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Relative transmission of different ions through shutter grid

M. Tabrizchi*, H.R. Shamlouei

Department of Chemistry, Isfahan University of Technology, Isfahan 84156-83111, Iran

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ABSTRACT

In this work, we study the transmission of different ions through a Bradbury–Nielson type shutter grid which is a key component in ion mobility instruments. It will be shown that the relative transmission of ions through the shutter grid depends not only on the opening time but also on the nature of ion and the voltage applied to the grid electrodes. The transmission of fast moving ions is higher than that of slow moving ions and, in general, applying a voltage greater than the blocking voltage reduces the transmission. A simple model is proposed to explain the results. Since slow-moving ions are lost in greater numbers than fast-moving ones, the intensity of ion peaks decreases as drift time increases. This can be corrected by multiplying the intensities by a factor of $(1+\alpha t_d)$ where α is a small correction factor which depends on the geometry of both the shutter grid and the drift tube and on the opening time.

1. Introduction

The Bradbury–Nielsen gate (BNG), originally introduced as an electron filter, is normally used to deflect or chop electron and ion beams before entering the drift region. BNG consists of two sets of parallel wires placed in one plane perpendicular to the moving direction of the charged particles [1]. The wires are biased to a potential, creating an orthogonal field, to deflect or block ion passage into the drift region. The operating principle of BNG is shown in S-1 (in the Supporting Information). BNG is widely used in Hadamard transform time-of-flight mass spectrometry [2–4] as well as in normal time-of-flight mass spectrometry [5–9]. It is also used for the determination of drift velocity of electrons in different gases [1,10–12] or in electron-swarm techniques for the study of electron attachment processes [13–15]. Several methods have been proposed for the production of BNG based on etching [16] or weaving [17–22].

One of the most important applications of BNG is in ion mobility spectrometry (IMS) where it is used as a shutter grid. IMS is similar to time-of-flight mass spectrometry except that it operates at atmospheric pressure. It consists of two main regions: the ionization and the drift region. The shutter grid is mounted between these two regions. Ions are generated in the ionization region and then penetrate into the drift region if the shutter grid is open. When the grid potential is removed for a short period of time, an ion pulse is admitted to the drift region. In fact, the shutter grid acts as an ion valve in IMS to allow only a small part of ions or electrons to enter the drift region. The ion packet then moves in the drift region at a velocity proportional to the electric field and ion mobility which depends on the cross-section of the ion under given conditions (pressure, temperature, and buffer gas).

IMS is a simple, sensitive, and fast analytical technique for the detection of trace levels of volatile organic compounds. It plays an important role in practical applications such as environmental monitoring and detection of drugs of abuse or explosives. The technique has also been used for both kinetic and thermodynamic studies of various gas-phase ion-molecule reactions at atmospheric pressure and for electron attachment reactions.

As in similar techniques, the signal intensity in IMS depends on the number of ions that are generated in the ionization region. It also depends on the number of ions that penetrate through the shutter grid and traverse the drift region. Low ion transmission either for the shutter grid or for the drift tube results in a poor signal-to-noise ratio, even at high initial ion current. Furthermore, if the transmission is not equal for all ions, the intensities are not a true measure of the number density of ions in the ionization region. Thus, information about transmission efficiency is needed to correct the intensities. Knowledge of transmission efficiencies may help to enhance the signal-to-noise ratio by allowing investigators to modify the parameters of the system in order to increase transmission of certain ions. The knowledge may also help in designing instruments optimized for specific applications. In our previous study of transmission in the drift tube, we concluded that most ions are lost in the drift tube [23]. Moreover, it was shown that the quantity of ions lost differs for different ions. In fact, the response factor in IMS is not the same for different ions because of their different transmission efficiencies through the drift tube. The response factor has been shown to depend linearly on $1/t_d$, where t_d is the drift time. A simple formula was proposed to adjust the intensities to take into account the transmission efficiency of different ions. This

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* Corresponding author. Tel.: +98 311 3913272; fax: +98 311 3912350.
E-mail address: m-tabriz@cc.iut.ac.ir (M. Tabrizchi).

