

A Different Way of Measuring Ion Mobility for Absolute Cross Sections at Ultra-High Resolution TOF MS

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Introduction

In classical drift tube IMS experiments an electric field accelerates ions while collisions with a stationary buffer gas lead to a frictional force: Ions drift with constant velocities and become separated depending on their mobility. Here, we present a different method: In the ion funnel interface of an electrospray-QTOF, ions are carried by a gas flow into the mass spectrometer and fly against an electric field barrier introduced to decelerate them (Fig. 1). This barrier repels the ions, and only those below a certain mobility threshold can be dragged into the mass spectrometer by the gas flow. With increasing barrier voltage, the threshold moves from high to low mobilities. When the threshold passes an ion's mobility its signal drops. Derivatives of decreasing signal curves form peaks. The aim of this study was to use the QTOF without any hardware changes to obtain IMS-mass spectrometry data.

Methods

The ion funnel interface in the conventional

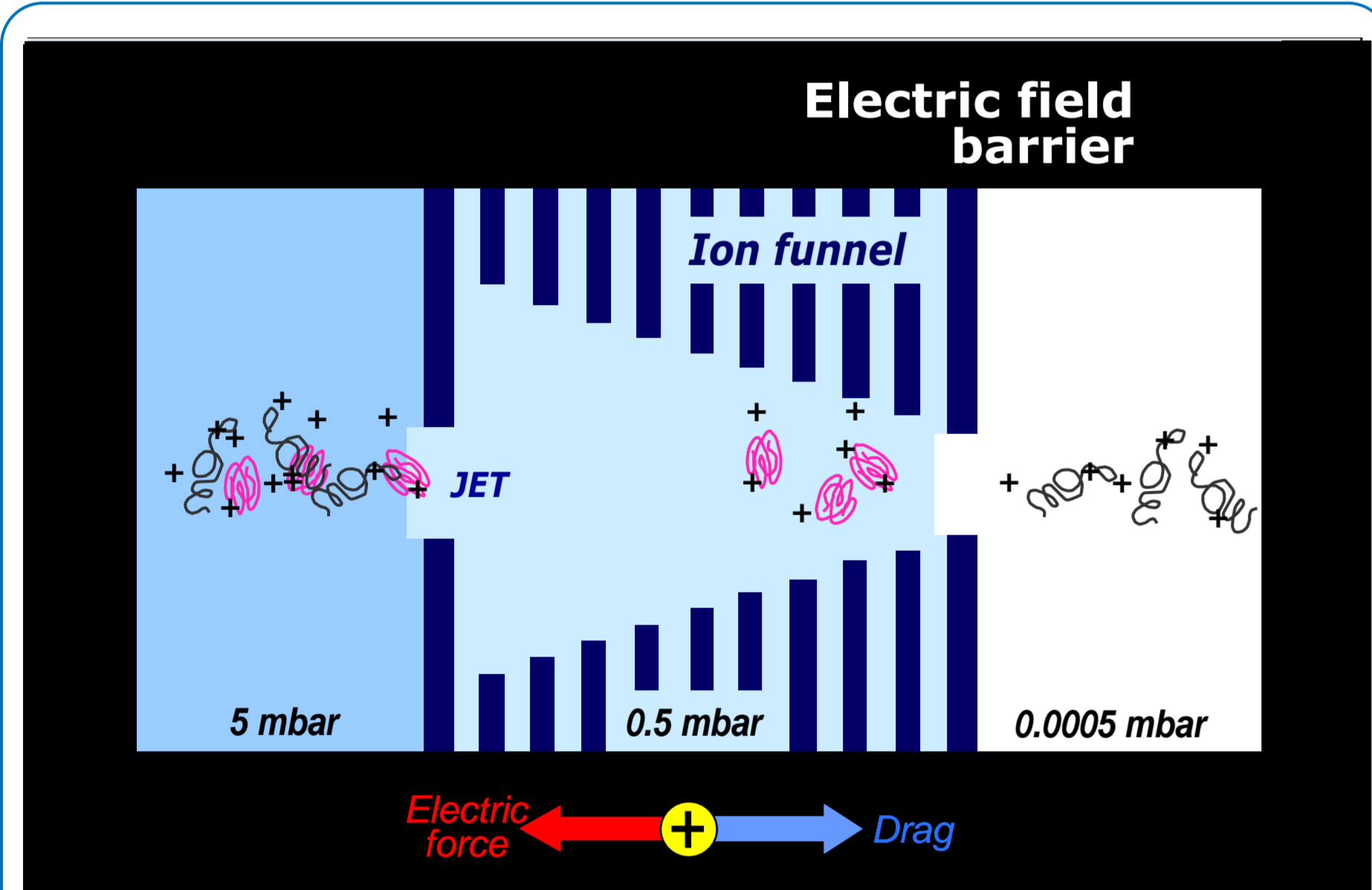


Fig. 1: Electric Field barrier in the second ion funnel of the ESI-QTOF maxis retards more mobile ions.

