U-Shaped Mobility Analyzer (UMA): A Compact and High-Resolution Counter-Flow Ion Mobility Spectrometer.

SUPPORTING INFORMATION

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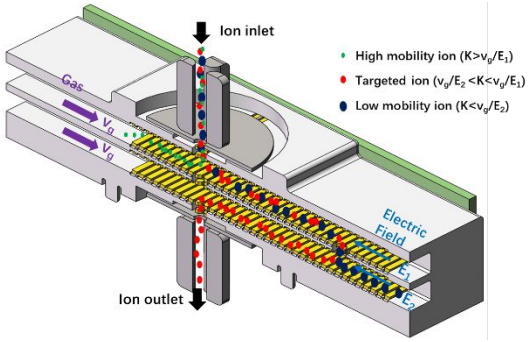

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Theoretical calculation of ion mobility resolving power in UMA

Table S-1. Parameter and Definition

Symbols	Definition
K	Ion mobility
E	Electric field
E_1	Electric field in the Channel 1 (CH1)
E_2	Electric field in the Channel 2 (CH2)
dE	Electric field difference between CH1 and CH2
β	Scan rate
m	Ion mass
q	Ion charge number
k_B	Boltzmann's constant
T	Temperature
D	Diffusion coefficient
v_g	Gas velocity
L_2	Length of CH2
L_t	Length of trap region (in trap-scan mode)
L_P	Length of plateau (in trap-scan mode)
R_f	Ion mobility resolving power in filter-scan mode defined by t/Δt

$R_{f,K}$	Ion mobility resolving power in filter-scan mode defined by K/ΔK
R_t	Ion mobility resolving power in trap-scan mode defined by t/Δt
$R_{t,K}$	Ion mobility resolving power in trap-scan mode defined by K/ΔK

S1. Resolving power in filter-scan mode

In filter-scan mode, electric field difference between two channels is kept a constant. Scan rate of E_1 and E_2 is β, and E_1 is started to scan from 0.

$$E_2 - E_1 = dE = const \tag{1}$$

Ion mobility resolving power in a time-intensity spectrum can be calculated as:

$$R_f = \frac{t_1 + t_2}{\Delta t} \ , \tag{2}$$

in which t_1 is not the ion drift time in CH1, but it is the scan time before $E_1=v_g/K$; t_2 is the ion drift time in CH2; Δt is the ion peak spread (FWHM) in spectrum.

For t_1, we have:

$$t_1 = \frac{v_g}{K\beta} \tag{3}$$

For t_2, we have: $v_2 = E_2K - v_g = \left(\frac{v_g}{K} + \beta t\right)K - v_g = K\beta * t$, so that ion drift in CH2 with a constant acceleration velocity, we can calculate t_2 as:

$$t_2 = \sqrt{\frac{2L_2}{K\beta}} \tag{4}$$

For Δt, we have:

$$\Delta t = \sqrt{{t_g}^2 + {t_d}^2} \ , \tag{5}$$

in which t_g is the time window when E is scanned in the window of dE, t_d is the diffusion spread of ions in CH2. And we have:

$$t_g = \frac{\mathrm{d}E}{\beta} \tag{6}$$

$$t_d = \sqrt{16ln2 \cdot D \cdot t_2}/v_2 \ , \tag{7}$$

in which $D = \frac{K \cdot k_B T}{q}$ [1], and v_2 is the ion velocity at the end of CH2, and we have:

$$v_2 = K\beta * t_2 \tag{8}$$

From Equation (2) to (8), we obtain the resolving power as:

$$R_f = \frac{\frac{v_g}{K\beta} + \sqrt{\frac{2L_2}{K\beta}}}{\sqrt{\frac{dE^2}{\beta^2} + \frac{16ln2 \cdot k_B T}{q} \frac{1}{\beta^{3/2}\sqrt{2L_2 K}}}} = \frac{v_g + \sqrt{2L_2 K\beta}}{\sqrt{dE^2 K^2 + \frac{16ln2 \cdot k_B T}{q}\sqrt{\frac{\beta}{2L_2}} K^{3/2}}} \tag{9}$$

Normally, t_1 is tens to hundreds of milliseconds, while t_2 is a few milliseconds. In the case of $t_1 >> t_2$, we have:

$$R_f \approx \frac{\frac{v_g}{K\beta}}{\sqrt{\frac{dE^2}{\beta^2} + \frac{16ln2 \cdot k_B T}{q} \frac{1}{\beta^{\frac{3}{2}}\sqrt{2L_2 K}}}} = \frac{v_g}{\sqrt{dE^2 K^2 + \frac{16ln2 \cdot k_B T}{q} K^{\frac{3}{2}}\sqrt{\frac{\beta}{2L_2}}}} \tag{10}$$

In this equation, the term of "dE^2" can be viewed as the effect of ion gate width, if analogous to a traditional ion mobility drift cell.

On the other hand, if mobility resolving power is defined by K/ΔK, where ΔK is the peak width (FWHM) in a mobility-intensity spectrum, we have:

$$R_{f,K} = \frac{K}{\Delta K} = \frac{K \cdot \frac{dt}{dK}}{\Delta t} = \frac{-\frac{v_g}{K\beta} + \sqrt{\frac{L_2}{2K\beta}}}{\sqrt{\frac{dE^2}{\beta^2} + \frac{16ln2 \cdot k_B T}{q} \frac{1}{\beta^{3/2}\sqrt{2L_2 K}}}} \tag{11}$$

$R_{f,K}$ is slightly lower than R_f. With a normal scan rate, $R_{f,K}$ is approximately the same as R_f.

