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Design and evaluation of a novel hemispherical FAIMS cell

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ABSTRACT

High-field asymmetric-waveform ion mobility spectrometry (FAIMS) is a rapidly growing gas-phase separation technique with a wide variety of applications. The geometry of the FAIMS cell influences ion transmission and resolution. Commercial FAIMS systems employ planar or cylindrical cell geometries. A spherical or hemispherical FAIMS cell would allow ions to travel equal path lengths through the FAIMS device while minimizing diffusional losses, improving ion resolution without sacrificing ion transmission. Here we detail the development of a novel hemispherical FAIMS cell and demonstrate the separation of a mixture of trinitrotoluene (TNT) and 3,4-dinitrotoluene (3,4-DNT). The resolution between TNT and 3,4-DNT using the hemispherical FAIMS cell is improved over that achieved with a commercial cylindrical cell while maintaining equivalent ion transmission. The novel hemispherical FAIMS cell provides improved resolution and resolving powers when compared to a commercially available cell.

1. Introduction

High-field asymmetric-waveform ion mobility spectrometry (FAIMS) is an important gas-phase atmospheric-pressure ion separation technique that has been utilized in a variety of fields including bioanalytical, forensic, geological, and homeland defense applications [1–8]. Frequently used in conjunction with mass spectrometry (MS), FAIMS-MS can provide rapid, selective detection of analytes in complex mixtures. The principles of FAIMS have been described elsewhere [2]. Briefly, ions produced by an atmospheric-pressure ionization source enter the FAIMS cell where they travel in a carrier gas between two electrodes towards the detector. One FAIMS electrode is held at a small bias or ground; an asymmetric waveform is applied to the other FAIMS electrode. The asymmetric waveform (typically at a frequency of 750 kHz) consists of a high field (>10,000 V/cm) applied for a short time, then a lower field (~500 V/cm) of opposite polarity applied for a long time. The time–voltage integral for both fields is equal; such that, if an ion's mobility were equal at high and low fields, the ion would encounter no net displacement between the electrodes over time, and would be transmitted through the cell. However, an ion's mobility is altered at high fields, causing a net displacement of the ion towards one of the electrodes. To counteract this drift and allow the ion to pass through the FAIMS cell without hitting an electrode, a direct current (DC) voltage called the compensation voltage (CV) is applied to one electrode in addition to the asymmetric waveform. The CV required for an ion to traverse the FAIMS device is compound-dependent, providing chemical selectivity and improvement in the signal-to-noise ratio.

The geometry of the FAIMS cell affects ion transmission and resolution. The first FAIMS cells employed planar electrodes developed by Buryakov et al. in 1993 [9]. Since then two other FAIMS cell geometries, the dome cell and cylindrical geometry, have been implemented [10,11]. The spherical cell design was proposed by Guevremont et al. [12] in 2004 but was never reduced to practice. Each cell geometry has its advantages and disadvantages in the optimization of resolution and ion transmission. In general, planar geometries can have higher resolution, whereas cylindrical geometries can offer higher ion transmission. Improved transmission in the cylindrical geometry is due to two-dimensional atmospheric-pressure ion focusing caused by the non-uniform electric field created by the curved surface of the electrodes that facilitates focusing ions into the center of the analytical gap [10,11]. Decreased collisions with the electrodes due to the enhanced focusing result in improved sensitivity.

However, the use of curved surfaces to increase sensitivity compromises resolution [11]. Guevremont and Purves [11] theorized that curved surfaces focus ions with a wide range of mobility behavior, which increases peak width and decreases resolution. As the radius of curvature increases, focusing improves and ion intensity increases at the expense of resolution. As the electrode curvature decreases, the focusing effect lessens and resolution improves at the expense of sensitivity. Planar geometry electrodes have no curvature, thus they exhibit the maximum attainable resolution but suffer from decreased ion transmission [11]. Clearly, there is a com-

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promise between resolution and transmission for both curved and planar cell geometries.

A spherical FAIMS cell, as proposed by Guevremont, could offer the optimum balance between resolution and transmission. A spherical FAIMS cell would provide decreased losses from ion diffusion, as all path lengths through the analytical gap would be identical, and therefore all ions would experience the same field, improving ion transmission. The increased ion transmission would allow larger electrode radii to be utilized, allowing for improved resolution. Unfortunately, we have found the construction of a robust spherical cell with precise positioning of the inner spherical electrode within the spherical cavity to be quite challenging [13]. We have therefore designed a hemispherical FAIMS cell which offers most of the advantages of a spherical cell in a more practical design. Here we report the construction and evaluation of that design.