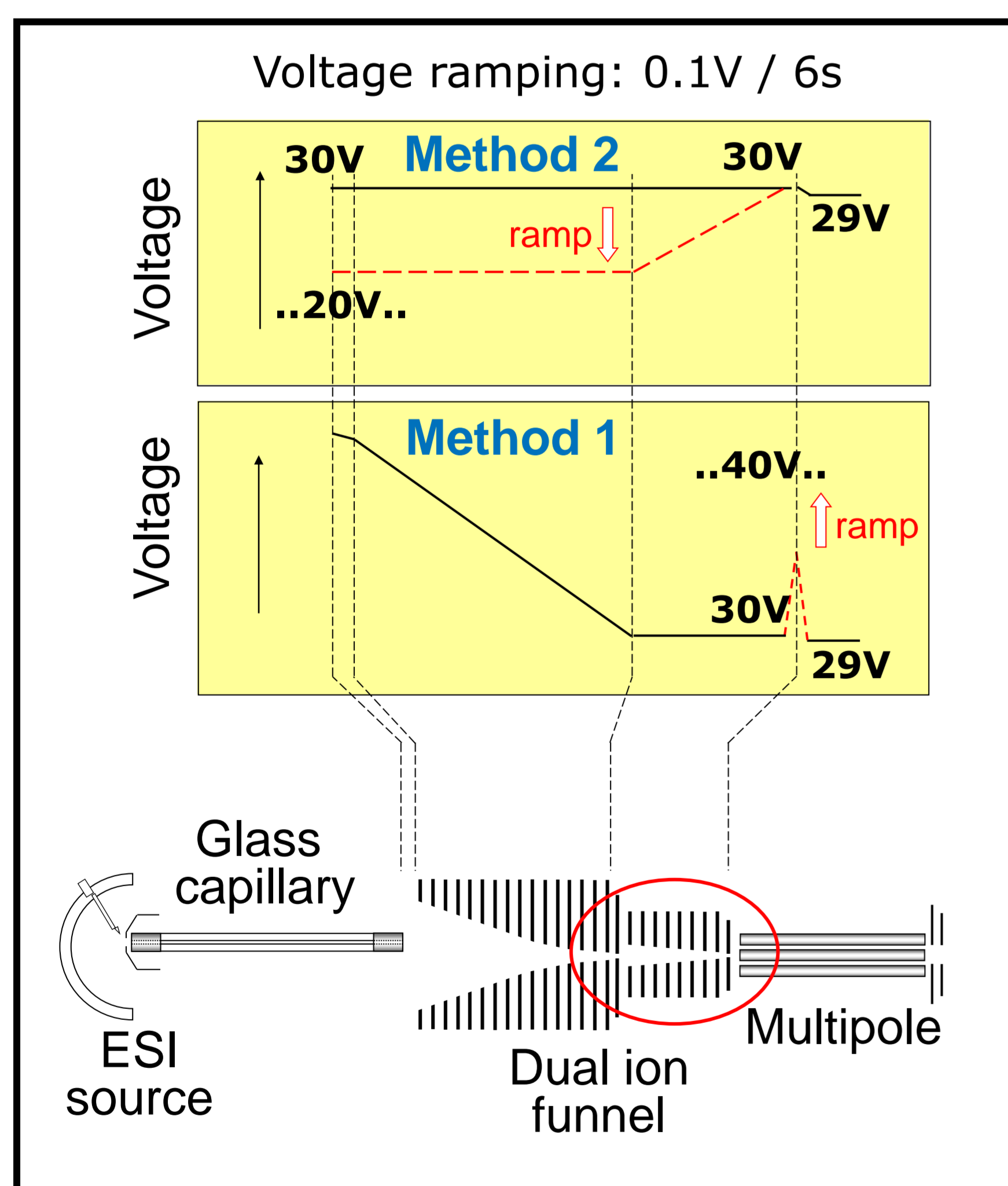


Fig. 2: Methods of barrier voltage ramping to obtain mobility information by retarding and blocking ions.

Conclusions

- Ion mobilities can be measured in an ion funnel and allow the separation of higher mobility ions from the rest.
- The mobility resolution is comparable or better than the resolution of small conventional drift cells or basic traveling wave mobility cells.
- The experiments could be performed without modifying the existing hardware of the ESI-QTOF maxis.

IMS, maxis

setup of the maxis UHR-QTOF (Bruker) was used for IMS experiments. For mobility measurements, ions were generated by ESI in 1:1 MeOH/H₂O solutions with 1% formic acid. The barrier voltage was stepwise increased (Fig. 2) and mass spectra were recorded. To calibrate the barrier voltage scale ions generated from reference peptides Bradykinin, Angiotensin I, Neurotensin, and Fibrinopeptide A were used, of which absolute cross section values in N₂ (from classical IMS experiments) were kindly provided by Erin Baker, PNNL, USA.

Results

Fig. 3 shows the signal drop curves and their derivatives for PEG 400 and prostaglandin E₁. Prostaglandin has a larger cross section while

