Comparison of the planar and coaxial field asymmetrical waveform ion mobility spectrometer (FAIMS)

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Abstract

A method and apparatus for ion separation in gases using the dependence of ion mobility coefficient on electric field strength are briefly described (including effect of ion focusing in apparatus with coaxial design of separation chamber). A mathematical model described ions transition for both coaxial and planar separation chamber design is proposed. The model has been verified by our own and published experimental data. Using the proposed model comparative analysis of the planar and coaxial apparatus is conducted by comparison of ion diffusion losses (sensitivity) and response time (speed of operation). Qualitative and quantitative advantages and disadvantages of both variants are considered.
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1. Introduction

The method and apparatus was proposed in Refs. [1–3] for separating ions in gases by the dependence of mobility coefficient on electric field strength. The method is easy to use, highly sensitive, fast and selective. Its disadvantage is that the physical parameter of ion separation (the dependence of ion mobility on electric field strength as compared with the mobility coefficient for conventional ion mobility spectrometer) is the subject of study rather than the characteristic of an ion. Over the last several years, however, there have appeared a lot of papers on this theme, which testifies that the method is highly promising. However, is still no commonly accepted terminology. Authors give different names to the apparatus used to realize this method of ion separation. We list here the names in a chronological order: gaseous analyzer of ions [1], drift spectrometer [4], field ion spectrometer [5], high field asymmetrical waveform ion mobility spectrometer [6], ion non-linearity drift spectrometer [7], radio frequency ion mobility spectrometer [8]. Below we use the name field asymmetrical waveform ion mobility spectrometer (FAIMS) and terms and notations close to those given in the book of Mason and McDaniel [9].

The two main types of apparatus are distinguished by planar (SDP-1, SIONEX, Waltham, MA) and coaxial (FIS, Mine Safety Appliance Company, Pittsburgh, PA) geometries of the ion separation chamber. The performance data for these apparatus are quite different. This paper studies and compares the analytical characteristics of both types of FAIMS apparatus.

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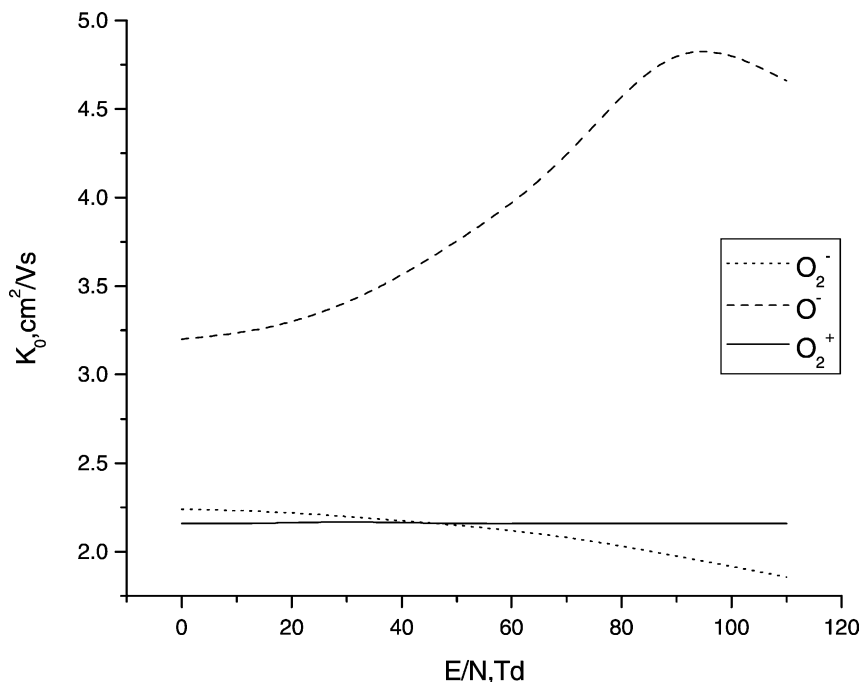*E-mail address:* ekrylov@nmsu.edu (E.V. Krylov).

Fig. 1. Electric field dependence of the coefficient of mobility for small ions. Plots [9] are for O_2^+ (solid line), O^- (dashed line) and O_2^- (dotted line) ions in oxygen carrier gas.

1.1. General principles

The motion of gas phase ions in electric fields at pressures greater than 1 Torr is measured as velocity (V, cm/s) in electric fields (E, V/cm) low enough so that velocity is proportional to the electric field through a constant, the coefficient of mobility (K, cm²/V s).

The mobility coefficient is influenced by collision frequency and energy obtained from the field by ions between collisions. The average energy acquired from the electric field is determined by parameter E/N and is considered negligible when E/N is small since any energy gained by the ion from the field is dissipated at high pressures by collisions with the supporting gas. Under such conditions, K is a constant and independent of E/N. However, the mobility coefficient becomes dependent on electric field with increasing values of E/N as shown in Eq. (1):

$$K\left(\frac{E}{N}\right) = K(0)\left[1 + \alpha\left(\frac{E}{N}\right)\right] \qquad (1)$$

where $K(0)$ is the mobility coefficient under low field conditions, E/N is in units of Td.[1] Fig. 1 shows plot, drawn from reference data [9], as example the electric field dependence of coefficient of mobility for positive (O_2^+), negative (O_2^-) molecular and atomic negative ions (O^-) in oxygen. Thus, the α parameter is a unique feature of ions, which is used for ions separation in field asymmetric waveform ion mobility spectrometry.