2. Experimental

2.1. Samples

A 10 ppm mixture of trinitrotoluene (TNT) and 3,4-dinitrotoluene (3,4-DNT) in 65/35 methanol/water was made. HPLC grade methanol and water (Fisher Scientific, Fair Lawn, NJ) were used. TNT and 3,4-DNT were obtained from the analytical laboratories of the Israeli Police Headquarters.

2.2. Instrumentation

An Ionalytics GPI 1000 alpha prototype waveform generator (Ionalytics, Ottawa, Canada) was used to generate the 750 kHz asymmetric waveform. The hemispherical FAIMS cell was fabricated by the Department of Chemistry Machine Shop at the University of Florida (Gainesville, FL). The radii of the hemispherical inner and outer electrodes were 12.7 mm and 14.7 mm, respectively. The curtain plate was set to −800 V with an entrance hole of 1 mm. Behind the curtain plate, the entrance hole to the FAIMS cell was 1.5 mm and the exit hole was 1 mm. The CV was scanned from 2 to 12 V at 4 V/min. The outer electrodes on the commercial and hemispherical devices were held at ground. Data were compared to a commercial Thermo-FAIMS cell (Thermo-Fisher Scientific, San Jose, CA) with cylindrical geometry with inner and outer electrode radii of 6.5 mm and 9.0 mm, respectively. The CV was scanned from 0 to 20 V at 10 V/min on the commercial cell. The carrier gas in all experiments was nitrogen (Airgas, Gainesville, FL) dried using a carbon/moisture trap (activated carbon/molecular sieve, Trigon Technologies). The carrier gas entered behind the curtain plate at a flow rate of 3.5 L/min.

A Thermo-Finnigan LCQ ion trap mass spectrometer was used in all experiments. The commercial Thermo-FAIMS cell is not designed to interface with the LCQ, so a homemade interface was devised employing a 83.9 mm long brass ion transfer tube with an inner diameter of 1.3 mm connected onto the heated capillary of the LCQ. All ions were formed by atmospheric-pressure chemical ionization (APCI) in negative ion mode.

3. Results and discussion

3.1. Design of the hemispherical FAIMS cell

The hemispherical FAIMS cell is shown in Fig. 1a. For comparison, a planar cell geometry is shown in Fig. 1b. The hemispherical design allows for accurate, robust inner electrode placement without field disruptions. The stainless steel inner electrode was machined from a 25.4 mm diameter stainless steel ball bearing into a near-hemisphere and secured to a Kel-F base plate, ensuring accurate centering and a uniform 2 mm analytical gap. The stainless steel outer electrode (29.4 mm in diameter) was mounted around the inner electrode in a Kel-F housing. The inner and outer electrodes were extended 2 mm more than a true hemisphere so that ions would enter the analytical gap away from the insulating baseplate. The asymmetric waveform and compensation voltage were applied through the screw that secured the inner electrode to the base plate.