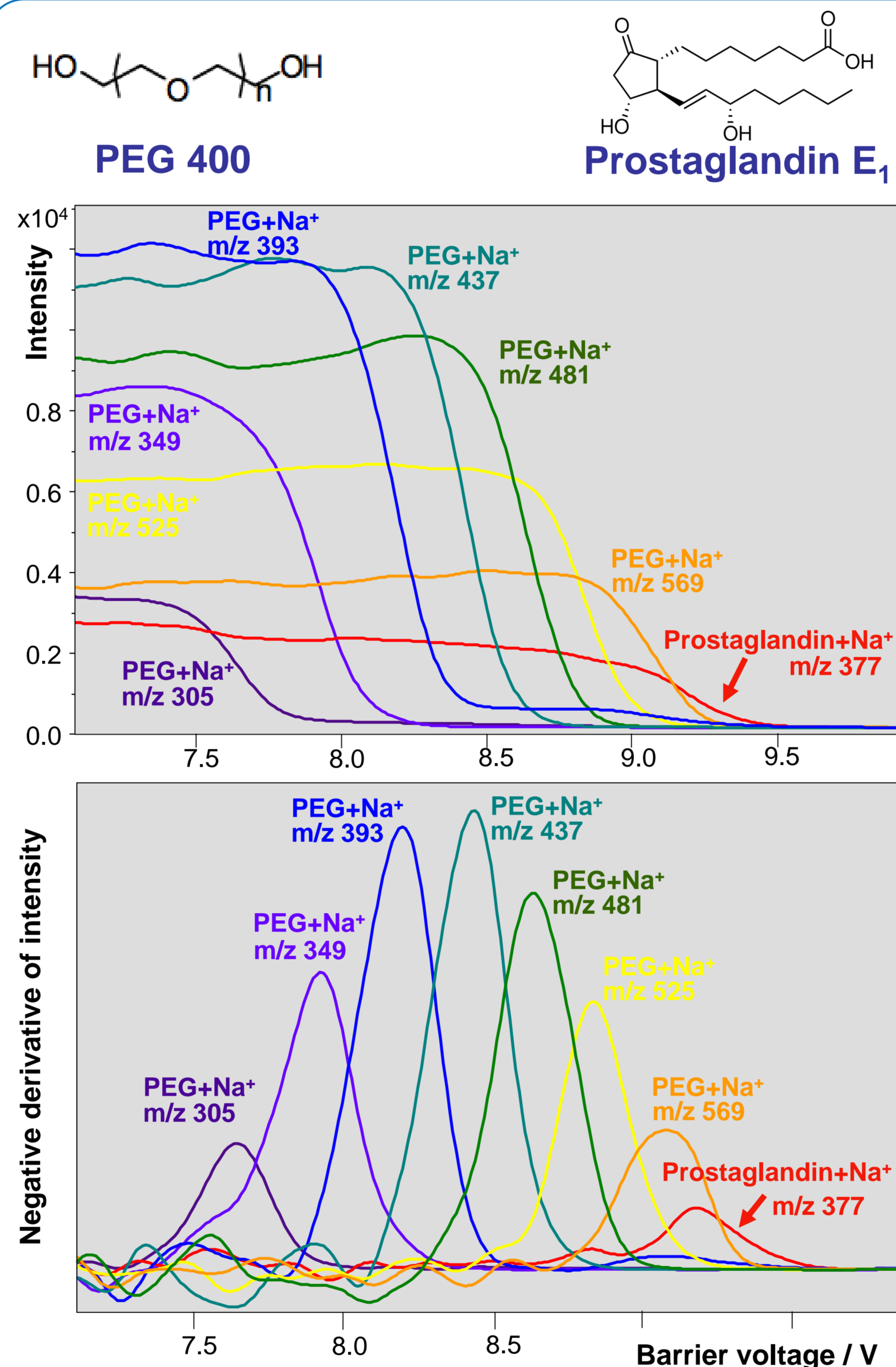


Fig. 3a: Separation of prostaglandin E₁ from a PEG 400 oligomer by ramping the barrier voltage. Due to its larger cross section, prostaglandin is blocked at a much higher voltage (top). Blocking voltages are determined in the negative derivative plot (bottom).

