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Peak Profile Analysis in High Field Asymmetric Wave Ion Mobility Spectrometry

Chi-lai Chen^{a,b*}, De-yi Kong^a, Xiao-hua Wang^a, Huan-qin Wang^a, Feng Shuang^a, Tao Mei^a

a. Institute of Intelligent Machines, Chinese Academy of Sciences, State Key Laboratory of Transducer Technology, Hefei 230031, China

b. Department of Precision Machine and Precision Instrument, University of Science and Technology of China, Hefei 230027, China

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High field asymmetric wave ion mobility spectrometry (FAIMS) is a powerful tool to detect and characterize gas-phase ions, while the unsolvable partial differential equation of ions moving in ion drift tube poses a big challenge to FAIMS spectral peak analysis. In this work, a universal and effective model of FAIMS spectral peak profile has been proposed by introducing ion trajectory and loss height. With this model, the influence of the structure of ion drift tube, dispersion voltages, compensation voltages, and carrier gas flow rate on the FAIMS spectral peak characteristics like peak shape, full width at half maximum and peak height is analyzed and discussed. The results show that the influence of different factors on the FAIMS spectral peak profile can be qualitatively described by the model which agrees with the experimental data.

Key words: High field asymmetric wave ion mobility spectrometry, Loss height, Ion trajectory, Spectral peak profile model, Parameter optimization

I. INTRODUCTION

High field asymmetric wave ion mobility spectrometry (FAIMS), also called differential ion mobility spectrometry (DMS), is an atmospheric-pressure ion separation and detection technique that separates and characterizes ions by the difference between their mobility in gases at high and low electric fields [1–3]. Since the end of the last century, FAIMS has been used extensively for the detection of explosives, drugs, air pollutants and toxic gases due to its high sensitivity and easy miniaturization [4–10]. The main research institutions of FAIMS include the Canada Institution of Research, the National Laboratory of Northwest Pacific and the New Mexico University of USA [11–14], and their research achievements have been transferred into products [15].

Spectra analysis is important for the application of FAIMS. However, a concise and unified spectral peak model does not exist due to the fact that the partial differential equation of ions moving in ion drift tube is unsolvable. By simplifying assumption on gas flow and operation boundary conditions, Krylov *et al.* built a solvable one-dimensional time-dependent diffusion equation, with which the model of peak height, the resolution and FWHM of FAIMS spectra were obtained [16]. However, the assumption that velocity of

gas is uniform distribution and density of ions at the entrance is cosine distribution has not been proved by any research. As a result, this model is not instructive or predictive. With software Simion and statistical diffusion simulation model, Prasad *et al.* simulated the ion movement in the ion drift tube and obtained the FAIMS spectral peak profile of hydroxyproline, leucine, hydrated oxygen, 2-propanone, and 2-dodecanone which were consistent with experimental results [17]. However, this method can only be adopted to solve specific problems and has no instructiveness for parameterization and peak analysis.

In this work, considering the structure of ion drift tube and voltages properties, a novel and effective method is proposed to analyze the spectral peak profile of FAIMS by introducing flow distribution, loss height and ion trajectory. Then model of FAIMS spectral peak is built, by which the spectral peak profile, peak heights, FWHM are analyzed and discussed.

II. FAIMS PRINCIPLE

A. General notions

The ion mobility is defined as the velocity attained by an ion moving through gas under unit electric field, as shown in Eq.(1).

$$K = \frac{v}{E} \quad (1)$$

* Author to whom correspondence should be addressed. E-mail: chlchen@iim.ac.cn

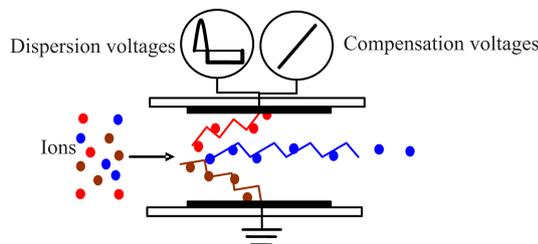


FIG. 1 Scheme of structure and mechanism of flat plate FAIMS.

where v is the velocity of ion, K is the mobility of ion and E is the electric field [1]. The mobility is dependent on the ratio of electric field to gas density as

$$K = K_0 \left[1 + \alpha_2 \left(\frac{E}{N} \right)^2 + \alpha_4 \left(\frac{E}{N} \right)^4 + \dots \right] \quad (2)$$

where N is the density of carrier gas [18]. The unit of E/N is Td (1 Td = 10^{-17} V/cm²). The K_0 is reduced mobility which changes little with values of E/N lower than 30 Td. The α_2 and α_4 are the 2nd and 4th order nonlinear coefficients, respectively, and the nonlinear coefficients higher than 4th order are small enough to be omitted.

