Accurate drift time determination by traveling wave ion mobility spectrometry: The concept of the diffusion calibration

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Introduction:

Ion Mobility Spectrometry (IMS) is a separation technique which allows separation of ion mainly depending on their three dimensional structure (described as Collision Cross Section or CCS)[1]. The main factor affecting the IMS resolution is the initial ion clouds size injected in IMS and its longitudinal extension due to diffusion[2]. Unresolved ion conformers by IMS lead to a spatial overlapping of their ionic cloud. In this case, the Arrival Time Distribution (ATD) corresponding to an ion is a sum of the contributions of each ion conformers and their diffusions[3]. Then a wider ATD than expected corresponds to the sum of different conformer distributions. This poster introduces a strategy of ATD signal deconvolution using the peak widths as *full width at half maximum* (FWHM).

Strategy:

A calibration using ionic compounds which are detected as a single conformer in gas phase allow the prediction of the *full width at half maximum* (FWHM) for a given ATD as a function of the intensity, the IMS settings and the drift time. The strategy is to use a modified gaussian equation, where the FWHM is set, to help the deconvolution process in TWIMS. In this case the fitting equation only depend on two parameters: a (correlated to the intensity) and b (correlated to the drift time). The standard deviation (correlated to FWHM) value becomes a function of these two parameters. This deconvolution process have been used to assist the study of two different kind of compound (crown ethers and peptides)

Estimation of the diffusion effects

Space Charge Effect

Coulomb repulsions between ions:
- **Depend on the intensity**
- **Depend on the charge**

Negligible effect on the peak width (< 1%) until intensity < 5.10^4 cps

(For monocharged ion only)

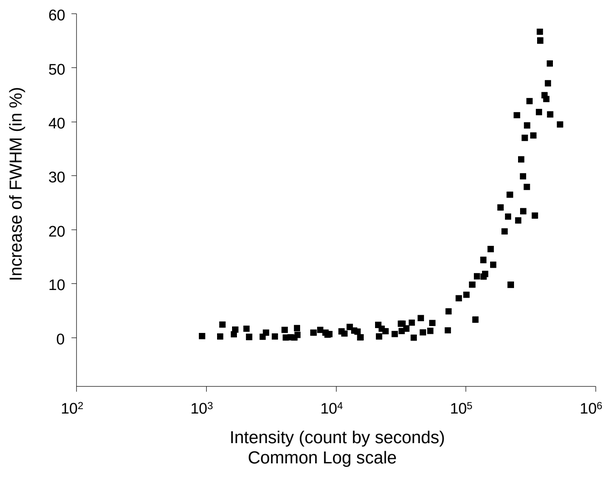

Figure 1: FWHM increase of the ATD of tetraalkylammonium compounds (in %) in function of the intensity (cps)

Temporal Axial Diffusion

Diffusion:
- **Depends on the drift time**
- **Depends on IMS settings**

Major factor on the peak width

→ Calibration of FWHM in function of drift time to estimate the correlation between drift time and FWHM

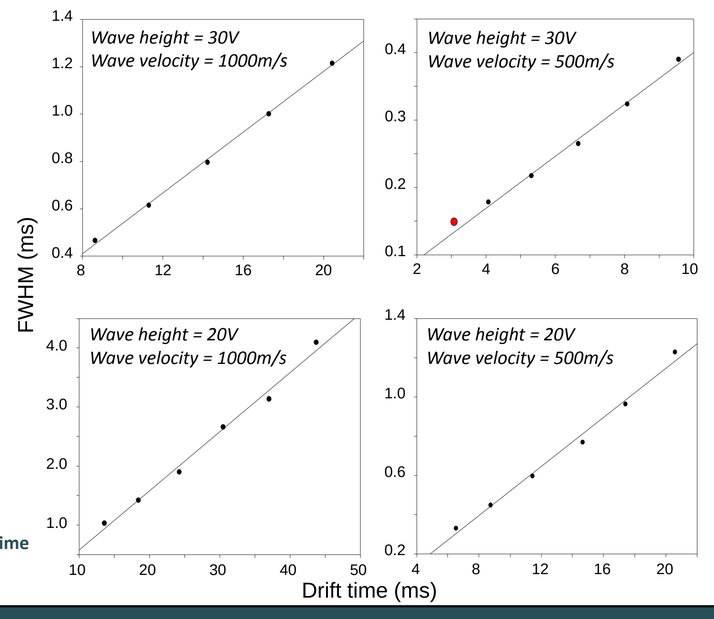

Fig. 2 : FWHM of ATD of tetraalkylammonium in function of drift time with different IMS settings.