The mobility coefficient should be expressed as an even power series in E/N due to symmetry considerations [9] (i.e., the absolute value for ion velocity is independent of electric field direction):

$$K\left(\frac{E}{N}\right) = K(0)\left[1 + \alpha_2\left(\frac{E}{N}\right)^2 + \alpha_4\left(\frac{E}{N}\right)^4 + \cdots\right] \qquad (2)$$

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[1] Under normal conditions, 1 Td is corresponded to $E = N_0 \times 10^{-17} = 268.67$ V/cm, N_0 is Loschmidt's constant.
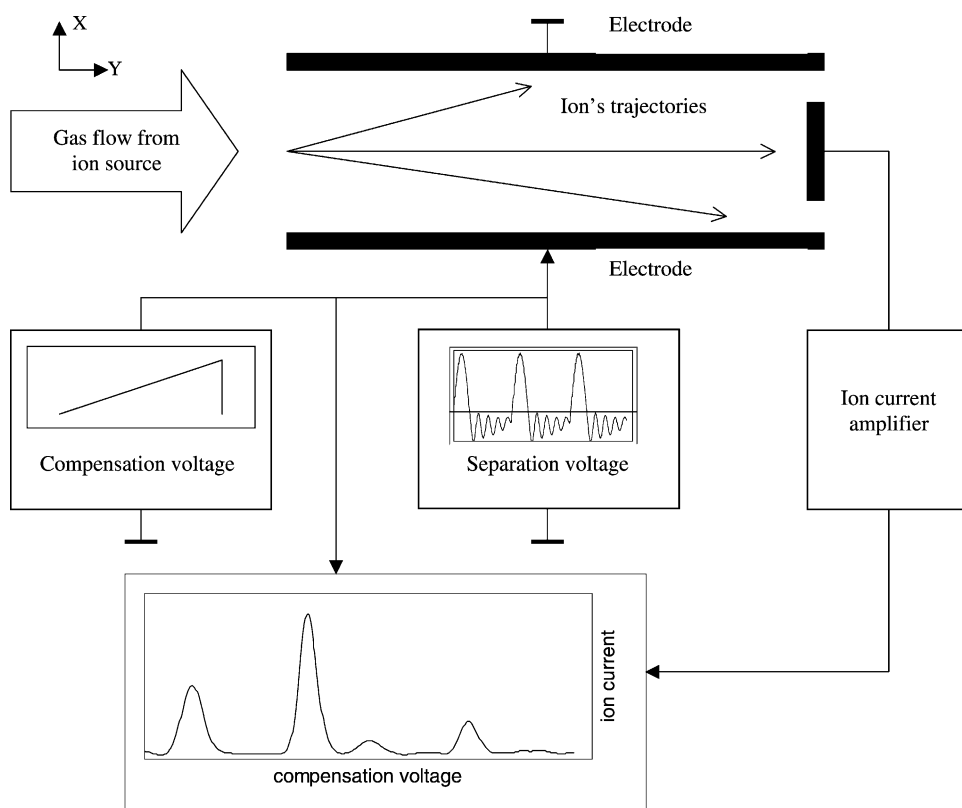
Fig. 2. Implementation of the method of ion separation in gases by their dependence of mobility coefficient on electric field strength.

where $\alpha_2, \alpha_4, \ldots, \alpha_{2n}$ are specific coefficients of an even powers of electric field.

In the FAIMS method, ions are introduced in a flow of gas that carries ion through a narrow gap between two electrodes as shown in Fig. 2. Under effect of high frequency, non-symmetric waveform electric field (the separation field, $S(t)$), which acted in perpendicular direction of gas flow movement different species of ions will have different trajectory and consequently may be separate.

Let us to consider ion motion under the action of the separation field. Ions undergo fast oscillations and slow drift perpendicular to the gas flow in response to the electric field. Ions will pass through the gap between the electrodes only when drift velocity is zero. Drifting ions will eventually reach one of the electrodes and undergo neutralization. If ion mobility significantly depends from electric field strength drift velocity of those ions will be not zero. Drift direction depends on sign of mobility dependence $\alpha(E/N)$ and separation field waveform. Drift velocity depends on field amplitude, field waveform, and absolute value of ion mobility dependence $\alpha(E/N)$.

A drifted ion can be restored to the center of the gap (i.e., compensated, with no drift for that ion) when a low strength constant electric field (the compensation field, C) is superimposed on the asymmetric waveform. Ions with differing drift velocities (owing to characteristic dependence of mobility in the high field condition) can be passed through the gap at compensation voltages characteristic of a particular ion and this is accomplished by applying various strengths of C. In this case, this system can function as continuous ion filter, or a scan of C will allow complete measure of ion species in the analyzer.