According to the structure of ion drift tube, there are two types of FAIMS: cylindrical FAIMS and flat plate FAIMS [19]. The cylindrical ones have been studied intensively in ion separation for high resolution mass spectrometry. In recent years, research has been focused on the flat plate ones due to their easy fabrication and high machining precision. The structure and working mechanism of flat plate FAIMS are illustrated in Fig.1.

The ion drift tube of FAIMS mainly consists of two closer pieces of electrodes on which dispersion voltages V_D and compensation voltages V_C are applied. The dispersion voltage produces an asymmetric waveform electric field with high frequency (about MHz) and high amplitude (higher than 10^4 V/cm). Under dispersion voltage, ions can be separated spatially due to the small difference between the amplitudes of traveling up and down caused by the change in ion mobility as shown in Eq.(2). The ions crossing electrodes will be neutralized and the remaining ions will flow out of the ion drift tube and produce ion current. Compared with dispersion voltage, the compensation voltage produces a low amplitude (lower than 10^3 V/cm) and low frequency electric field (lower than 1 Hz). This voltage is used to control the types of ions flowing out of the ion drift tube. The FAIMS spectra describe the relationship between compensation voltage and the ion current intensity. We do not care about the absolute position of FAIMS spectral peak, so the center position of spectrum is set to be 0.

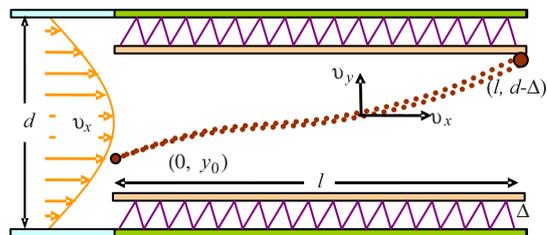


FIG. 2 Scheme of the moving trajectory of ion in the ion drift tube. l is the length of ion drift tube, d is the height of ion drift tube, v_y is the longitudinal velocity of ions, v_x is the transverse velocity of ions, Δ is the loss height caused by dispersion voltage.

B. Model of operation

The moving trajectory of ion in the ion drift tube is illustrated in Fig.2.

A Cartesian coordinate system is adopted in which the x -axis is the gas flow direction, the y -axis is perpendicular to electrodes and the origin is at the bottom of the entrance of ion drift tube.

The transverse velocity v_x is determined by the gas velocity which exhibits a parabolic distribution:

$$v_x = \frac{21.6Q}{d^3h} y(d-y) \quad (3)$$

where h is the width of ion drift with unit of cm and Q is the flow rate of carrier gas. Theoretically, the longitudinal velocity v_y is determined by V_C and V_D as

$$v_y = \frac{1}{T} \int_0^T K(V_C + V_D) dt \quad (4)$$

However, the velocity caused by V_D is far less than the velocity caused by V_C due to their waveform [20], so the v_y is mainly determined by compensation voltage as

$$v_y = \frac{K_0 V_C}{d} \quad (5)$$

The loss height Δ is defined as the peak-to-peak amplitude of y -axis vibration of ions in a single period under V_D . The ions with y -coordinate in the interval $[0, y_0]$ and $[d-\Delta, d]$ will reach the electrodes and be neutralized. Δ can be calculated as

$$\Delta = \int_{\Omega} \frac{K f(V_D)}{d} dt \quad (6)$$

where Ω is the zone in which the V_D is positive in a single period and $f(V_D)$ is the wave profile function of V_D .