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correction is particularly useful when trying to calculate the relative number densities of two species in the ionization zone. For example, in calculating the ratio [H_3O^+]/[NH_4^+], the relative corresponding intensities should be corrected by a factor of 1.3, as the reduced mobility is 2.5 and 3.25 $cm^2/V\,s$ for H_3O^+ and NH_4^+, respectively. Without such correction, the calculation is expected to show a 30% error. In our previous work, the number of ions lost on the shutter grid was assumed to be the same for all ions. However, this was not true since even after correction, the intensity of different ions was observed to decrease slowly with their drift time. This was believed to be due to the effect of the shutter grid on ion transmission efficiency which is the subject of the present work.

Shutter grid is normally 99% optically transmitting. However, a simple experiment showed that about 30% of ions are lost on a fully open shutter grid. The question now is whether the loss is the same for all ions or different for different types of ions. Little is known about the loss of ions or ion transmission through the shutter grid. Puton [24] is the only study having investigated in 1989 the penetration of ions through the shutter grid of an ion mobility spectrometer. He determined the permeability of the grid as a function of blocking potential and wire diameter as well as the dynamic ion concentration distribution in the vicinity of the grid. Recently, he presented the results of computer calculations concerning electric field and ion concentration distributions in the neighborhood of grid electrodes. His proposed model and methods of calculation make it possible to estimate the permeability of the grid and to determine the ion concentration profile behind the grid as a function of grid dimensions and voltage controlling parameters [25]. Unfortunately, there is no information about ion losses on the shutter grid for different ions. The main aim of this work is to investigate the transmission efficiency of different ions through the shutter grid. If the relative transmission efficiency of two ions through the shutter grid is known, the intensities can be corrected accordingly to represent the true relative number densities.

2. Experimental

2.1. Ion mobility spectrometer

The ion mobility spectrometer used in this study was constructed in our laboratory at Isfahan University of Technology. The ionization region consisted of five 9.5-mm thick aluminum rings, 20 mm in ID and 55 mm in OD. The drift tube consisted of 11 aluminum rings with the same OD size and 36 mm in ID. Each ring was connected to the adjacent one via a 5-MΩ resistor to create a potential gradient. A continuous corona discharge was used to produce ions, and a Faraday cup type collector plate (10 mm in diameter) with an aperture grid was used to register the ion current. The IMS cell was housed in a thermostatic oven where temperature could be adjusted from room temperature to 473 K within 1 K. All experiments were carried out at 333 K. Nitrogen gas, after passing through a 13× molecular sieve (Fluka), was passed through the cell as the carrier and the drift gas. The spectrometer was operated in the positive mode with various drift fields from 312 to 500 V/cm. The ion current reaching the end of the drift tube was registered by a Faraday cup, amplified using a home-made amplifier, and digitized by an A/D converter (Picoscope, UK). A home-made pulse generator was used to apply a pulsed voltage to the shutter grid. The applied voltage and its duration were adjustable from 0 to 160 V and 20 to 800 μs, respectively. The pulse generator could operate in three modes; closed, open, and pulsed. In the closed mode, a continuous voltage was applied to the grid; in the open mode, the voltage went to zero; and in the pulsed mode, the voltage was removed for a short period of time.

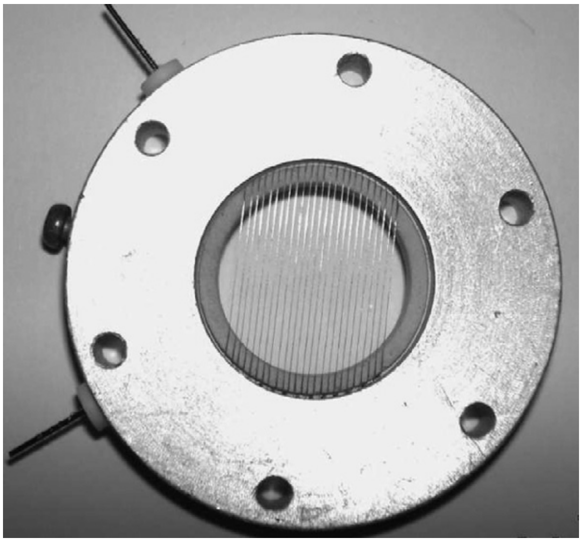

Fig. 1. The shutter grid constructed at Isfahan University of Technology.