1.2. Mathematical description

A brief mathematical description of the method is presented below and a comprehensive treatment can be found elsewhere [3,10]. The separation field in a field asymmetric waveform mobility spectrometer is must satisfy the following conditions:

$$\frac{1}{T}\int_0^T S\,f(t)\,\mathrm{d}t \equiv S\langle f(t)\rangle = 0 \qquad (3a)$$

$$\langle f^{2n+1}(t)\rangle \neq 0 \qquad (3b)$$

where $f(t)$ is a normalized function which describes the waveform (normalized waveform), S the maximal amplitude of the separation field, triangular brackets denote the averaging over the period of separation field. The waveform is designed such that its average period value is zero (Eq. (3a)) while the amplitude of positive portion is not equal to negative (asymmetry condition—Eq. (3b)). The addition of the compensation field, C, to the separation field $Sf(t)$ yields Eq. (4):

$$E(t) = S\,f(t) + C \qquad (4)$$

where $E(t)$ is electric field affected ions between the electrodes. Under the action of this field ions are fast oscillating and slow drifting perpendicular to the carrier gas flow toward the electrodes. The average ion drift velocity can be written as:

$$V = \langle V(t)\rangle = \langle K(E)(S\,f(t) + C)\rangle \qquad (5)$$

Only ions with average velocity equal zero will pass through the gap without neutralization. An expression for the compensation field required to enable an ion to pass through the gap can be obtained by substituting Eqs. (2)–(4) into Eq. (5) as shown here [3]:

$$C = \frac{\langle \alpha S\,f(t)\rangle}{1 + \langle \alpha\rangle + \langle(\partial\alpha/\partial E)S\,f(t)\rangle} \qquad (6)$$

The value of this compensation electric field can be predicted precisely when the α parameter for the ion species, the normalized waveform $f(t)$, and the amplitude of the separation field S are known. Authors [3] also give the method for solving inverse problem. Deriving experimentally the approximation of function

$C(S)$ as the expansion into a series of odd S degrees, one can calculate the expansion of function $\alpha(E/N)$ into a series of even E/N degrees.

When ions are separated in the spatially inhomogeneous (coaxial or spherical) electric field, the field strength and thus, the ion drift velocity become the space coordinate function. It has been found [2,10] that under certain conditions, the ion-focusing effect arises which decreases the diffusion losses of ions. This means that the ions diffusing along the field lines from the point of equilibrium, r_0, where the compensation condition is fulfilled are subject to the restoring force. In other words, under the action of separation field, the ions start drifting from the walls of the chamber to the center. In the linear approximation, drift velocity, V_{focus}, proportional to the small shift, Δr, of ion from equilibrium position r_0 is

$$V_{\text{focus}} = K\left(C - \frac{\mathrm{d}C}{\mathrm{d}S}S\right)\frac{\nabla E}{E(r_0)}\Delta r \equiv \gamma\,\Delta r \qquad (7)$$

where $E(r_0)$ is electric field in the point of equilibrium, ∇E the field gradient, γ the focusing factor, C the compensation field and S is the separation field amplitude.

For the field inside the coaxial separation chamber, the focusing factor is

$$\gamma = \frac{K}{\rho}\left(C - \frac{\mathrm{d}C}{\mathrm{d}S}S\right) \qquad (8)$$

where C is compensation field, S the separation field amplitude, K the ion mobility and ρ is the medial radius of the separation chamber.

2. Model of FAIMS

The field asymmetrical waveform ion mobility spectrometer, which realizes the method of ion separation, gives information about an analyzed ion mixture in a spectral form. Position of the spectrum peak (or compensation field for these ions) depends on the ion properties (see Eq. (6)); peak height (or ion current measured at the exit of separation chamber) depends on the quantity of the ions. What is the influence of the apparatus parameters (carrier gas flow rate,

amplitude and form of separating field, dimensions and form of separation chamber) and ion characteristics (diffusion, mobility and field mobility dependence) on spectral peaks height?

Let us to determine the coefficient of ion transition through separation chamber, L, as a ratio between the integrals of ion density by cross-section at the input and output of the separation chamber. The transition coefficient is equal to the output current of the FAIMS normalized to the input ion current. Thus, transition coefficient equal zero corresponds to total ions loss (no output ion current); transition coefficient equal 1 corresponds to loss free passage through separation chamber (output ion current is equal to input current). When C satisfies the compensation condition, peak height A is proportionate to the transition coefficient L.

To determine dependence of L from parameters we have to calculate the ion density distribution in the separation chamber. We make the following simplifying assumptions:

(1) A spectrum peak corresponds to one ion type. There are no ion–molecular reactions in the separation chamber.
(2) An electric field which affects ions in the separation chamber leads to the fact that:
   (a) The diffusion and mobility coefficients become a values depending on field strength [9]. The generalized Einstein relation correlates $D(E)$ with $K(E)$ [9].
   (b) The effective gap between electrodes decreases, because the ions, approaching electrodes to a distance equal to the amplitude of their fast oscillations, neutralize:

$$g = d - SK\frac{1}{2}\int_0^T |f(t)|\,dt \qquad (9)$$

   where g is value of effective gap, d the distance between electrodes, S the separation field amplitude, K the ion mobility and $f(t)$ is the separation field normalized waveform.
(3) Ion diffusion in the direction of carrier gas flow is neglected.
(4) The influence of spatial inhomogeneous field on the process of ion separation results in the ion

drift proportional to ion shift from the point of equilibrium (Eqs. (7) and (8)).

In the framework of this assumption and considering Fick's second law, the problem of calculating the ion density in separation chamber resolves itself into a solution of the one-dimensional diffusion equation with zero boundary conditions:

$$\frac{\partial n}{\partial t} + \nabla(-D\,\nabla n + \gamma xn) = 0, \quad n\left(\pm\frac{g}{2}\right) = 0 \quad (10)$$

where n is ion density, D the coefficient of diffusion, x the coordinate along the electric field and γ is the focusing factor.

This differential equitation may be solved in the assumption of independent variables. Then, the spatial part of the solution describes the established profile of ion density in separation chamber. The time part determines coefficient of ion transition in separation chamber and by that spectrum peak height dependence. Let us consider the different cases.