The influence of ion diffusion on the movement of ions in drift tube can be estimated by the ratio of diffusion radius to the height of the ion drift tube. The diffusion radius r is equal to $(2D\tau)^{1/2}$, where D is the diffusion coefficient of ion and τ (about 1 ms) is the time interval

of ion flowing through the ion drift tube. Under the same condition, D is much less than that of molecules [21]. A straightforward calculation can obtain a value of about 0.1 for the ratio r/d . So the diffusion has no obvious effect on the spectral peak profile.

From Fig.2 and the above discussion, it is obvious that only the ions under a certain position can pass through the ion drift tube. This position is defined as $(0, y_0)$ at which ions will reach the top of the outlet of the ion drift tube whose coordinate is $(l, d-\Delta)$. According to Eqs. (3) and (5), the motion of ion satisfies the following equation

$$\begin{aligned} l &= \int_0^\tau v_x dt \\ &= \int_{y_0}^l \frac{v_x}{v_y} dy \\ &= \int_{y_0}^l \frac{21.6Qy(d-y)}{hd^2K_0V_C} dy \end{aligned} \quad (7)$$

It can be recast as

$$\frac{y_0^3}{3} - \frac{dy_0^2}{2} = \frac{ld^2hK_0V_C}{21.6Q} + \frac{(d-\Delta)^3}{3} - \frac{d(d-\Delta)^2}{2} \quad (8)$$

The ratio of ions flowing out of the ion drift tube to all ions is

$$\frac{\int_{\Delta}^{y_0} J dy}{\int_0^d J dy} = \frac{\int_{\Delta}^{y_0} n_0 v_x dy}{\int_0^d n_0 v_x dy} = \frac{\int_{\Delta}^{y_0} v_x dy}{\int_0^d v_x dy} \quad (9)$$

where J is the ion current density, and n_0 is the ion density at the entrance of ion drift tube. Because the height of the ion drift tube is far less than the distance between the ion source and the entrance, n_0 could be considered to be uniform. We do not care the absolute value of FAIMS spectral peak, so n_0 is set to be 1. Then the ion current intensity I can be gained from Eqs. (8) and (9) as follows:

$$I = \left(1 - 2\frac{\Delta}{d}\right) \left[1 - 2\frac{\Delta}{d} - 2\left(\frac{\Delta}{d}\right)^2\right] - \frac{K_0V_Chl}{3.6dQ} \quad (10)$$

The above equation describes FAIMS spectral peak profile and Δ can be calculated from Eq.(6).

III. EXPERIMENTS

The device of FAIMS was made by ourselves and the ion drift tube was fabricated by micro-electro-mechanical systems (MEMS) technology.

Nitrogen (99.99%, NanJing Special Gases Factory Co., Ltd.) was used as carrier gas. The detection substances were purchased from Sinopharm Chemical Reagent Co., Ltd. and their purity was higher than

99.5%. The ion drift tube of FAIMS was kept at 20 °C under ambient pressure.

V_D is clipped-sinusoidal which can be described by the following equation:

$$V_D = V_1 \sin\left(\frac{\pi t}{rT}\right) - 2r\frac{V_1}{\pi} \quad (0 \leq t \leq rT) \quad (11)$$

$$V_D = -\frac{2rV_1}{\pi} \quad (rT \leq t \leq T) \quad (12)$$

The experimental parameters of FAIMS are $T=0.2 \mu\text{s}$, $r=0.36$, $d=0.05 \text{ cm}$, $l=1.5 \text{ cm}$, $h=1.0 \text{ cm}$.

IV. RESULTS AND DISCUSSION

A. The model of FAIMS spectral peak profile

Combining Eqs. (11), (12), and (6), Δ can be gained as

$$\Delta = \frac{0.15K_0V_1T}{d} \quad (13)$$

Then the FAIMS spectral peak profile, which describes how the ion current intensity I varies with V_C , can be obtained from Eq.(13) as:

$$\begin{aligned} I &= \left(1 - 2\frac{\Delta}{d}\right) \left[1 - 2\frac{\Delta}{d} - 2\left(\frac{\Delta}{d}\right)^2\right] - \frac{lhK_0V_C}{3.6dQ} \\ &= \left(1 - \frac{0.3K_0V_1T}{d^2}\right) \left[1 - \frac{0.3K_0V_1T}{d^2} - 2\left(\frac{0.15K_0V_1T}{d^2}\right)^2\right] - \frac{lhK_0V_C}{3.6dQ} \end{aligned} \quad (14)$$