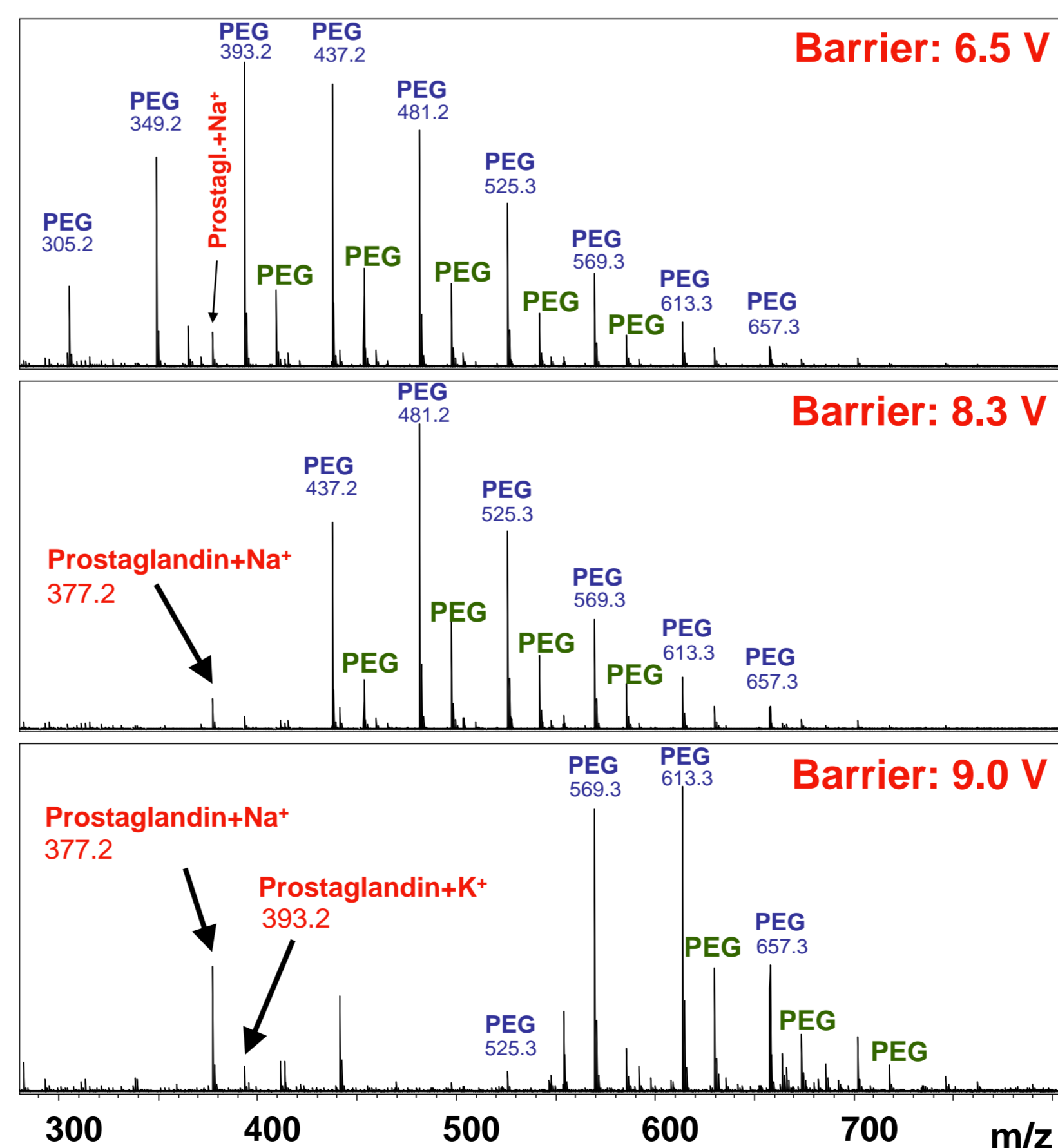


Fig. 3b: Mass spectra of the mixture PEG 400 with prostaglandin at different barrier voltages. At the voltage 9V, Prostaglandin E₁ is clearly separated from PEG and can be detected with a much improved S/N. In the mass spectra above blue PEGs stand for PEG+Na⁺ and green PEGs for PEG+K⁺.

alkali ion-attached PEGs form compact spherical structures. Fig. 4 shows the derivative plots of [Arg⁸]-vasopressin and [des-Glu¹]-LHRH, which have very similar masses but different cross sections, thus different mobility values.

From absolute cross sections of the reference ions the K₀ values in N₂ were calculated and the barrier voltage scale was calibrated. The calibration curve of the barrier voltage vs. K₀ was linear in the range of mobilities measured. Ion mobilities and cross sections of peptide ions were determined. As preliminary examples, mobilities and cross sections of ions generated from Angiotensin II, Bombesin, Substance P, Melittin, were determined using this dynamic method (Fig. 5). In these experiments IMS resolving power values up to 30 were obtained.