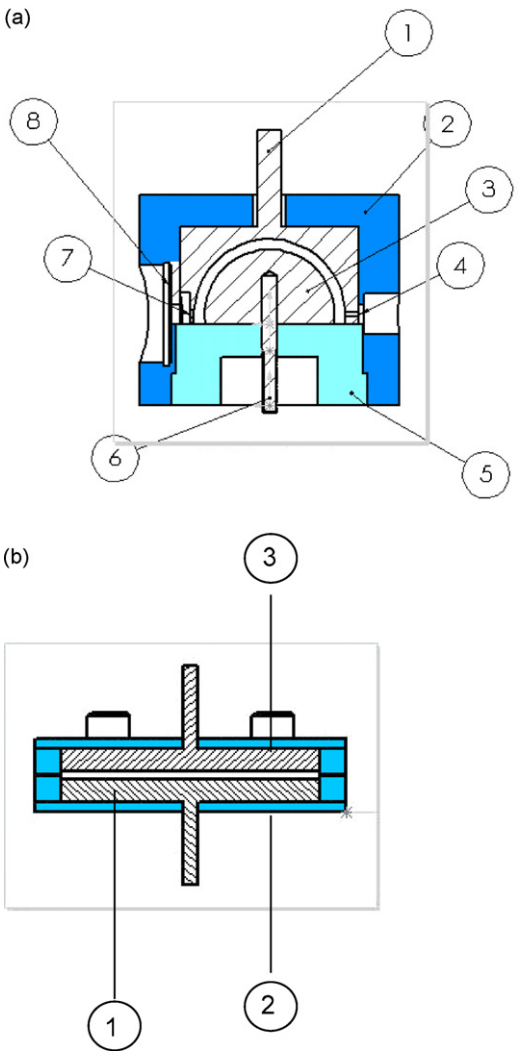

Fig. 1. (a) Schematic of hemispherical FAIMS electrodes. (b) Schematic of planar FAIMS electrodes. 1, Outer electrode; 2, outer housing; 3, inner electrode; 4, exit port; 5, base; 6, inner electrode connection; 7, entrance port; 8, curtain plate.

3.2. Separation of explosives using hemispherical FAIMS electrodes

The performance of hemispherical FAIMS electrodes was evaluated on a mixture of explosives. The highest attainable field using the hemispherical electrodes and the Ionalytics waveform generator was −83 Td (1 Td = 10^{-17} V/cm^2; The townsend (Td) unit can be used to compare electric field strength at different electrode gap sizes and at different pressures and volumes). The resolution between 3,4-DNT and TNT at −83 Td was 3.3, as shown in Fig. 2. The resolving powers for the two peaks were 14.8 and 14.6, respectively. The equations for resolution (R_s) and resolving power (R_p) are shown in Eqs. (1) and (2), where *CV* is the compensation voltage, W_b is the width at 10% of the base, and $W_{1/2max}$ is the width at half

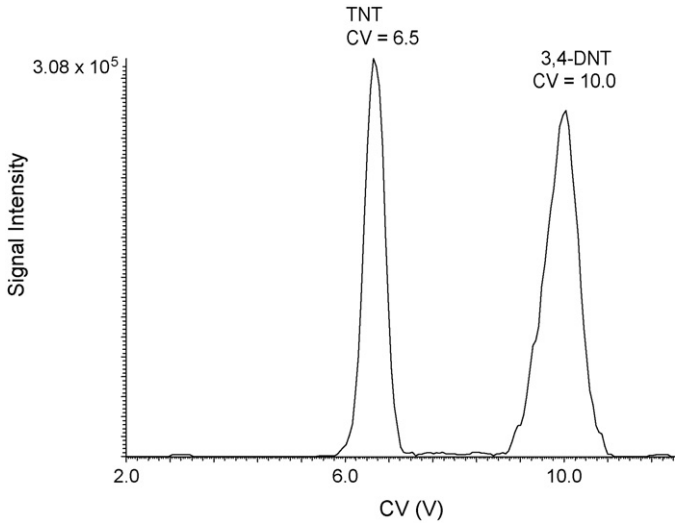

Fig. 2. CV scans from 2.0 to 12.0 V at 4 V/min showing the separation of a mixture of TNT (m/z 227) and 3,4-DNT (m/z 182) using hemispherical FAIMS cell at −83 Td. Resolution of 3.3 was achieved between the two ions.

max. Fig. 3 shows the mass spectra obtained with the hemispherical FAIMS cell (from the CV scan in Fig. 2).

$$R_s = \frac{2\,\Delta CV}{W_{b1} + W_{b2}} \quad (1)$$

$$R_p = \frac{CV}{W_{1/2\,max}} \quad (2)$$

The data obtained using the hemispherical FAIMS cell were then compared to the commercial cylindrical FAIMS cell as shown in Table 1. The highest maintainable field on our Thermo-FAIMS cylindrical cell and waveform generator was determined to be −73 Td. Resolution achieved at this field on the cylindrical FAIMS cell was 1.0 and resolving powers for TNT and 3,4-DNT were 4.2 and 4.9, respectively. However, when using the hemispherical FAIMS cell at this same −73 Td, the resolution obtained for the mixture was 1.9, nearly double that of the cylindrical cell. The resolving powers for TNT and DNT were also two times higher, 10.6 and 10.7, respectively, when using hemispherical cell at −73 Td. One might expect the difference in resolution between the two geometries