2.2. Shutter grid

The shutter grid employed in this instrument was of the Bradbury–Neilson type, mounted between the ionization region and the drift tube. It was constructed by weaving thin wires (0.05 mm in diameter) at 0.7 mm intervals on a ceramic frame (Fig. 1).

2.3. Selection of compounds

In order to individually measure the transmission of different ions, a specific type of ion ought to be produced in the ionization region. As for the previous work, the samples were chosen so that their corresponding ion mobility spectra contained only one peak. Ketones possess high proton affinity; hence, at low temperatures and at sufficiently high concentrations, they react fully with the reactant ion, (H_3O^+), to form proton-bound dimers. A series of 9 different ketones, the dimers of which showed a range of drift times between 8 and 22 ms, were selected (Table 1). Ion mobility spectra of the selected ketones are shown in Fig. 2. The concentration of the samples was high enough for the reactant ion and protonated monomer peaks to disappear so that only the dimer peak remained in the spectrum. The selected compounds used in this experiment, presented in Table 1, were purchased from Fluka and used without further purification.

Table 1
List of selected ketones used in this study. The drift time for the dimer peak is given for each compound.

No.	Compound	Drift time (ms)
0	Reactant ion	9.01
1	Acetone	10.17
2	Pentanone	12.07
3	Cyclohexanone	13.38
4	Methyl isobutyl ketone	13.95
5	Acetophenone	13.50
6	Methyl heptanone	15.53
7	Octanone	15.74
8	Nonanone	16.53
9	Decanone	17.22

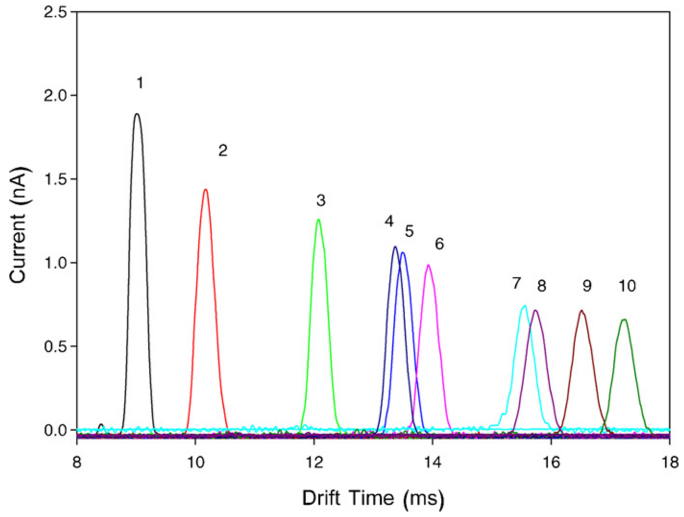

Fig. 2. Selected ion mobility spectra of ketones (listed in Table 1) at high concentrations.

3. Results and discussion

The results are presented in three parts. Firstly, the threshold voltage for closing the shutter grid at different drift fields was determined. Then, the effect of overvoltage was evaluated on ion transmission. Finally, the transmission of different ions through the shutter grid was studied and a model was developed to explain the results.

3.1. Threshold voltage for blocking ions

In order to obtain the threshold voltage for closing the shutter grid, a variable DC voltage was applied to the shutter grid while the total ion current was being measured. The ion current is plotted against the applied voltage to the shutter grid in Fig. 3 for different drift fields. All the plots fit very well into a second order function. The threshold voltage, in which the ion current goes to zero, was extracted by extrapolation of each plot to the zero current.

Fig. 3 demonstrates that the threshold voltage changes with increasing drift field. This is similar to the observation by Puton et al. [25].

The nominal field between the shutter grid wires for blocking threshold was calculated by dividing the threshold voltage by the distance between the adjacent wires (0.7 mm). The results were plotted as a function of the drift field, presented in S-2 (in the Supporting Information). The plot reveals that the field required to close the shutter grid increases linearly with the drift field with a slope of 2. This means that to block ions, the shutter grid field should be at least 2 times as much as the drift field. This is almost consistent with the findings of Puton et al. [25] and Siems et al. [26].