S2. Resolving power in trap-scan mode

In this case, ion motion in a gas flow with an opposed electric filed can be described by the Nernest-Planck equation

$$\frac{\partial n}{\partial t} - \nabla \cdot \left(\overline{D} \cdot \nabla n - (\vec{v}_g - K\vec{E})n\right) = 0 \ , \tag{12}$$

in which n(r,x,t) is the ion concentration, $\overline{D}$ is the isotropic diffusion tensor. If we only considering a simple 1D model in x direction and neglecting the radial electric field and diffusion, the Nernst-Planck equation will be

$$\frac{\partial n(x,t)}{\partial t} - \frac{\partial}{\partial x}\left(D \cdot \frac{\partial}{\partial x}\mathrm{n(x,t)} - (v_g - KE(x,t)) \cdot n(x,t)\right) = 0 \qquad (13)$$

In UMA trap-scan mode, CH1 is for the ion accumulation (Figure 4a in the paper). The beginning of CH2 is as the receptor of those accumulated ions and also as the temporal trapping region (Figure 4b), and this region can be called as the “trap region”. The other part of CH2 is for ion elution and for mobility separation, and it is so-called “plateau”.

The ion elution time t_e after the “trap region” but before the “plateau”, with a scan rate β, can be determined by the timing for ions being upon the same electric force and the drag force:

$$t_e = \frac{v_g/K}{\beta} \qquad (14)$$

Those eluted ions will drift in the “plateau” for a relatively long time. Ion motion in the plateau of CH2 is similar to that in filter-scan mode, which has a constant acceleration Kβ, so that the ion drift time in the plateau of CH2 t_p is:

$$t_P = \sqrt{\frac{2L_P}{K\beta}} \qquad (15)$$

The ion motion in the “trap region” has been dealt with in several papers by solving the equation (14), in which the electric field is linearly increased in space [2, 3, 4]. Here we will directly use the result in [2] for the ion spatial spread after the “trap region” but before the “plateau”:

$$\Delta \mathrm{x}_t = \sqrt{\frac{8ln2k_BT}{q} \cdot \frac{KL_t}{v_g}} \qquad (16)$$

The next step is to calculate the ion spatial spread after the “plateau”. For an ion packet

which has a very small narrow distribution, such as the case after UMA “trap region”, the ion spatial width can be easily solved from the diffusion equation,

$$\Delta x_p = \sqrt{\Delta x_t{}^2 + 16ln2t_p} \tag{17}$$

Ion drift speed at the end of “plateau” is also similar to that in filter-scan mode $v_P = K\beta * t_P$. Hence the temporal ion distribution can be obtained:

$$\Delta t = \frac{\Delta x_p}{K\beta t_P} \tag{18}$$

If the resolving power in trap-scan mode is also defined as t/Δt, then it can be calculated according to equation (14) to (18)

$$R_t = \frac{\frac{v_g}{\sqrt{K\beta}}\sqrt{2L_P} + 2L_P}{\sqrt{\frac{8ln2k_BT}{q}\cdot\frac{KL_t}{v_g} + 16ln2\sqrt{\frac{2L_P}{K\beta}}}} \tag{19}$$

In UMA, the length of “trap region” is only 4mm, which is much less than that of “plateau” 36mm, so that approximately we can let $L_t \approx 0,\ L_P \approx L_2$. On the other side, in a normal scan rate, $t_e << t_p$, so that the resolution $R_{t,K}$ which is defined by K/ΔK is approximately the same as the resolution R_t which is defined by t/Δt. The equation for mobility resolving power can be simply deduced as:

$$R_t \approx R_{t,K} = \frac{v_g}{\sqrt{\frac{16ln2\cdot k_BT}{q}K^{3/2}\sqrt{\frac{\beta}{2L_2}}}} \tag{20}$$

In order to compare the equation to that for the filter-scan mode, we can isolate the initial ion spread in space in the “trap region” Δx_t, the resolving power will be obtained as:

$$R_t \approx \frac{v_g}{\sqrt{\frac{\Delta x_t^2}{2L_2}K\beta + \frac{16ln2\cdot k_BT}{q}K^{3/2}\sqrt{\frac{\beta}{2L_2}}}} \tag{21}$$

Compare the Equation (21) to (10), there is no “ion gate width” in trap-scan mode, while there is no “ion initial space spread” in filter-scan mode. In a normal analysis, the effect of “ion initial space spread” is much less than that of space spread in plateau [2].

The latter is usually less than the effect of “ion gate width” to degradation of resolving power. Therefore, the absolute value of R_f is usually lower than R_t. For example, if v_g=150 m/s, L_2=4 cm, β=30 V/mm/s and the electric field is started to scan from 0, T=300 K, ion mobility K=250 cm^2/V/s, ΔE=0.01 V/mm in filter-scan mode and Δx_t=1 mm in trap-scan mode, then the calculated R_f= 181.3, and R_t=188.0.

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