Application to protonated crown ethers

ATD of some protonated crown ethers are larger than expected compare to the ATD of crown ether and alkalin cation complexes…

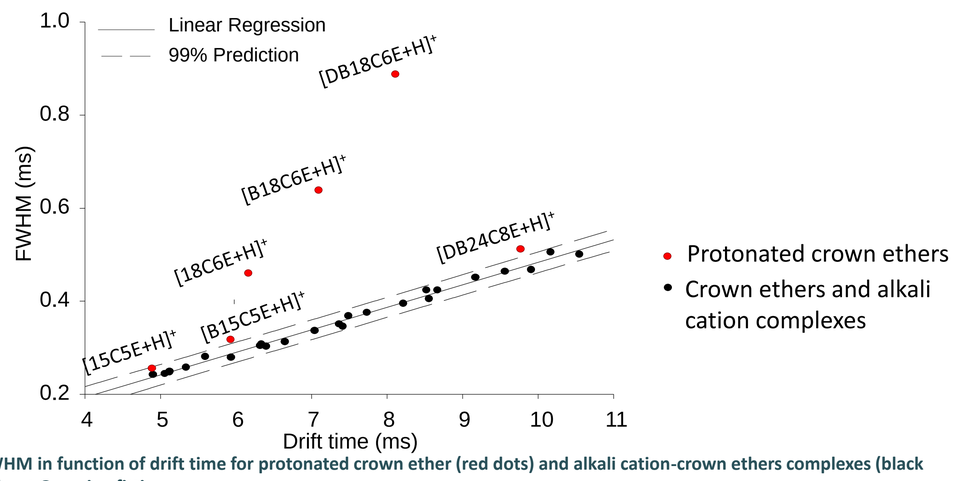

Fig.3 : FWHM in function of drift time for protonated crown ether (red dots) and alkali cation-crown ethers complexes (black dots) without Gaussian fitting process.

… explained by the presence of two different distributions:

1. ATD of Initial protonated crown ether

2. ATD of protonated crown ether formed after IMS separation
(from crown ether complexes with H_3O+

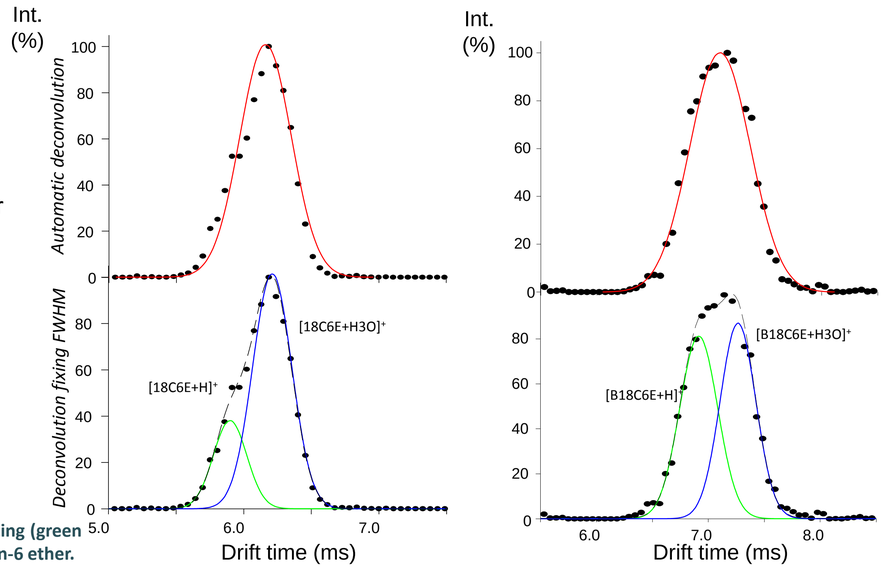

Fig.4: Normal Gaussian fitting (red) and modified Gaussian fitting (green and blue) for protonated 18-crown-6 ether and benzo 18-crown-6 ether.