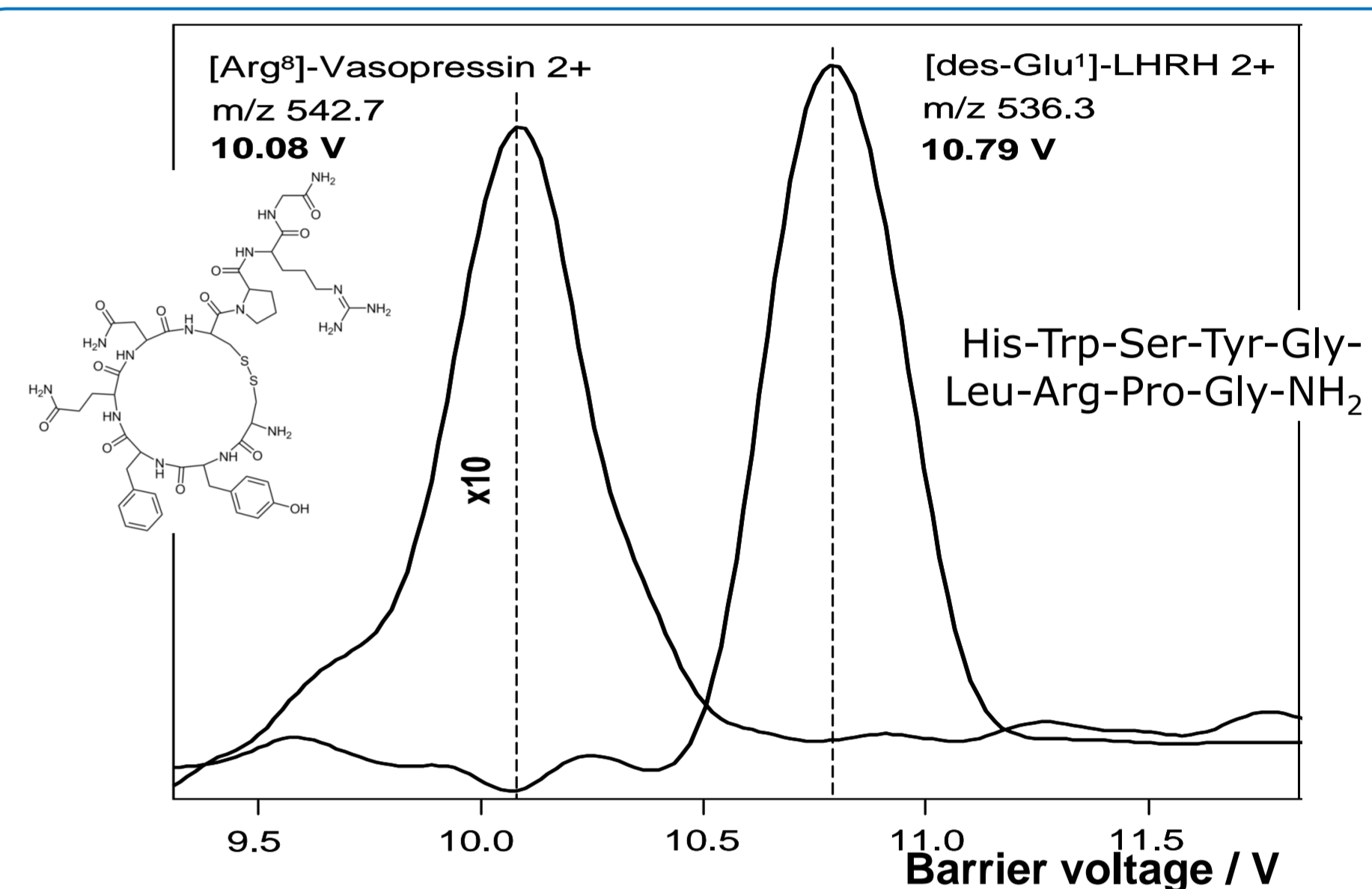


Fig. 4: Separation of an open-chain peptide from an S-S bridged one with a very similar mass. Note that [Arg⁸]-vasopressin with even slightly larger mass than [des-Glu¹]-LHRH is more mobile.