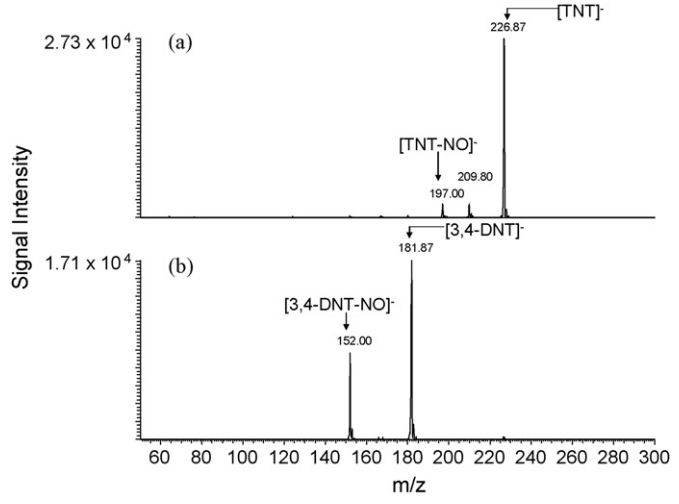

Fig. 3. Mass spectra obtained with the hemispherical FAIMS cell. (a) Mass spectrum of TNT (CV scanned from 6.2 to 6.8 V). (b) Mass spectrum of 3,4-DNT (CV scanned from 9.5 to 10.4 V).

Table 1
Comparison of resolution and resolving power of cylindrical cell to hemispherical cell at −73 Td.

	Hemispherical cell[a]	Thermo-cylindrical cell[b]
Resolution between DNT and TNT	1.9	1.0
Resolving power		
TNT	10.6	4.2
3,4-DNT	10.7	4.9

[a] For hemispherical cell at −73 Td, DV = −3600 V, and gap = 2 mm.
[b] For cylindrical cell at −73 Td, DV = −4500 V, and gap = 2.5 mm.

is due to a difference in the field gradient; however, the field gradients between the inner and outer electrodes for the hemispherical and cylindrical cell were very similar at 73 Td, 5283 V/cm and 5909 V/cm, respectively. The local field gradient for a cylindrical geometry cell can be calculated from Eq. (3) [14]. The local field gradient for the hemispherical cell can be calculated from Eq. (4). In both equations, V_a is the applied voltage, r is any point between the electrodes, a is the radius of the inner electrode and b is the radius of the outer electrode. Therefore, the improvement in resolution does not simply result from a difference in field gradient between the two geometries. The improvement in resolution in the hemispherical design is due to the increased path length through the cell. As the radius of the electrodes gets larger, the path length of the ions must travel to traverse the cell increases and the difference in ion mobility between ions is magnified as they are influenced by an increased number of waveform cycles.

$$E_{cylindrical} = \frac{-V_a}{r \ln(a/b)} \quad (3)$$

$$E_{hemispherical} = \frac{-V_a}{((1/b) - (1/a))r^2} \quad (4)$$

Despite the improvement in resolution and resolving power when using hemispherical FAIMS electrodes, signal intensity was not sacrificed. Comparable signal intensities were achieved on both cells at a field of −73 Td. On the cylindrical cell, the signal intensities for TNT and 3,4-DNT were 6.5×10^4 and 3.0×10^4 counts, respectively. However, ion loss studies indicate the homemade ion transfer tube used to connect the Thermo-cylindrical FAIMS cell to the Thermo-LCQ reduces analyte signal by 70%, so the actual values are approximately three times higher (1.9×10^5 and 9.0×10^4, respectively). For comparison, the signal intensities for TNT and 3,4-DNT using the hemispherical FAIMS electrodes were determined to be 2.9×10^5 and 1.8×10^5, respectively. Thus, the ion transmission of the hemispherical FAIMS cell is approximately two times higher than that for the cylindrical FAIMS cell. The two times higher transmission of the hemispherical cell presumably results from all path lengths around the inner electrodes being equivalent and decreased lateral diffusion in the hemispherical cell.

4. Conclusion

A novel hemispherical FAIMS cell has been developed that demonstrates improved resolution and ion transmission. This novel design minimizes ion losses due to ion diffusion, while allowing a larger radius on the inner electrode for improved resolution. The resolving powers and resolution were doubled for the hemispherical electrodes compared to the Thermo-cylindrical electrodes at the same field. Hemispherical electrodes showed improved balance between resolution and ion transmission over a commercially available cylindrical FAIMS cell. Future work will further evaluate the capabilities and limitations of the hemispherical cell design.

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