Improvement of the Resolving Power of Ion Mobility Spectrometers: A Simulation Study

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Abstract. Ion mobility spectrometers (IMS) are well known devices for the detection of explosives, drugs, chemical warfare agents and many other hazardous trace gases in environmental monitoring. Their benefits are small size, robustness, fast response time and high sensitivity in the ppbv range. One disadvantage is the reduced selectivity, especially the resolving power is in commercial devices with a maximum of 40 rather low. In this paper we investigate how with the help of the necessary operating voltages the resolving power can be increased. The study has been performed using the finite element solver COMSOL.

Keywords: ion mobility spectrometry, resolving power, finite element solver, diffusion

1. Introduction

Ion mobility spectrometers work by the time of flight principle. Ions are accelerated by an electric field and drift through ambient air. Depending on their mobility, which in turn depends on numerous quantities (e.g. mass and collision cross section), analyte ions drift with different velocities and reach the detector after a certain characteristic time. The flight time t can then be used to calculate the mobility if the length of the drift region is known [1]:

$$v = k \cdot t \tag{1}$$

$$t = \frac{l}{v} = \frac{l^2}{k \cdot U} \tag{2}$$

E is the electric field strength in the drift region, k is the mobility constant, l the length of the drift region and U the voltage supplied to the drift region. The resolving power is defined as the flight time divided by the full width at half maximum (FWHM) of the signal:

$$R = \frac{t}{w} \tag{3}$$

An IMS consists or three sections, i.e. a reaction region where the ionization of the analyte takes place, the drift region and at the end a collector region where the ions a further accelerated towards the detector [1,2]. From the reaction region the ions are accelerated into the drift region by an injection field, which is formed by supplying a certain injection voltage. Due to the width of the reaction region, and the velocity of the ions reached due to the supplied injection voltage, the ion packet has initially a certain temporal width which is determined by the spatial width (normally the length of the reaction region since it is assumed that the whole reaction region is initially filled with ions) and the velocity reached due to the injection voltage and the corresponding mobility. From theoretic calculations a certain maximum resolving power can be calculated [2,3]:

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$$R = \frac{\dfrac{l^2}{k \cdot U}}{\sqrt{w_{inj}^{\ 2} + \dfrac{16 k_B T \ln 2}{eU}\left(\dfrac{l^2}{kU}\right)^2}} \qquad (4)$$

Factors determining the resolving power are thus the initial ion packet width w_{inj}, the temperature T, length of drift tube l and drift voltage U. Since varying T is more difficult, and the length l is normally a given device parameter, the drift voltage U is one convenient way to increase the resolving power, and similarly the injection voltage.

In general, the resolving power of IMS devices is low. Especially in environmental monitoring with its huge number of substances to be detected for a manifold of different reasons, improving this low resolving power is very important. Since equation 4 is based on theoretic principles neglecting certain peculiarities [4,5], we have simulated with help of a finite element solver (COMSOL, www.comsol.com) and the corresponding differential equations (Fick's Law for the diffusion, Maxwell-Equations for the motion in the electric field) the resolving power and its dependence on the injection and the drift voltage. The focus is on the contribution of the different effects (injection width, diffusion width) to the final signal width and thus to the resolving power with the final goal to find out (simple) ways of improving this quantity.

2. Experimental

The IMS has typically three distinct sections: The reaction region is 0.35 cm wide, the drift region 5.0 cm and the collector region 0.2 cm wide. These are the dimensions of the IMS used in our laboratories [6,7]. The injection voltage is assumed to be supplied to the reaction region long enough so that all ions can leave the reaction region. An initial ion packet that just left the reaction region thus has the rectangular shape that it had in the similarly shaped reaction region since after such a short time the diffusion did not yet have a strong effect. At the end of the drift region, the shape has changed due to diffusion. This effect becomes stronger the longer the ion packet travels. Since Fick's Law states that the diffusion depends on the gradient of the analyte concentration, the initial spatial packet width is thus important, especially if the electric fields in reaction region and drift region are very different from each other, e.g. in order to minimize the initial temporal packet width. The final width is, based on the assumption of Gaussian shaped signals which is at least at the end of the drift tube the case, following this equation:

$$t = \sqrt{t_{inj}^2 + t_{diff}^2} \qquad (5)$$

We have simulated for different injection voltages and drift voltages this final package width in order to find out trends that allow increasing the resolving power.

3. Results and Discussion

A typical set up has a injection voltage of 200 V and a drift voltage of 1800 V over a collector voltage of 200 V. This leads to an injection field of ca. 700 V/cm, a drift field of ca. 400 V/cm and a collector field of 1000 V/cm. The resolving power assuming that all the ions from the reaction region reach the detector is then 25.