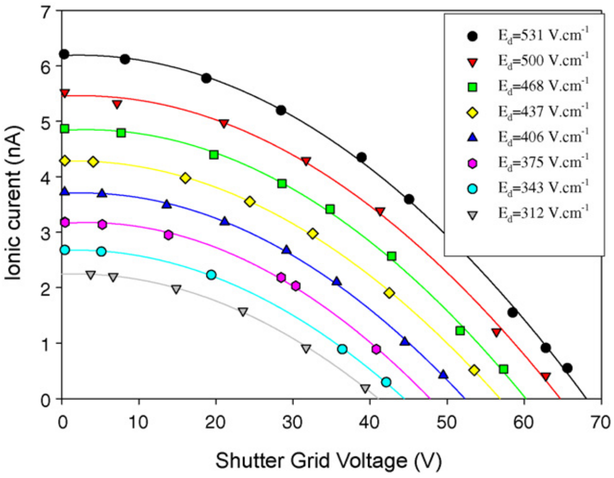

Fig. 3. Plots of ionic current versus applied voltage to the shutter grid at various drift fields.

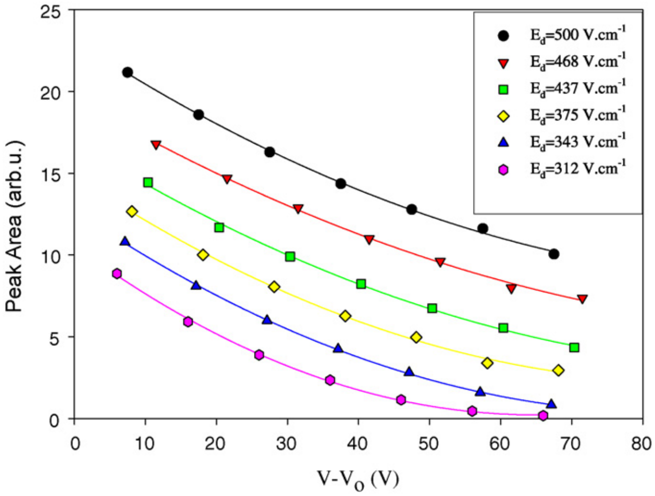

Fig. 4. Peak area versus the overvoltage applied to the shutter grid at several drift fields. V_o is the blocking voltage at the corresponding drift field.

3.2. Applying additional voltage to the shutter grid

Applying a pulsed voltage as high as the threshold voltage to the shutter grid is sufficient to obtain a zero background spectrum. However, it was observed that if the magnitude of the pulse applied is greater than the blocking voltage, signal intensity decreases. This is demonstrated in Fig. 4 where the signal intensity for the reactant ion peak was plotted versus the overvoltage applied to the shutter grid at various drift fields. The decrease is believed to be due to the penetration of the orthogonal field outside the shutter grid plane, which causes fewer ions to escape during the opening time. This will be further discussed in Section 3.5 where the effective thickness of the shutter grid will be considered.

It was found that the peak area presented in Fig. 4 is a linear function of the reciprocal overvoltage. It is also a linear function of the ratio of E_d/E_s where E_d and E_s are the drift and shutter grid fields, respectively. This is demonstrated in S-3 (in the Supporting Information).

3.3. Transmission of different ions

In order to measure the relative transmission of different ions, a procedure similar to the one described in Ref. [23] was employed. Different ketones, given in Table 1, were injected into the ionization region to produce various proton bound dimmers via the following reactions:

$$\mathrm{M} + \mathrm{H_3O^+} \rightarrow \mathrm{MH^+} + \mathrm{H_2O} \quad \text{(R1)}$$

$$\mathrm{MH^+} + \mathrm{M} \rightarrow \mathrm{MHM^+} \quad \text{(R2)}$$

where M denotes ketone, H_3O^+ is the reactant ion, and MH^+ and MHM^+ are the protonated ketone and the proton bound dimer, respectively. In order to ensure that the same number density of all ions is present in the ionization region, the ketones were injected at adequate concentrations so that only a single peak of dimer was observed, i.e., all reactant ions were converted to product ions. In such conditions, the number of ions reaching the shutter grid