Application to peptides

ATD of Glu-Fib is larger than expected compare to the trend of BSA tryptic digest

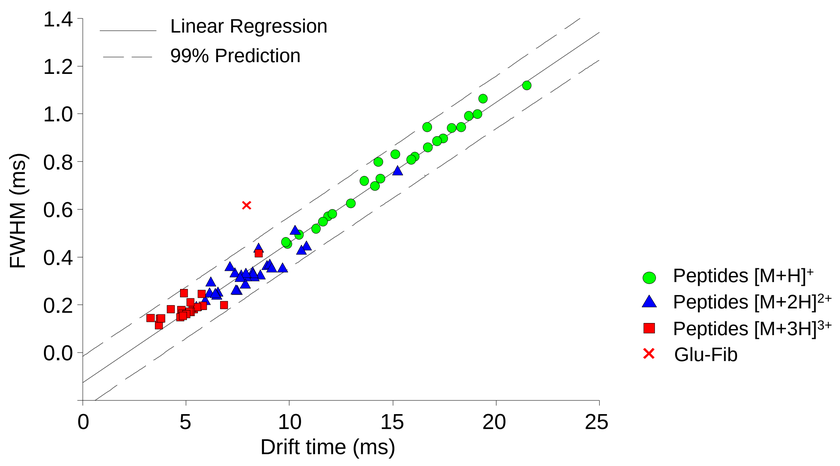

Fig. 5: FWHM in function of drift time for BSA tryptic digest peptides and doubly charged Glu-Fib (red cross)

… explained by the presence of two different distributions:

Confirmed by the use of different IMS settings

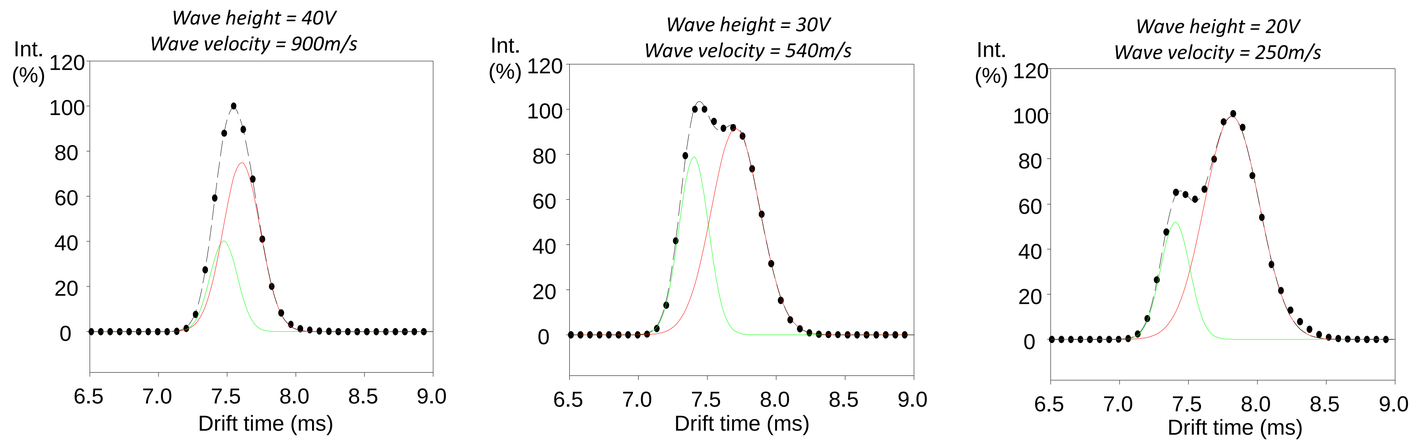

Fig. 6 : ATD of GluFIB^{2+} in function of IMS settings.

Conclusion:

Data shown suggest that the deconvolution of arrival time distribution (ATD) peaks can be helped by using the full width at half maximum (FWHM) to detect unresolved ion conformers in travelling wave ion mobility spectrometry (TWIMS). The ATD for a given conformers is assumed as a Gaussian function where the amplitude depends on the intensity, the mean value depend on the ionic mobility and the standard deviation, or peak width, depends on the diffusion described as the Coulomb expansion and the temporal diffusion. The experimental determination of the diffusion lead to the possibility of predicting the FWHM of the ATD for a given conformer ion as shown with crown ethers and peptides.

References:

1.Kanu, A. B., Dwivedi, P., Tam, M., Matz, L. & Hill Jr., H. H., *J. Mass Spectrom.* **43,** 1–22 (2008).
2.Shvartsburg, A. A. & Smith, R. D., *Anal. Chem.* **80,** 9689–9699 (2008).
3.Yamagaki, T. & Sato, A., *J. Mass Spectrom.* **44,** 1509–1517 (2009).

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