For the separation chamber with planar geometry focusing factor is negligible. In this case diffusion equation has accurate solution:

$$|\gamma| \ll \frac{D}{g^2} \qquad (11a)$$

$$n(x;t) = \cos\left(\frac{\pi x}{g}\right)\exp\left\{-t\frac{D\pi^2}{g^2}\right\} \qquad (11b)$$

Eq. (11b) integrates to the following expression for the coefficient of ion transition through separation chamber, L:

$$L = \exp\left\{-\frac{WD\pi^2}{Qg^2}\right\} \qquad (12)$$

where W is the volume of separation chamber, Q the carrier gas flow rate, g the effective gap and D is the diffusion coefficient.

Eq. (12) gives the dependence of the spectrum peak height on the amplitude of separating field and ion mobility (via the effective gap according to Eq. (9)), diffusion coefficient, carrier gas flow rate and volume of separation chamber.

For the separation chamber with coaxial geometry focusing factor is significant. Only the time part

of the solution can be expressed analytically. In this case coefficient of ion transition through separation chamber, L:

$$|\gamma| \approx \frac{D}{g^2} \tag{13a}$$

$$L = \exp\left\{-\frac{WD\pi^2}{Qg^2}\exp\left(\frac{g^2\gamma}{2\pi^2 D}\right)\right\} \tag{13b}$$

where W is the volume of separation chamber, Q the carrier gas flow rate, g the effective gap, D the diffusion coefficient and γ is the focusing factor (see Eq. (8)).

Eq. (13b) determines the dependence of coefficient of ion transition (and thus, of peak height) on separating field strength, ion properties, separation chamber geometry, and carrier gas flow rate.

3. Experimental verification

The model has been verified by both our own experiments with planar FAIMS and published experimental data for coaxial FAIMS separation of various ions under different conditions.

3.1. Planar FAIMS

Studies here were completed using planar field asymmetric waveform ion mobility spectrometry. Planar FAIMS was interfaced to a tandem mass spectrometer (Sciex TAGA 6000, Toronto, Ont., Canada) for identification of the core ions from peaks in mobility scans. Details of this planar FAIMS drift tube/MS/MS interface have already been given [11]. A width of 0.5 mm was used for the gap between the electrodes of 5 mm width and 15 mm length. Air at 1 L/min was used for gas flow through the analyzer. Air was provided using a pure air generator (Mode 737, Addco Corp., Miami, FL) and was further purified through beds of activated charcoal and $13\times$ molecular sieve. The ion sources were UV-lamp (10.6 eV) or ^{63}Ni β-source (5 mCi). The drift tube was operated using specialized electronics containing a separation voltage

generator, a sweeping voltage generator, and an electrometer. The separation voltage generator was based on a soft-switched, semi-resonant circuit that incorporates a flyback transformer [12] and allowed variable amplitudes of the asymmetric waveform from 200 to 1100 V without altering the waveform shape. The operating frequency of the generator was 1.3 MHz and the amplitudes were 1000 V. A compensation voltage ramp was synchronized with the data collection system and provided a scan of compensation voltage from −35 to +10 V. Custom software and hardware was used to display the results as spectra.

Ions identifications of the peaks in mobility scan were made by setting the compensation voltage to pass only certain sort of ions into the MS/MS. In FAIMS–MS/MS measurements, individual neat chemicals were placed in a vapor generator and headspace vapors were diluted and split to the planar FAIMS drift tube. The vapor generator was a hermetically sealed, glass container (200 mL), which was thermostated in an aluminum block with a Minco CT 137 controller. Glass diffusion tubes or Teflon permeation tubes was placed in the glass container and temperatures ranged from 35 to 80 °C. All supply lines from the vapor generator to the drift tube were 60 °C or more to minimize wall-adsorption by vapors. This flow system allowed a constant gas flow to be delivered to the drift tube and permitted changes in vapor concentration by adjusting the ratio of sample to diluent flows or the sample temperature. The diffusion or permeation tubes were weighed over time to determine gravimetrically concentrations in the sample flow.

The ions from a ^{63}Ni source in a planar FAIMS drift tube in the absence of chemicals appeared at compensation voltage of −9.5 V with m/z values of 19, 37, 55 and 73 amu. These were identified as $(H_3O)^+(H_2O)_n$ where $n = 0$–3 at ambient temperature and moisture of ~1 mg/m^3. Though the identification of the core ion (i.e., a hydrated proton) can be considered reliable, uncertainty exists in the exact composition of the ion population from clustering and declustering in the interface region for ambient pressure and high vacuum. Thus, the fractional composition of ions for

values of n may not be quantitative derived from intensities in mass spectra. The mass spectra also cannot accurately account for short lived ion clusters such as $(H_3O)^+(H_2O)_n(N_2)_n$ which also are altered in the supersonic jet expansion region of the IMS/MS. Thus, mass spectra from this experiment are suitable for qualitative interpretations and assignment of identity for the core ion. Nonetheless, the ion chemistry of positive polarity ions in clean air at ambient pressure are well-known and the results here are consistent such prior findings [13,14].

For verification of our computation, we have carried out experiments with simple ions in dry (0.1 ppm moisture) air. In this experiments we change separation field amplitude within 30–110 Td in conditions of atmosphere pressure and measure height of peak corresponding to certain ions. Ion transition coefficient, L, was considered to be proportional to peak height. Then actual parameters of planar FAIMS experimental set and properties of the ions under investigation

were used to calculate theoretical curve. Experimental point and theoretical curve were compared to check proposed model validity.