Figure 1 shows the development of the signal width over the drift length, as obtained from our simulations. For low injection / drift voltage, the diffusion broadening is small and thus the peak shape does not change, i.e. the signal width stays constant while traveling down the drift region. An increase of the injection voltage to 2700 V and thus of the injection field from ca. 600 V/cm to 2000 V/cm has two effects: Since the injection field is higher, the drift velocity of the analyte ions from the reaction region into the drift region increases. Thus the temporal width t_{inj} decreases. When entering the drift region, the ions experience a different field (here from 2000 V/cm in the reaction region they enter the drift region with ca. 350 V/cm), reach thus a different (here lower) velocity and thus a reduced spatial width, since the temporal width stays the same. A reduced spatial width on the other hand leads to a higher spatial analyte concentration (no losses assumed), which leads due to Fick's Laws to a stronger diffusion broadening. Since the initial temporal width t_{inj} is lower, the influence of the diffusion broadening is stronger. Figure 1 shows this in the curves which

show an increasing total width with increasing flight distance in the drift region. The higher the injection voltage (with constant drift voltage), the stronger the increase of the total temporal signal width at the end of the drift region since the initial spatial width has been increased. If the drift voltage is also increased (in figure 1 from 2000V to 3000V), the total flight time is reduced since the ions fly faster, and so is the broadening of the signal.
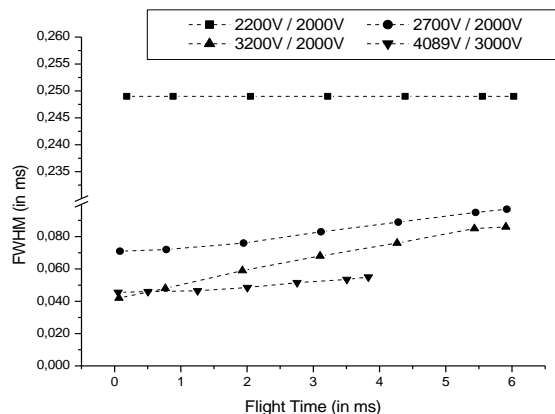

Figure 1: Development of total signal width over flight time, i.e. drift length (the flight time of ca. 6 ms means the end of the drift region); the voltages given indicate the injection/drift voltages

Thus there exist two possibilities to reduce the temporal ion packet width, based on equation 5: The injection width t_{inj} can be reduced by using a higher injection voltage. The diffusion width can be reduced by using a higher drift voltage since a shorter flight time leads to less diffusion broadening. A strong difference in injection- and drift field strength on the other hand leads to stronger diffusion broadening if the drift field is weaker than the injection field due to an increase of analyte concentration when the spatial ion packet width is decreased due to the field difference (that leads to different velocities in each region).

Figure 2 shows how for a constant drift voltage of 2000 V (which leads to a drift field strength of 360 V/cm since 200 volts of these 2000 volts are for the collector region) the total signal width decreases with increasing injection voltage, but the diffusion broadening becomes stronger due to the increased analyte concentration gradient (which is increased since the spatial ion packet width decreases when the temporal width decreases due to the increased injection voltage). From a certain injection field strength and thus from a certain low temporal width on the diffusion width is the dominant part of the total width, so that a increase of the resolving power cannot be achieved anymore by just increasing the injection voltage. For the dimensions of the reaction region used here this means 5000 V/cm (or a voltage drop of ca. 15000 V).

