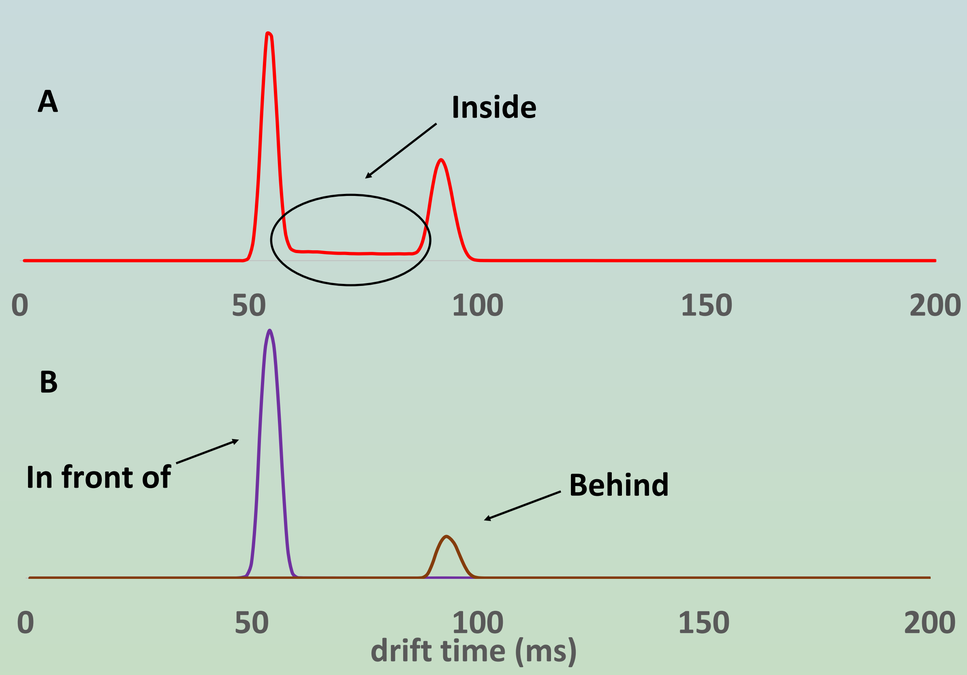

Figure 3 Mobilograms showing the fragmentation of 4-(trifluoromethyl)benzylamine in different regions relative to the mobility cell.

Conclusion

The fragmentation process can be significantly affected by the settings of the electrospray and ion optics, but also by the setting of the cyclic ion mobility cell.

Since traveling wave velocity has little effect on fragmentation, compared to wave height, its tuning can allow ion manipulation with less impact on parent ion signals. However, the effect of the time the ions spend in the mobility cell needs to be studied.

Proper adjustment of the parameters studied can mimimize the effect of fragmentation on the ATD profiles of precursor ions, which can improve the repeatability of ATD profiles and support their use in isomer ratio determination.

Reference: [1] L. Borovcová, et al. Anal. Chim. Acta, 981 (2017) 71-79. [2] A. Kováč, et al. J. Am. Soc. Mass. Spectrom., 34 (2023) 394-400. [3] J. Wan, et al. J. Am. Soc. Mass. Spectrom., 34 (2023) 2323-2340. [4] C. Ieritano, et al. J. Am. Soc. Mass. Spectrom., 31 (2020) 582-593. [5] D. Morsa, et al. J. Am. Soc. Mass. Spectrom., 25 (2014) 1384-1393.

The research was supported by the Czech Science Foundation (grant 23-07254S).