Fig. 3a shows coefficient of ion transition L vs. separation field amplitude S for $M^+(H_2O)_n$ xylene ions obtained by photoionization in purified air (solid line, theoretical computation; circles, experimental results).

Fig. 3b shows result of our determination of ion transition coefficient L vs. separation field amplitude S for $(H_3O)^+(H_2O)_n$ ions obtained by β-ionization of purified air (solid line, theoretical computation; squares, experimental results).

Good agreement of these sets of data is the direct verification of the mathematical model of planar FAIMS proposed in this work.

3.2. Coaxial FAIMS

In Ref. [5] results are given for $M^+(H_2O)_n$ ions obtained from xylene photoionization in purified air. This

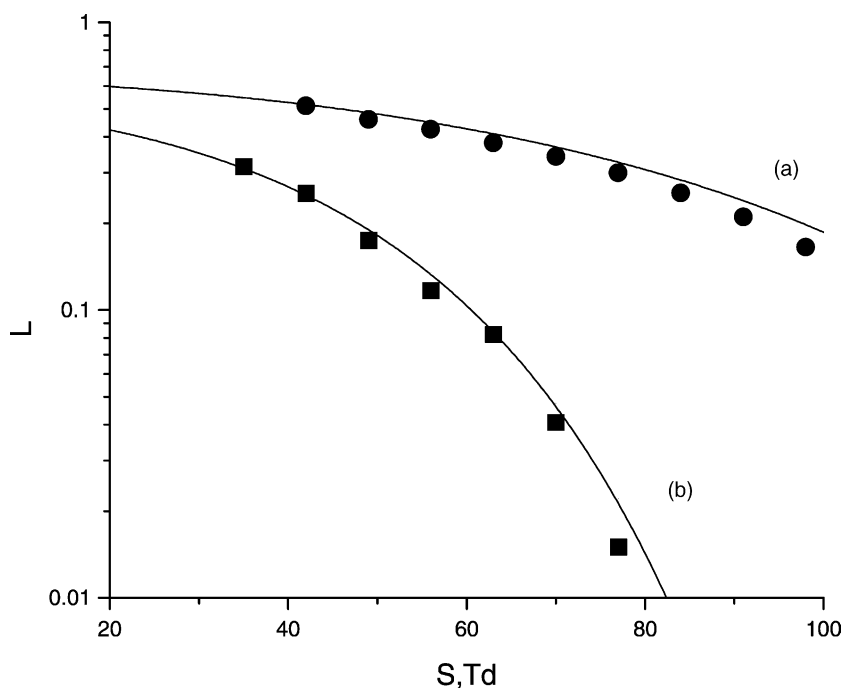Fig. 3. Coefficient of ion transition vs. separation field amplitude for planar FAIMS: (a) $M^+(H_2O)_n$ xylene ions obtained by photoionization of purified air (solid line, theoretical computation; circles, experimental results); (b) $(H_3O)^+(H_2O)_n$ ions obtained by β-ionization of purified air (solid line, theoretical computation; squares, experimental results).

experiment used the apparatus with the coaxial separation chamber (FIS, Mine Safety Appliance Company, Pittsburgh, PA).

The coaxial FAIMS device was composed of inner and outer cylinders, which are coaxially aligned. The inner cylinder is 14 mm o.d., the outer cylinder is 18 mm i.d., and cylinders are about 90 mm long. Ion separation takes place in the 2 mm annular space between the inner cylinder and the outer cylinder. Carrier gas flow rate through separation chamber is 1.5 L/min.

The outer cylinder of the coaxial FAIMS is held at ground electrical potential. During operation, a high frequency 200–250 kHz, high-voltage up to 5000 V p–p maximum asymmetric waveform was applied to the inner cylinder to establish separation electric fields in the separation chamber. The separation voltage generator was based on a principle of two-frequency resonance [4,12]. In addition to this high-frequency

waveform, a dc offset voltage (the compensation voltage) was applied to the inner cylinder. This results in the separation of ions in the manner discussed in Section 1.

Fig. 4a shows both a theoretical curve of ion transition coefficient L vs. separation field amplitude S and experimental points obtained from published spectrums for these ions (solid line, theoretical computation; circles, experimental results).

Experimental spectra for $(H_3O)^+(H_2O)_n$ ions obtained by corona discharge ionization of purified nitrogen were presented in Ref. [15]. Parameters of coaxial FAIMS used in this work are in general the same as were described above. Separation field dependence of ion transition coefficient can be extracted from experimental data. The comparison of experimental and theoretical results is shown in Fig. 4b (solid line, theoretical computation; squares, experimental results).
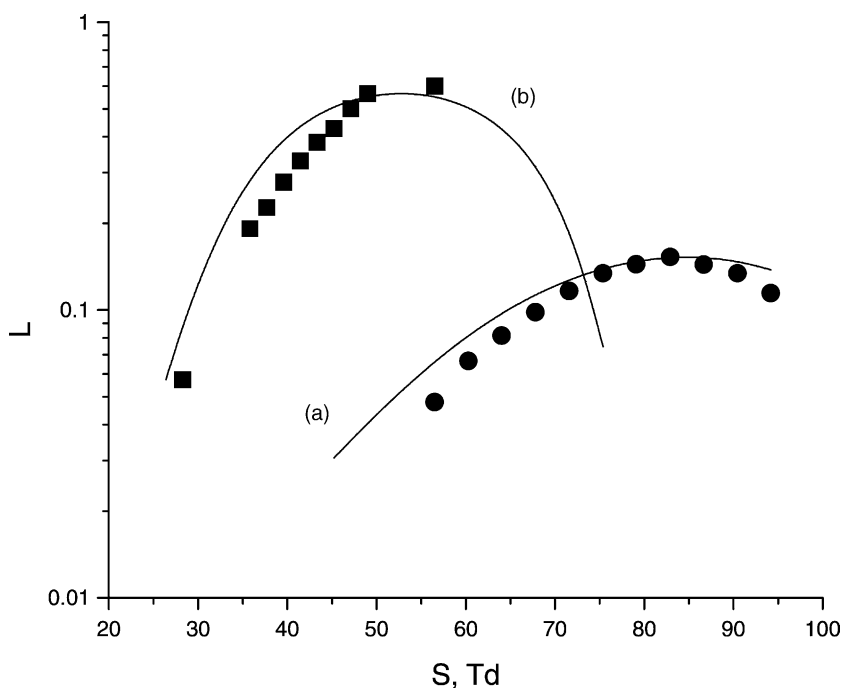