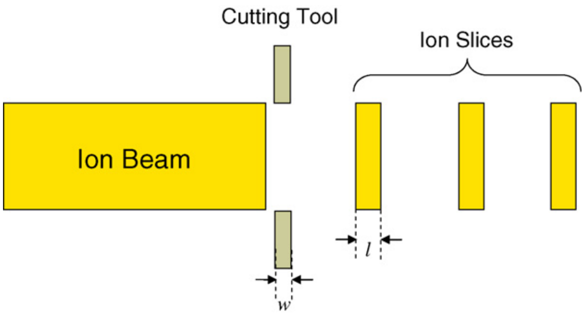

Fig. 5. Schematic diagram for chopping of ions by the shutter grid.

depends on their transmissions since the originally number density of ions for all the ketones are the same. Hence, the spectra were corrected for transmission based on our previous findings presented in Ref. [23], i.e., the intensities were multiplied by a factor of t/t_{RI} where t is the corresponding drift time and t_{RI} is the drift time of the reactant ion. The corrected peaks were then integrated and plotted versus drift time. The results are presented in S-4 (in the Supporting Information). In principle, the plot is expected to be flat since the number of initial ions was the same for all different ketones and their loss in the drift tube was compensated. However, as shown, the plot has a small negative slop. The signal intensity for heavier ions is less than those for light ions even after the correction. This means that ion transmission through the shutter grid is not the same for all ions. A model is presented here to describe the loss mechanism and the way to correct the intensities.

3.4. The model

The shutter grid can be assumed as a chopper that cuts the ion beam. The beam is converted into successive slices of ions after passing through the shutter grid which is repeatedly opened. This is shown in Fig. 5. Apparently, the cutter is not infinitely sharp. If the width of the cutter is comparable to that of the slice, some parts of the slice is lost during the cutting process.

Designating the cutting width of the shutter grid to be w, then the thickness of the ion slice will be:

$$l = u \cdot t_{on} - w \tag{1}$$

where u is the velocity of the ion beam and t_{on} is the opening time of the shutter grid. Obviously, the value of $u \cdot t_{on}$ must be greater than that of w in order for an ion slice to be formed. The number of ions in each slice is $N^* \cdot A \cdot l$, where N^* is the number density of ions and A is the cross-section of the slice. Considering the charge of each ion (e), the total charge, Q, in each slice is given by;

$$Q = N^* A (u \cdot t_{on} - w) \cdot e \tag{2}$$

When the shutter grid is fully open, the total current (I_{op}) is;

$$I_{op} = N^* A \cdot u \cdot e \tag{3}$$

Substitution of $u = t_d/D$ in Eq. (2) where D is the drift length and using Eq. (3) gives;

$$\frac{Q}{I_{op}} = t_{on} - \frac{w}{D} \cdot t_d \tag{4}$$

In Eq. (4), Q is the total charge registered for each ion packet which corresponds to the peak area and I_{op} is the total current for the corresponding ion when the shutter grid is fully open. Eq. (4) suggests that the peak area over the total current increases with the opening time of the shutter grid (t_{on}), and decreases with the drift time of the ion (t_d) that is passing through the shutter grid, i.e., less heavy ions penetrate through the shutter grid than light ones. The extent of ion loss depends on the ratio of w/D as well as on the drift time for the ion. The ratio w/D is usually very small. Hence, for fast moving ions with small t_d, the ion lost due to the cutting edge is negligible. However, for heavy ions, the term t_d becomes large enough to make the extent of ion loss considerable. Eq. (4) also proposes that the ion loss depends on the sharpness of the shutter grid represented by w.

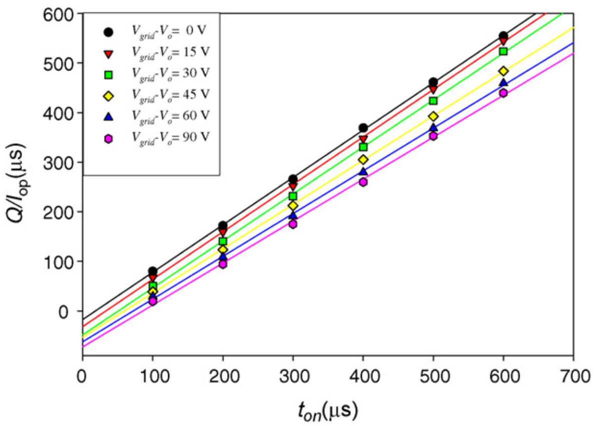

Fig. 6. Plots of Q/I_{op} versus t_{on} for various voltages applied to the shutter grid.