From this model, we can see that the ion current consists of two terms. The first term is $(1-2\Delta/d)[1-2\Delta/d-2(\Delta/d)^2]$, which represents I when V_C is 0. In this term, Δ is determined by V_D in the form of $0.15K_0V_1T/d$. The second term can be written as $-1/3.6(lh/d^2)[(K_0V_C/d)/Q]$ which is determined by the FAIMS structure parameters, the compensation voltage, the ion mobility, and the flow rate. In one word, I is inversely proportional to V_C and the mobility of ion K_0 , the width of ion drift tube h , while proportional to the carrier gas flow rate Q , the length of ion drift tube l , the height of ion drift tube d , and dispersion voltage V_1 .

The testing sample is acetone whose ion mobility is $1.84 \text{ cm}^2/(\text{V}\cdot\text{s})$ [22]. V_D is 1.3 kV and Q is 250 L/h.

The theoretical prediction and experimental results are compared as shown in Fig.3. The peak height is set to be 1.

From Fig.3, it can be seen that the theoretical model agrees well with the experimental data. The deviation mainly exists at the bottom of the peak, and this is because the ion diffusion becomes dominant when the ion flowing out of the ion drift tube is nearly zero. However, this deviation does not affect the judgment of FAIMS peaks.

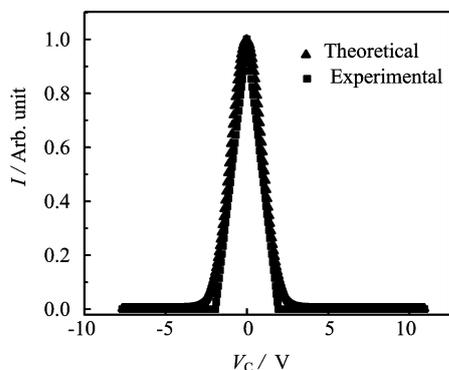


FIG. 3 FAIMS spectral peak profile of acetone.

B. The peak height of FAIMS spectra

The peak height is the critical index to measure the sensitivity of FAIMS, which refers to I when the V_C approaches 0 in this work. According to the FAIMS spectral peak profile model, the relative peak height H is:

$$\begin{aligned}
 H &= \left(1 - 2\frac{\Delta}{d}\right) \left[1 - 2\frac{\Delta}{d} - 2\left(\frac{\Delta}{d}\right)^2\right] \\
 &= \left(1 - \frac{0.3K_0V_1T}{d^2}\right) \left[1 - \frac{0.3K_0V_1T}{d^2} - 2\left(\frac{0.15K_0V_1T}{d^2}\right)^2\right] \quad (15)
 \end{aligned}$$

From Eq.(15), it can be seen that H is totally determined by Δ/d in the form $0.15K_0V_1T/d^2$. Thus, the relative peak height is inversely proportional to ion mobility K_0 , peak value of dispersion voltage V_1 , and period of dispersion voltage, and proportional to the height of ion drift tube d .

The testing samples are acetone and chlorobenzene. The ion mobility of chlorobenzene is 1.96 [23]. The experimental parameters are the same as mentioned above except V_1 which is variable in this part. The H value corresponding to $V_1=500$ V is set to be 1. According to our model, the theoretical and experimental data of acetone and chlorobenzene are shown in Fig.4.

As can be seen from Fig.4, the peak height is inversely proportional to dispersion voltage, which is consistent with our model. The experimental data are a little lower than the theoretical data, which is probably caused by ion diffusion.