Fig. 4. Coefficient of ion transition vs. separation field amplitude for coaxial FAIMS: (a) $M^+(H_2O)_n$ xylene ions obtained by photoionization in purified air [5] (solid line, theoretical computation; squares, experimental results); (b) $(H_3O)^+(H_2O)_n$ ions obtained by corona discharge ionization of purified nitrogen [15] (solid line, theoretical computation; circles, experimental results).

4. Comparative characteristics of planar and coaxial FAIMS

The proposed model of FAIMS appears to be in fair agreement (accurate up to a normalization factor) with the experiment performed for the different types of apparatus. It proves that the model can be used as a basis for comparing the characteristics of two types of the FAIMS (planar and coaxial).

4.1. Response time

The response time or the speed of response for both planar and coaxial FAIMS is determined by the time that ions spend in the separation chamber (residence time).

For the planar FAIMS this time is limited from below by the requirement on the full separation of the ion mixture. The ions, for which the compensation condition is not met, must reach electrodes upon their flight through the separation chamber. This allows one to estimate the minimum or the response time of the planar FAIMS:

$$t_r \geq \frac{g}{KM} \tag{14}$$

where t_r is the response time, M the peak width (V/cm), K the ion mobility, g the effective gap. Substituting the real values, we numerically estimate that the minimum response time is 2.5 ms.

For the coaxial FAIMS, the response time is determined by the time necessary for ion focusing. For ions to focus into a beam, the residence time in the coaxial FAIMS separation chamber must be much longer than the characteristic time of ion focusing:

$$t_r \gg t_f = \frac{\rho}{(C - C'S)K} \tag{15}$$

where t_r is the response time, t_f the characteristic focusing time, C the compensation field, S the separation field amplitude, K the ion mobility and ρ is the medial radius of the separation chamber. Substituting the real values, we numerically estimate that the minimum response time is about 0.2 s.

Response time determines time of spectrum scanning. In practice, period of full range compensation voltage scan should be approximately 100 times more then response time.

4.2. Ion losses in a separation chamber

Even though the compensation condition in the planar FAIMS is fulfilled for particular ions, some of these ions still diffuse during the flight through the separation chamber onto its walls lose their charge and cannot be detected. Since diffusion ion losses exponentially increase with time, the residence time in the chamber should be decreased to improve not only the speed of operation (response time) but also the sensitivity of the FAIMS.

Besides, ions losses grow drastically with the amplitude of their fast oscillations resulted from the action of the separation field (see Eqs. (3a) and (3b)). Concept of the effective gap (see Eq. (9)) reflects this consideration. Oscillation amplitude is proportionate to the ion mobility, separation field period and amplitude. It means that under the equal separation conditions the higher mobility the higher losses.

Separation field polarity, ions polarity and α-dependence have no noticeable effect on the ion diffusion losses in the planar FAIMS. Such tolerance of the planar FAIMS results in the possibility of simultaneous separation of positive and negative ions as it had been done in the work [16]. Only one scan of the compensation voltage is necessary to get spectral information about all sorts of ions, i.e., both positive and negative with all possible α-dependencies.

The spatially inhomogeneous electric field in the coaxial FAIMS not only separates ions but also focuses the ions meeting the condition of compensation. However, the focusing effect of the coaxial FAIMS causes a decrease in diffusion losses (up to full disappearance) for some ion types. In terms of ion transition, it means that ion transition coefficient, L, tend to 1 (see Eqs. (13a) and (13b)). But focusing is possible only for the ions with a noticeable α-dependence in a fairly high field. The ions with weak α-dependence or in a weak field cannot be focused.

Moreover, in order that the focusing effect appears, the separating field polarity must correspond to the polarity and α-dependence of the separated ion. In terms of Eq. (7) it means that the sign of focusing factor γ must be negative. Otherwise, the focusing changes into defocusing, i.e., the separating field causes ions to drift from the center of the chamber to its walls. Defocusing results in the total ion losses, i.e., ion transition coefficient, L, tend to 0. The reason is in the fact that now there is a dedicated direction in the system, the gradient of electric field strength [10].

Let us to summarize above-mentioned considerations as a simple logical rule for determining the focusing conditions in a coaxial FAIMS. The appearance of ion focusing is known to depend on:

- Ion polarity.
- α-Dependence sign (positive sign corresponds to an increase in ion mobility with increasing field strength).
- Separation field polarity.