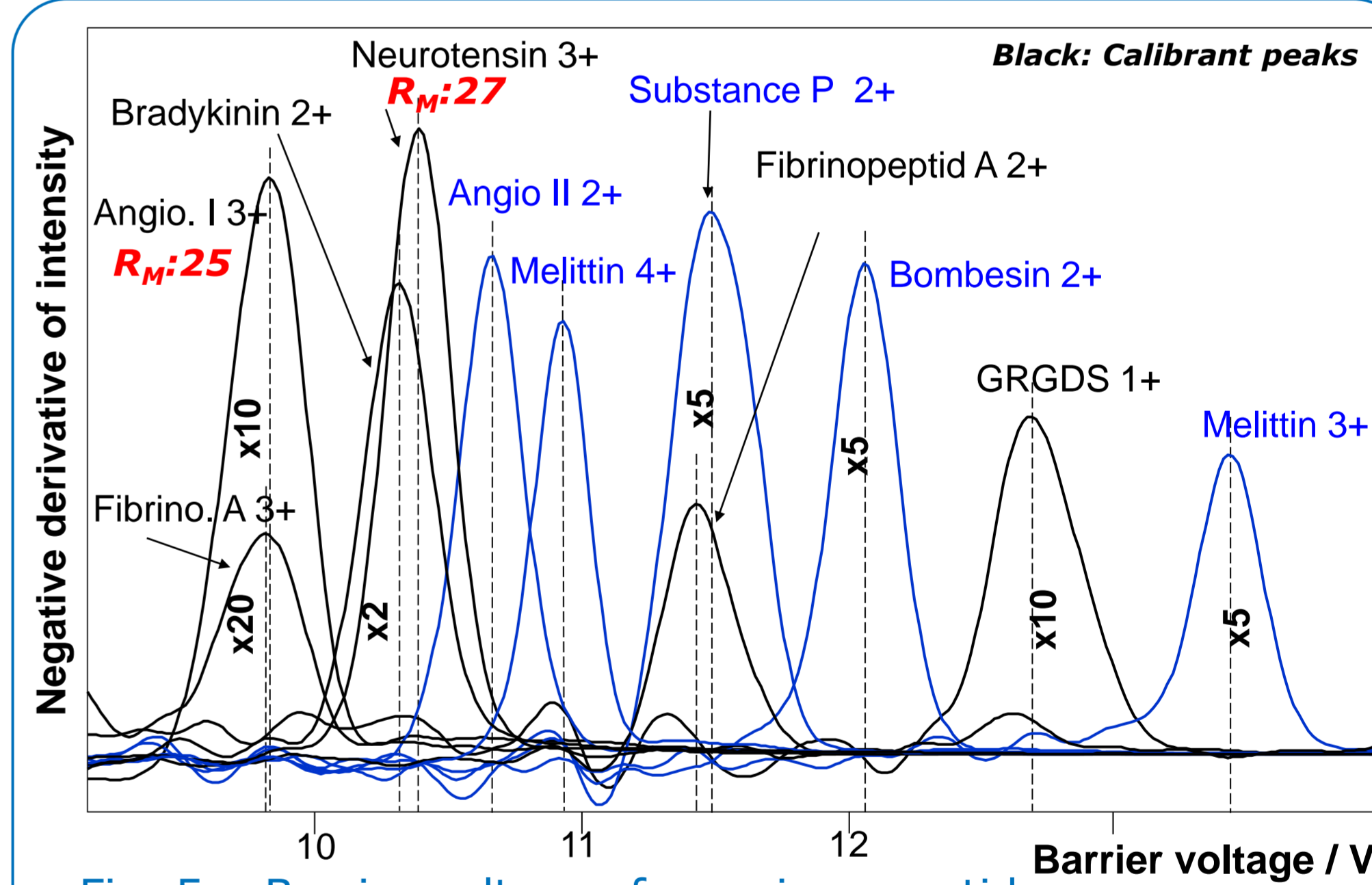


Fig. 5a: Barrier voltages for various peptides.

