

Ability of conductance limiting electrode **40** of ion funnel **10** to perform selective low-mass filtering was tested on a single quadrupole mass spectrometer (e.g., model 1100 quadrupole MS, Agilent, Palo Alto, Calif., USA) modified with an ESI/ion funnel source. The ESI/ion funnel configuration described in reference to FIG. **2b** was employed. Ion funnel **10** was operated by applying an RF voltage of 500 kHz at 90 V peak-to-peak ( $90 V_{p-p}$ ), but was not limited thereto. DC voltage applied to funnel plates **35** of ion funnel **10** yielded a constant gradient of 200 V at inlet **55** down to 5 V at exit aperture **65** of ion funnel **10**. Pressure in funnel **10** was 1.9 Torr. ESI emitters were made by pulling sections of 100- $\mu$ m i.d./200- $\mu$ m o.d. fused silica capillary (Polymicro Technologies, Phoenix, Ariz., USA) either by hand with a butane torch or with a Model 2000 capillary puller (Sutter Instrument Company, Novato, Calif., USA). For infusion experiments, the ESI emitter was connected to a transfer capillary and a 25 mL syringe (Hamilton, Las Vegas, Nev., USA) by a stainless steel union, which also served as the connection point for the ESI voltage. Solutions were infused at a 0.3  $\mu$ L/min flow rate from a Harvard Apparatus Model 22 syringe pump (Holliston, Mass., USA). Voltages from 1.4 kV to 1.5 kV were applied to the ESI emitter via a Burtan high voltage power supply (e.g., Model 205B-03R, Hicksville, N.Y.). Terminal RF/DC plate **40** of funnel **10** was set to 5 V DC and the energy barrier was generated by biasing filter plate **40** to voltages above this value. An Agilent MS calibration solution (product code number G2421A, Palo Alto, Calif., USA) containing 7 fluorinated compounds producing singly charged ions in the ESI source was infused and electrosprayed into mass spectrometer **30**. Mass spectra were acquired as the voltage to filter plate **40** was incremented. Mass spectra were acquired in positive ESI mode with a  $m/z$  step size of 0.1.

FIGS. **3a-3c** present mass spectra from three representative MS analyses of the MS calibration solution at three different voltage settings applied to low- $m/z$  filter **40** of ion funnel **10**, i.e., 8 volts, 13.6 volts, and 17.6 volts, respectively. FIG. **3a** shows that when voltage to filter plate **40** was set to 8 V, the barrier potential was too low to effectively block any ions from entering the quadrupole of the mass spectrometer. FIG. **3b** presents the mass spectrum acquired using a filter plate **40** voltage of 13.6 V, showing the increase of 6 volts was sufficient to block most of the  $m/z$  118.1 peak. FIG. **3c** presents the mass spectrum acquired using a filter plate **40** voltage of 17.6 V. At 17.6 V, the voltage increased the effective range of low-mass filtering achieved by filter plate **40**. A majority of the  $m/z$  322.1 calibration peak was blocked without affecting the  $m/z$  622.1 peak. Results show filter plate **40** provides a simple low-mass filter, generated by adding a barrier potential to exit aperture **65** of ion funnel **10**.

#### Example 2

Example 2 describes tests relating  $m/z$  cut-off of filter plate **40** to the potential applied to filter plate **40** necessary to achieve filtering of low  $m/z$  ions.

A solvent mixture was prepared by combining methanol (Fisher Scientific, Pittsburgh, Pa., USA) and water (Nanopure Infinity Purification system, Barnstead, Dubuque, Iowa, USA) in a 50:50 ratio by volume and adding 1% by volume acetic acid (Sigma-Aldrich, St. Louis, Mo., USA). Filtering capacity of filter plate **40** was characterized by infusing and electrospraying (i.e., using an ESI/ion funnel source **25**) the solvent mixture and acquiring mass spectra with the instrument described in Example 1. By observing the  $m/z$  cut-off at which chemical noise in the acquired mass spectra was eliminated, cut-off threshold could be ascertained as a function of

voltage applied to filter plate **40**. Filter plate **40** voltages were adjusted in one-volt increments in the range from about 12 V to about 18 V.

FIG. **4a** presents a mass spectrum acquired from mass analysis of the solvent solution taken without use of filter plate **40** and associated low-mass filtering. Spectral peaks correspond to solvent clusters and impurities. FIG. **4b** is a mass spectrum of the same solvent solution taken in conjunction with filter plate **40** at an applied voltage sufficient to provide for low-mass filtering. As shown by intensity scales in FIG. **4b**, when voltage was applied to filter plate **40**, noise in the low-mass region was virtually eliminated. Cut-off value ( $m/z$ ) corresponding to a particular filter voltage was determined by observing where a large drop-off of any displayed chemical noise occurred. Drop off in noise observed in FIG. **4a** (without filtering) occurred in FIG. **4b** at an  $m/z$  value of about 200.

FIG. **4c** shows a plot relating  $m/z$  cut-off values to applied filter voltages over the range from about 12 V to about 18 V. Results show the data to be substantially linear. In short, the effect of energy barrier potential to the upper limit of mass filter **40** is substantially linear.

Results provide an easy and useful method for calculating the voltage required to provide any desired  $m/z$  filtering in conjunction with filter plate **40**. The ability to dynamically adjust potentials applied to filter **40** thereby achieving a desired mass filter range allows for quick adjustments to the analysis instrument based upon the sample properties, making the method available for dynamic low- $m/z$  filtering in an automated process. Results further show that a simple low-mass filter can be created by adding a potential energy barrier at the exit aperture **65** of ion funnel **10**.

#### Example 3

Example 3 describes the distribution of DC voltages and electric fields generated in the region near exit aperture **65** of filter plate **40** at an applied voltage of 15 V to filter plate **40**. The DC electric field  $E$  was estimated using calculations based on the geometry shown in FIG. **1**. As illustrated, e.g., in FIG. **2a**, filter plate **40** can be considered a 3-dimensional plate having left and right surface planes (surfaces **40-L** and **40-R**, respectively, and any suitable thickness (e.g., 0.5 mm), the left surface plane **40-L** facing into the interior of ion funnel **10**.

FIG. **5a** shows the distribution of DC potentials observed for radial distances ( $r$ ) of 0, 0.25, 0.5, 0.75 and 1 mm, respectively from the center of exit aperture **65** of filter plate **40** toward the radial edge of aperture **65** of filtering plate **40** as a function of axial coordinate " $z$ " for rear section **45** of funnel **10**. The origin of axial coordinate " $z$ " is positioned at left-most surface plane **40-L** (left surface) of filter plate **40**. Small variations in DC potential are observed as a function of distance from the center of aperture **65**, with slight increases in potential observed at positive displacements up to about 1 mm from the center of aperture **65**. At an applied potential of 15 V, for example, results show a DC potential of from about 13 V to about 15 V at aperture **65**, with a potential difference or spread of about 2 V.

FIG. **5b** shows the electric field  $E$  (V/cm) strength associated with the applied barrier potential, calculated as the derivative of the potential over the axial displacement  $z$ . Data show a peak field  $E$  with a slight negative axial displacement, indicating the actual placement of the potential barrier exerted near exit aperture **65** of plate **40** where low  $m/z$  ions are filtered. FIG. **5c** shows the maximum axial electric field ( $E_{max}$ ) as a function of applied filter plate voltage ( $V_{fp}$ ). The