We consider the separation field polarity to be positive, if the vector of field gradient is opposite to the vector of field during the half-period of greater strength. In the coaxial chamber the vector of field gradient is directed from the outer to the inner electrodes. When (as for the coaxial FAIMSes described in Refs. [5–7,15,17]) the voltage is supplied to the inner cylinder, and the outer cylinder is grounded, the separation field polarity coincides with the sign of separation field amplitude S. And, vice versa, if voltage is supplied to outer cylinder sign of field polarity inverts relatively sign of S.

All three factors of focusing can be taken as logical (two-valued) variables. The logical multiplication of these variables will result in a logical variable corresponding to focusing. All possible combinations of parameters are shown in Table 1. Experimental data [15] sustain a theory for described configurations of the coaxial FAIMS.

Thus, phenomenon of focusing along with ion losses decreasing imposes some limitations concerning to the analytical performance. Focusing conditions cannot be met simultaneously for all sorts of ions. In

Table 1
Focusing condition

No.	Field polarity	Ion polarity	$\alpha(E/N)$	Focusing
1	−	−	+	+
2	−	+	−	+
3	−	−	−	−
4	−	+	+	−
5	+	−	−	+
6	+	+	+	+
7	+	−	+	−
8	+	+	−	−

terms of focusing effect all ions can be divided into three large groups. First group is positive ions with positive α-dependence and negative ions with negative α-dependence. Second group is negative ions with positive α-dependence and positive ions with negative α-dependence. Third group is the ions with weak α-dependence.

If polarity of the separation field is positive, ions of first group are focused but ions of second group are defocused and visa versa. To get spectral information about both groups of ions one must do one scan of compensation field, switch polarity of the separation field and do second scan of compensation field. In practice, to switch separation field polarity one needs to commutate high-voltage high-frequency circuits for reversing the separation voltage polarity. The diffusion losses of third group ions obey the same laws as for planar FAIMS. As residence time for coaxial FAIMS is much more then for planar FAIMS, losses of third group ions are huge and they cannot be detected by the coaxial FAIMS under typical experimental conditions.

Proposed mathematical model of FAIMS allows not only qualitative but also quantitative estimation of ion losses both in coaxial FAIMS and planar FAIMS. Knowing ion's properties (mobility dependence) we can calculate ion transition coefficient, L, for any configuration of FAIMS apparatus.

Fig. 5 shows the calculated ion transition coefficient vs. separation field amplitude for ions with weak α-dependence (protonated ions of lysine $(M + H)^+$ obtained by electrospray ionization in air [17]; dashed line, planar FAIMS; solid line, coaxial FAIMS;
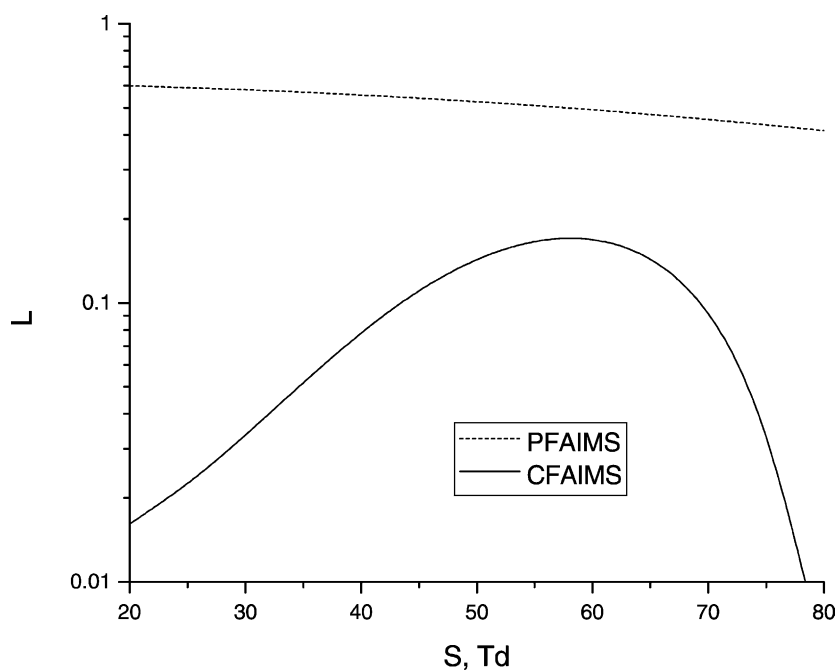
Fig. 5. Calculated coefficient of ion transition vs. separation field amplitude for low mobility dependence ions (protonated ions of lysine $(M + H)^+$ in air [17]); dashed line, planar FAIMS; solid line, coaxial FAIMS.
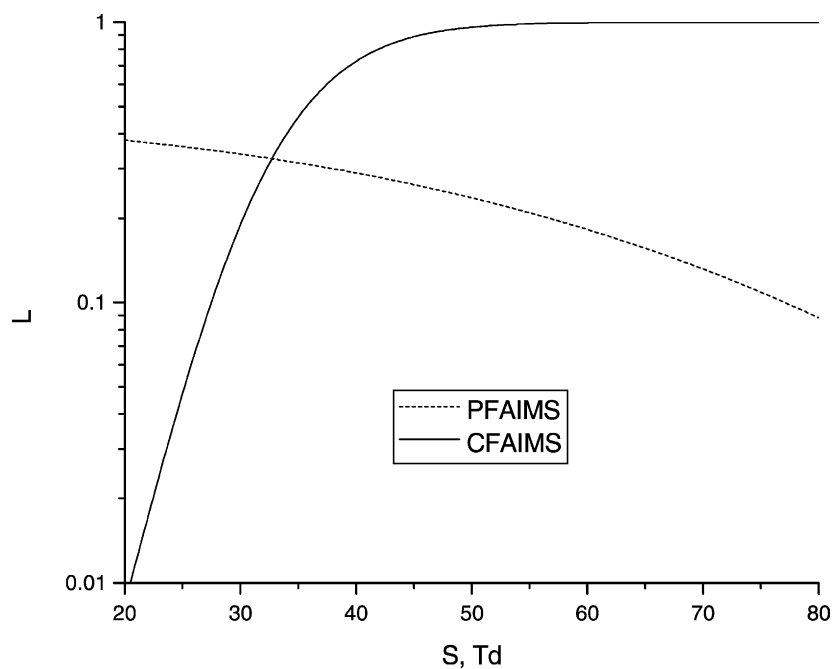