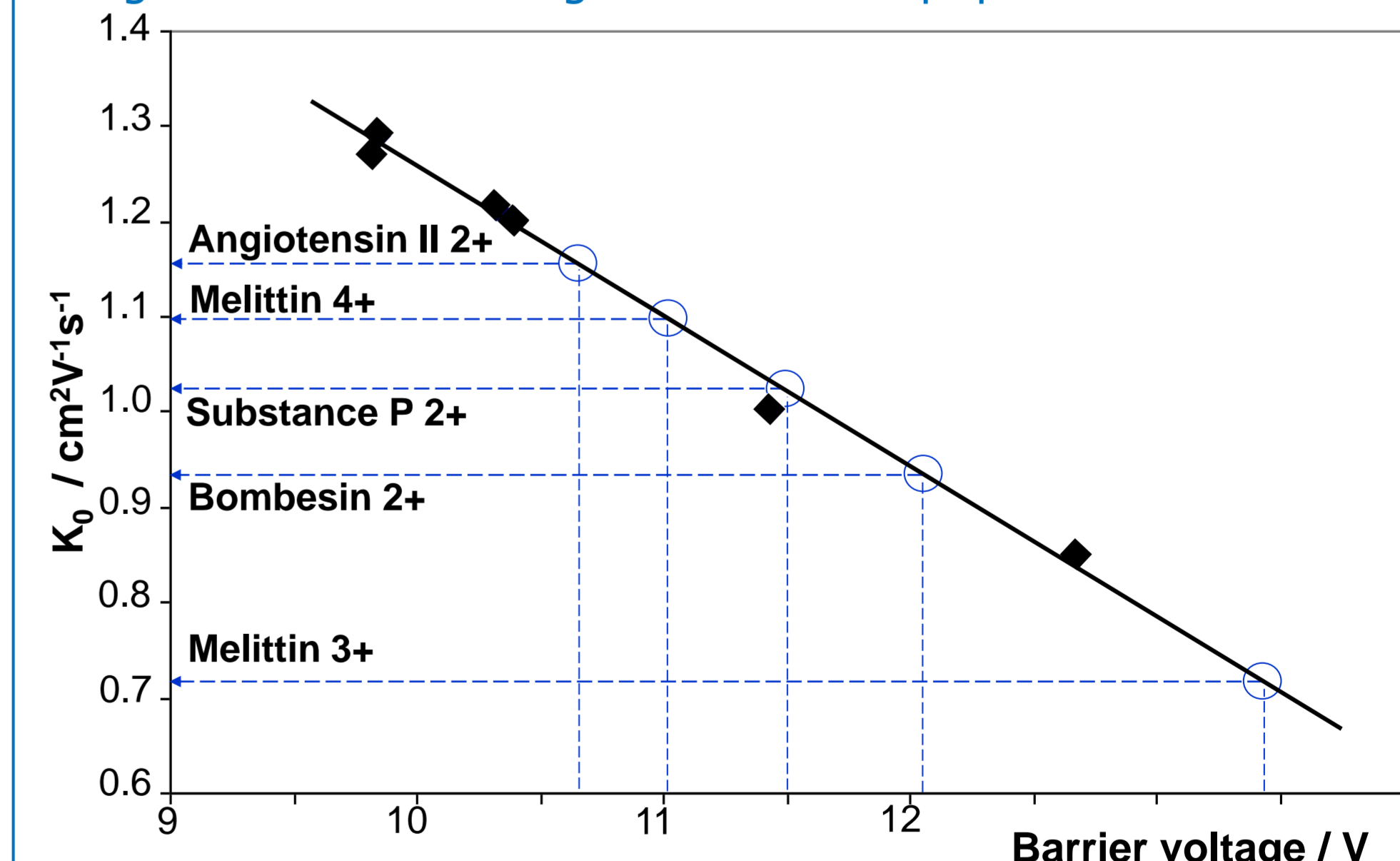


Fig. 5b: Calibration curve (black diamonds: calibrant peptides) and determination of mobilities for the investigated peptides.

Peptide	m/z	Reduced mobility K ₀ (cm ² V ⁻¹ s ⁻¹) by calibration	Calculated cross section in N ₂ (Å ²)
Angiotensin I+2H ⁺	648.9	1.065	384
Neurotensin+2H ⁺	837.0	0.912	447
[Arg ⁸]-Vasopressin+2H ⁺	542.7	1.259	326
[Des-Glu ¹]-LHRH+2H ⁺	536.3	1.152	356
Angiotensin II+2H ⁺	523.8	1.155	355
Substance P+2H ⁺	674.4	1.022	400
Bombesin+2H ⁺	810.4	0.932	438
Melittin+3H ⁺	949.6	0.717	850
Melittin+4H ⁺	712.4	1.097	741

Table 1: Mobilities and cross sections of the investigated peptides determined by the barrier voltage method.