Since the diffusion broadening depends on the flight time, i.e. the longer the flight, the stronger the peak broadening, reducing the flight time by increasing the drift voltage reduces the diffusion width. On the other hand, the total flight time is thus also reduced. Figure 3 shows the corresponding changes. By increasing the drift field, the diffusion width can be lowered to ca. 0.004 ms from 0.08 ms. At these values, the diffusion width becomes comparable to the injection width at 5000 V/cm, as can be seen in the graph since the diffusion width separates a little from the total width (before they are nearly identical since the injection width is so small compared to the diffusion width at the corresponding drift field strengths). Since the total flight time decreases, the resolving power decreases (see equation 3). Since both decrease nearly in the same fashion, as can be seen in figure 3, the gain for the resolving power by reducing the diffusion width is nearly lost due to the reduction in flight time, i.e. at high drift fields the diffusion width and the flight time depend on each other in a linear fashion. Thus a limit has also been reached regarding improving the resolving power. Table 1 gives an overview over the achieved results.
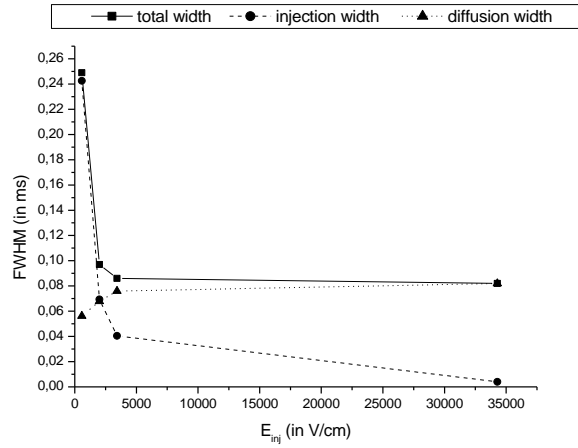
Figure 2. Development of total signal width, injection width (determined by injection field) and diffusion width at the end of the drift tube in dependence on the injection field, shown for a drift voltage of 1800 V.
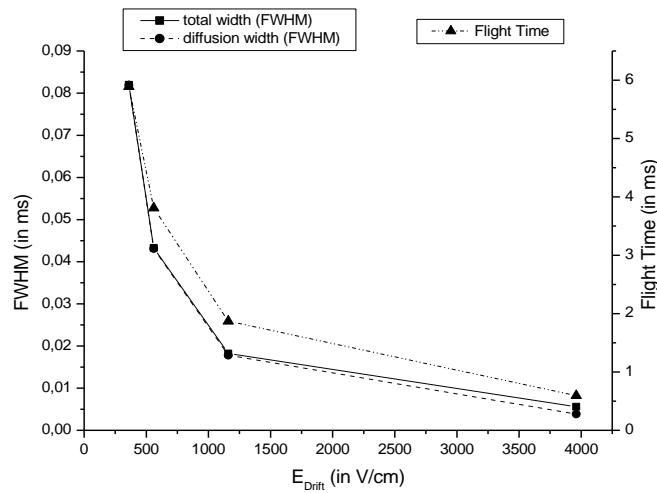

Figure 3. Development of total signal width and diffusion width depending on the drift field strength. Diffusion width and flight time and reduced in a similar fashion, thus the resolving power is only slightly changed at higher drift fields.

Table 1:   Achieved resolving powers

E_{Inj} [V/cm]	E_{Drift} [V/cm]	w_{inj} [ms]	w_{diff} [ms]	Flight Time [ms]	Resolving Power
571	360	0.242	0.056	6.30	24.2
2000	360	0.069	0.068	5.92	61.1
3428	360	0.040	0.076	5.91	68.7
3111	560	0.046	0.032	3.83	69.7
34285	360	0.004	0.082	5.89	71.8
34285	560	0.004	0.043	3.81	88.0
34285	1160	0.004	0.018	1.87	102.5
34285	3960	0.004	0.004	0.59	106.1

As can be seen, the improvement is rather small when the resolving power reaches 90. The decrease of diffusion width and flight time lead only to small changes, so that by just adjusting the voltages, a limit of nearly 110 is reached. The injection field is here already so strong that in normal air the break-down limit has

been reached (ca. 30000 V/cm). A further improvement could only be reached by further reducing the injection width with help of voltage pulses, so that not all the ions leave the reaction region. The temporal packet width would then be determined by the temporal voltage pulse width. Since the concentration is then lower, the diffusion width would be lower. A drawback would be the reduced signal intensity since not all ions reach the detector anymore. An improved resolving power leads on the other hand to stronger peaks (since the ions concentrate on a smaller time window), so that this drawback could be theoretically compensated. But even with this set up described here, i.e. an injection voltage of ca. 10000V and a drift voltage of ca. 20000V for a device with the described dimensions, the resolving power could already be increased from ca. 30 as it is typically achieved in commercial devices to 110. This is achieved without any disadvantage in terms of ion loss (losses created by the device are ignored).

4. Conclusion

In this contribution the resolving power of a standard IMS device was calculated by simulation. The injection voltage and the drift voltage have been changed, two parameters which are easily accessible and thus allow for a simple way to change the resolving power. With the injection field strength near the break down limit in air, i.e. 30 kV/cm, the injection width reaches ca. 5 µs. In order for the diffusion width to reach similar values, the drift field needs to be around 4 kV/cm. With these settings, a resolving power of 106 can be achieved. A further increase of the drift field only marginally leads to an increase of the resolving power, sine the decrease of diffusion happens in parallel with a similar reduction of flight time, so that the resulting resolving power changes only little. 106 can thus be seen as a limit achievable with just changing the mentioned voltages. A further increase would require a gated voltage pulse so that not all the ions leave the reaction region. Thus the injection width would be similar to the voltage pulse's duration, and the diffusion broadening could be reduced due to a reduced analyte concentration in the ion packet. The disadvantage would be that since not all the ions leave the reaction region, the signal intensity would be less. Further investigations should find out how strong this reduction would be, and if it could not be compensated by the stronger signal intensity caused by the smaller peak width. But already know the results presented here show that an impressive increase of over 250% in resolving power is possible with simple voltage adjustments, leading to a correspondingly improved application potential in environmental monitoring.

5. References

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