Fig. 6. Calculated coefficient of ion transition vs. separation field amplitude for strong mobility dependence ions (deprotonated ions of glycine (M^-) in air [17]); dashed line, planar FAIMS; solid line, coaxial FAIMS.

characteristics of the devices were described above). A drastic decrease in ion transition coefficient with increasing separating field amplitude in coaxial FAIMS results from that the focusing is substituted by defocusing. This is typical of all real ions and is assigned to the fact that all real ions at fairly high field strengths have a decreasing dependence of mobility on field strength. Changing the sign of mobility dependence derivative leads to substitution of defocusing for focusing. According to Eq. (8), the focusing effect vanishes at point where compensation field satisfies condition:

$$C = \frac{\partial C}{\partial S} S \tag{16}$$

where C is compensation field and S is the separation field amplitude

Fig. 6 shows the calculated ion transition coefficient vs. separation field amplitude for ions with strong α-dependence (deprotonated ions of glycine (M^-) ob-

tained by electrospray ionization in air [16]; dashed line, planar FAIMS; solid line, coaxial FAIMS; characteristics of the devices were described above). Extremely strong α-dependence for these ions result in full focusing in the coaxial FAIMS (solid line), i.e., diffusion losses disappear. Function L asymptotically tends to one.

Ion α-dependence appears to have an effect on ion transition coefficient (compare Figs. 5 and 6). To illustrate the correlation between ion α-dependence and ion transition coefficient let us to consider FAIMS separation of the ion mixture consists of ions with the same properties, distinguishing only by α-dependencies. Then difference of ions diffusion losses is determined by α-value only. Every sort of ions can be characterized by α-value under certain electric field strength (for example 70 Td). Fig. 7 shows the calculated logarithm of ion transition coefficient vs. $\alpha(70)$ value for that hypothetic ion mixture.
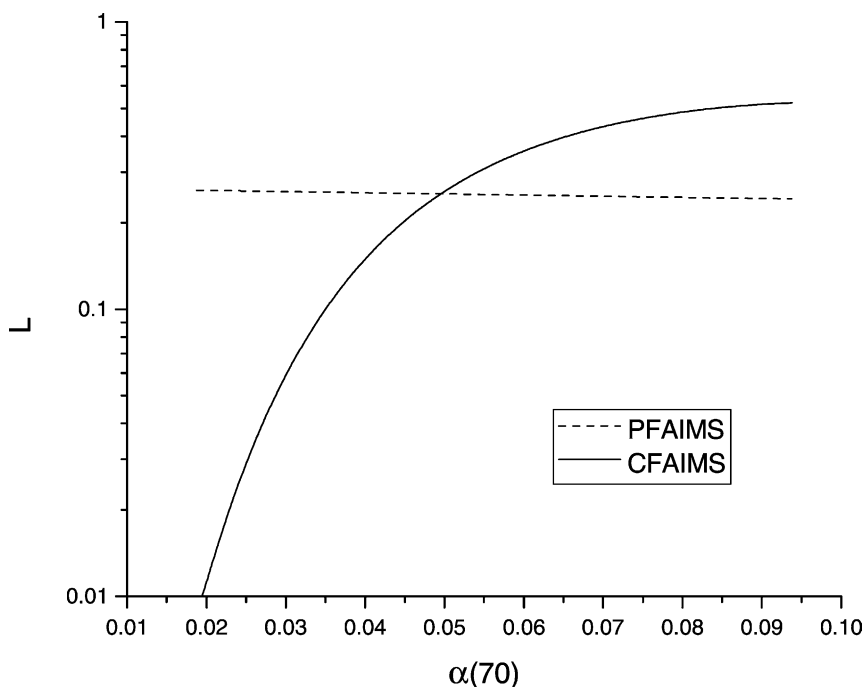

Fig. 7. Calculated coefficient of ion transition vs. ion properties (α-value under 70 Td of electric field strength); dashed line, planar FAIMS; solid line, coaxial FAIMS.

5. Conclusions

The experimentally tested model proposed for separating and focusing ions in field asymmetrical waveform ion mobility spectrometer (FAIMS) allows the following conclusions on the characteristics of coaxial FAIMS and planar FAIMS.

- The response time of coaxial FAIMS is two orders of magnitude more than for planar FAIMS.
- When the focusing conditions are met, the coefficient of ion transition in coaxial FAIMS becomes more than those in planar FAIMS and vice versa.
- Only the ions with substantial field dependence of mobility can be effectively focused.
- The focusing conditions in coaxial FAIMS cannot be met simultaneously for all sorts of ions.
- Planar FAIMS separates all types of ions without discrimination in the features of α-dependence or ion polarity.

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