C. The FWHM of FAIMS spectral peak

The FWHM of FAIMS spectral peak profile directly describes the resolution of FAIMS, which is one of the critical parameters in analysis and detection. The

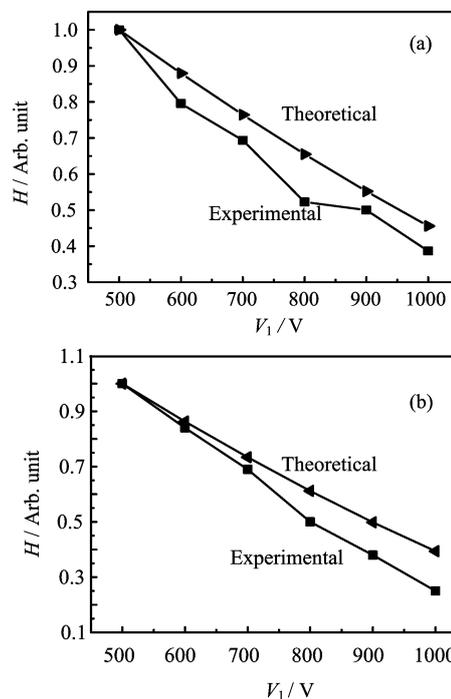


FIG. 4 Dependence of FAIMS spectral peak height of acetone (a) and chlorobenzene (b) on dispersion voltage.

FWHM of FAIMS is defined as the difference of two values of compensation voltage V_C at which the ion current intensity equals to $1/2$ peak height H . Using Eqs. (14) and (15), the FWHM is obtained as

$$\begin{aligned}
 \text{FWHM} &= \frac{3.6dQ}{lhK_0} \left(1 - 2\frac{\Delta}{d}\right) \left[1 - 2\frac{\Delta}{d} - 2\left(\frac{\Delta}{d}\right)^2\right] \\
 &= \frac{3.6dQ}{lhK_0} \left(1 - \frac{0.3K_0V_1T}{d^2}\right) \cdot \\
 &\quad \left[1 - \frac{0.3K_0V_1T}{d^2} - 2\left(\frac{0.15K_0V_1T}{d^2}\right)^2\right] \quad (16)
 \end{aligned}$$

From Eq.(16), we can see that the FWHM is related to almost all FAIMS operation parameters, such as the structure of ion drift tube, dispersion voltages, compensation voltages, and carrier gas flow rate. As d/l increases, the voltage needed to move ions up and down, electrodes becomes high, which leads to the increase of FWHM. Similarly, with the increase of carrier gas flow rate Q , it takes less time for the ions to flow out of ion drift tube, so the compensation voltage must be increased in order to move ions up and down electrodes. The fact that FWHM is proportional to $(1-2\Delta/d)[1-2\Delta/d-2(\Delta/d)^2]$ can be explained as the following: when loss height increases, the effective height of ion drift tube decreases, and FWHM decreases consequently. The testing sample is benzene whose ion mobility is 2.27 [24]. The relation between FWHM of benzene's FAIMS spectral peak and carrier gas flow rate

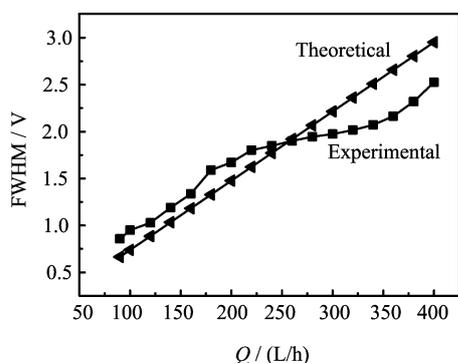


FIG. 5 The relation between FWHM of benzene's FAIMS spectral peak and carrier gas flow rate.

is shown in Fig.5. From Fig.5, we can see that FWHM increases with carrier gas flow rate, which is the same as predicted by Eq.(16).

When the carrier gas flow rate reaches 250 L/h, the experimental data deviate slightly from the predicted value, which is probably caused by weak turbulence at high flow rate. This phenomenon needs to be further studied.

D. The parameters optimization of FAIMS

Sensitivity and resolution are the two critical parameters for analysis and detection technique, and can be expressed as the peak height and half height width, respectively. The FAIMS spectral peak profile model in this work provides a clear description about them. Through this model, the peak height and FWHM can be expressed as the function of the structure parameters of ion drift tube, parameters of electric field and parameters of gas flow. This affords a theoretical instruction to optimize the parameters of FAIMS.

V. CONCLUSION

There is no simple and universal spectral peak profile model in the research of FAIMS. In this work, avoiding solving the partial differential equation problems, we get an easy-dealing FAIMS spectral peak profile model from the ions' moving trajectories. Peak profile, peak height, and FWHM of FAIMS spectra are analyzed and discussed based on this model, which was testified by experimental data. This model provides a theoretical basis for FAIMS spectral analysis and parameter optimization.