3.5. Evaluation of the model

To evaluate the model, the total ion current (I_{op}) was measured. Then, the shutter grid opening time (t_{on}) was changed and the peak area for the reactant ion was measured. The experiment was repeated with different overvoltages. The results are plotted in Fig. 6.

All plots in Fig. 6 are linear with similar slopes close to unity as predicted by Eq. (4). The cutting width of the shutter grid, w, is obtained from the intercepts of the plots. For the zero overvoltage

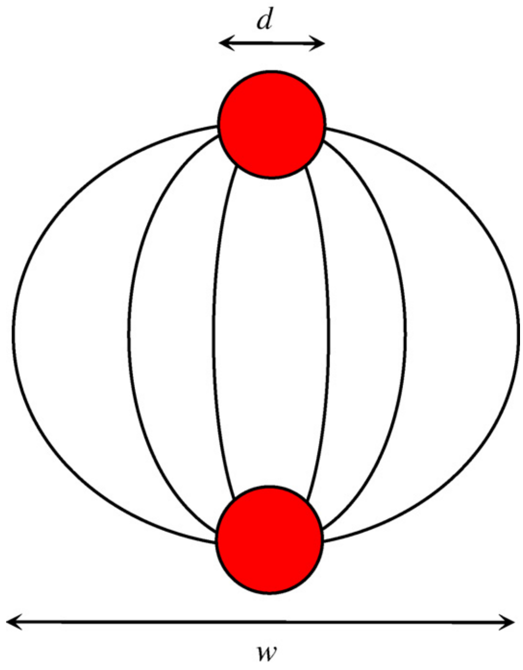

Fig. 7. Penetration of the electric field created between the shutter grid wires outside the shutter plane.

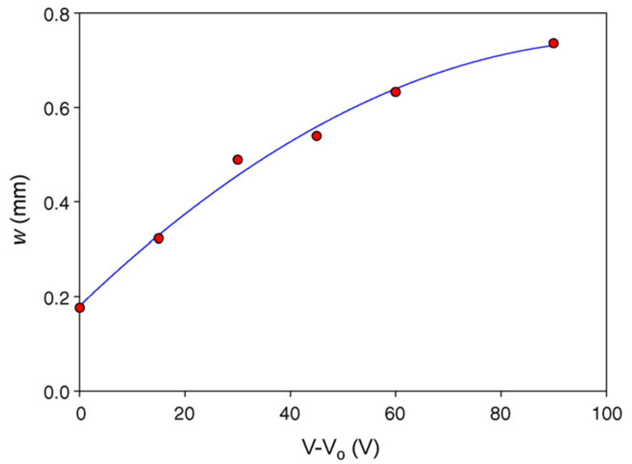

Fig. 8. Plot of the effective shutter grid width, w, versus the overvoltage applied to the shutter grid.

plot, w was obtained to be 0.17 mm. This is much larger than the actual width of the shutter grid (0.05 mm). The difference could be due to the fact that the field between the wires penetrates outside of the shutter plane as depicted in Fig. 7.

The penetrated field contributes to the effective width of the shutter grid. It is expected that the field penetrates deeper if the voltage applied to the wires is increased. This effect was observed indeed. In Fig. 6, the lines show different intercepts which is attributed to different ws. In other words, the cutting width of the shutter grid depends on the overvoltage. This dependency is demonstrated in Fig. 8. Based on Eq. (1), the increase in w results in a shorter ion slice and a weaker signal. Hence, peak intensity reduces with increasing overvoltage, as experimentally observed in Fig. 4.

Eq. (4) shows that, in addition to t_{on}, the peak area is affected by t_d, i.e., more heavier ions are lost by the shutter grid. To examine this, the peak areas for various ketones were measured at several fixed values of t_{on}. The results of Q/I_{op} versus drift time (t_d) are plotted versus drift time in Fig. 9. The plots show a negative slope as predicted by the model. The lines are also parallel since the overvoltages were the same resulting in a constant w/D. The average value of w, obtained from these plots is 0.25 mm which is comparable to that obtained from Fig. 6.