VI. ACKNOWLEDGMENTS

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- [1] G. A. Eiceman and Z. Karpas, *Ion Mobility Spectrometry*, 2nd edn., Boca Raton: CRC Press Taylor & Francis Group, 1 (2005).
- [2] R. A. Miller, G. A. Eiceman, E. G. Nazarov, and A. T. King, *Sens. Actuators B* **67**, 300 (2000).
- [3] E. V. Krylov, S. L. Coy, J. Vandermeij, B. B. Schneider, T. R. Covey, and E. G. Nazarov, *Rev. Sci. Instrum.* **81**, 024101 (2010).
- [4] Z. Karpas, G. A. Eiceman, E. V. Krylov, and N. Krylova, *Int. J. Ion Mobil. Spec.* **7**, 1 (2004).
- [5] N. Krylova, E. Krylov, G. A. Eiceman, and J. A. Stone, *J. Phys. Chem. A* **107**, 3648 (2003).
- [6] B. M. Kolakowski and Z. Mester, *Analyst* **132**, 842 (2007).
- [7] J. Kapron and R. A. Thakur, *LCGC Eur.* **19**, 27 (2006).
- [8] D. S. Levin, P. Vouros, R. A. Miller, and E. G. Nazarov, *J. Am. Soc. Mass Spectrom.* **18**, 502 (2007).
- [9] B. Ells, D. A. Barnett, R. W. Purves, and R. Guevremont, *Anal. Chem.* **72**, 4555 (2000).
- [10] G. A. Eiceman, H. Schmidt, J. E. Rodriguez, and C. R. White, *Instrum. Sci. Technol.* **35**, 365 (2007).
- [11] R. Guevremont and R. Purves, *Faseb J.* **19**, A767 (2005).
- [12] G. A. Eiceman, E. V. Krylov, N. S. Krylova, E. G. Nazarov, and R. A. Miller, *Anal. Chem.* **76**, 4937 (2004).
- [13] A. A. Shvartsburg, K. Q. Tang, and R. D. Smith, *J. Am. Soc. Mass Spectrom.* **15**, 1487 (2004).
- [14] H. Li, X. H. Wang, F. Tang, J. Yang, and L. Ding, *Chin. J. Chem. Phys.* **23**, 125 (2010).
- [15] M. D. Krebs, A. M. Zapata, E. G. Nazarov, R. A. Miller, I. S. Costa, A. L. Sonenshein, and C. E. Davis, *IEEE Sens. J.* **5**, 696 (2005).
- [16] E. V. Krylov, E. G. Nazarov, and R. A. Miller, *Int. J. Mass Spectrom.* **266**, 76 (2007).
- [17] S. Prasad, K. Q. Tang, D. Manura, D. Papanastasiou, and R. D. Smith, *Anal. Chem.* **81**, 8749 (2009).
- [18] A. A. Shvartsburg, *Differential Ion Mobility Spectrometry*, 1st Edn., Boca Raton: CRC Press Taylor & Francis Group, 57 (2009).
- [19] E. V. Krylov, *Int. J. Mass Spectrom.* **225**, 39 (2003).
- [20] A. A. Shvartsburg, S. V. Mashkevich, and R. D. Smith, *J. Phys. Chem. A* **110**, 2663 (2006).
- [21] A. A. Shvartsburg, *Differential Ion Mobility Spectrometry*, 1st edn., Boca Raton: CRC Press Taylor & Francis Group, 6 (2009).
- [22] W. Vautz, B. Bödeker, J. Baumbach, S. Bader, M. Westhoff, and T. Perl, *Int. J. Ion Mobil. Spec.* **12**, 47 (2009).
- [23] H. Borsdorf, A. Raemmler, D. Schulze, O. K. Boadu, B. Feist, and H. Wei, *Anal. Chim. Acta* **440**, 63 (2001).
- [24] S. Sielemann, I. J. Baumbach, H. Schmidt, and P. Pilzcker, *Field Anal. Chem. Technol.* **4**, 157 (2000).