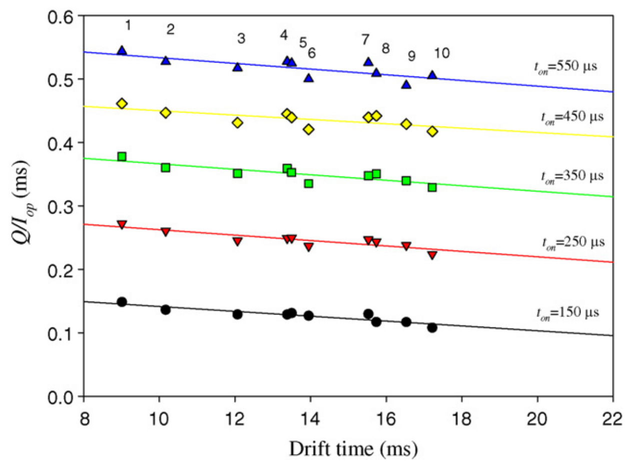

Fig. 9. Q/I_{op} versus t_d at various t_{on} for the shutter grid. Numbers are listed in Table 1.

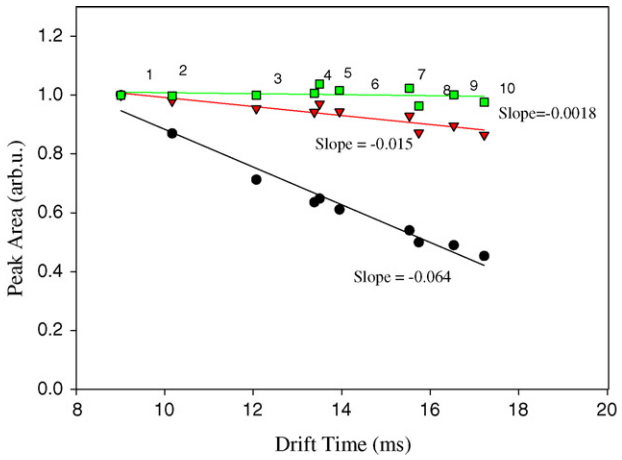

Fig. 10. Peak area as a function of drift time (a) actual recorded spectra, (b) after correction for drift tube, and (c) after correction for shutter grid.

3.6. Correction of intensities

Eq. (4) may be used to compensate for the loss due to the shutter grid. If Eq. (4) is rearranged to

$$Q = I_{op} \cdot t_{on} \left(1 - \frac{w}{D \cdot t_{on}} \cdot t_d\right) \qquad (5)$$

the value of $I_{op} \cdot t_{on}$ is the peak area, neglecting the shutter grid effect ($w = 0$). Thus, the actual peak area should be divided by $(1 - \alpha \cdot t_d)$, where $\alpha = w/(D \cdot t_{on})$ is a small coefficient and w is the effective shutter grid width. Since the correction coefficient, α, is small, the peak area can be simply multiplied by a factor of $(1 + \alpha \cdot t_d)$. As an approximation, the ion mobility spectra can be compensated for the effect of the shutter grid by multiplying the intensity axis by the factor of $(1 + \alpha \cdot t_d)$. This was done after the first correction for the drift tube. Considering a 15 V overvoltage, the value of α was extracted from Fig. 8. The raw spectra for the selected ketones are shown in Fig. 2. Fig. 10 compares the peak areas of ketones after the first correction (drift tube) and the second correction (shutter grid). The slope goes from −0.065 to −0.018 after the first correction and nears zero after the final correction.

4. Conclusion

Ions are lost during their passage through the shutter grid. It was shown that the extent of the loss depends on the nature of the ion (its velocity) as well as the opening time and the effective width of the shutter grid. A model was developed to explain this behavior. According to Eq. (4), ion mobility spectra can be compensated for by multiplying the intensities by a factor of $(1 + \alpha \cdot t_d)$. This further correction, albeit slight, is essential for deriving accurate information from peak areas about the number density of ions in the ionization region which is the basis of calculations in thermodynamic and kinetic measurements using IMS. This work also shows that as t_d is too big for very large ions, the loss is considerable for heavy ions. Thus, the opening time, t_{on}, should be increased for large ions to see a detectable signal.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ijms.2010.01.011.

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