

performance evaluation. The concentrations for each component in Agilent tuning mix were 1.17 ng/uL for ion at m/z 118, 9.19 ng/uL for ion at m/z 322, 9.32 ng/uL for ion at m/z 622, 18.42 ng/uL for ion at m/z 922, 22.81 ng/uL for ion at m/z 1522, and 46.66 ng/uL for ion at m/z 2122.16 The solvent used for the Agilent tuning mix was 95:5 acetonitrile/water +2 mM TFA. The electrospray was operated at a flow rate of 2 uL/min. The temperature of the dual heated capillary inlet was fixed at 150° C. A DC bias at 220 V was applied to the dual heated capillary block. The RF frequency and the amplitude applied to the ion funnel were 500 kHz and 70 Vp-p, respectively. The DC biases on the first ion funnel plate and the last ion funnel plate were 200 and 35 V, respectively, which resulted in an axial DC field of 16 V/cm in the ion funnel. A variable DC bias and a square waveform voltage with variable frequency and duty cycle were applied to the jet disturber for both static and dynamic modulations of the ion transmission through the ion funnel. Because of the increased gas throughput of the dual capillary inlet, an additional mechanical pump (Edwards E1M18) was used to pump the ion funnel chamber. The ion funnel pressure was measured at 1.33 Torr, and the analyzer chamber pressure, at 4.5×10^{-6} Torr. The mass spectrometer was operated in the positive ESI mode.

Strong space charge effects in electrosprays limit the speed or utility of ion transmission modulation at atmospheric pressure, and mechanical switching of dual electrospray is relatively slow for ion inlet manipulation. The capability for ion transmission modulation through the dual channel ESI interface was first investigated experimentally by changing the jet disturber DC bias. The Agilent ESI tuning mix was introduced to the main channel electrospray. The reserpine solution was used for the jet disturber channel electrospray inlet. Mass spectra at both the optimum jet disturber voltage for maximum ion transmission and the voltage corresponding to maximum suppression of ion transmission are shown in FIGS. 4a and b. At the optimum jet disturber voltage of 165 V, the reserpine ion intensity m/z 609 accounted for approximately 40% of the base peak (FIG. 4a). The reserpine ions were almost completely suppressed when the jet disrupter voltage was at 110 V (FIG. 4b), demonstrating the effective electric modulation of ion transmission through the jet disturber channel of the ion funnel. Once effective ion transmission modulation was observed, the ion transmission through the jet disturber channel was further characterized. FIG. 4c shows variations of the base peak percentage of reserpine ion and the ratio of maximum reserpine ion intensity to the reserpine ion intensity, I_{max}/I , at different jet disturber voltages. As shown in FIG. 2c, the ion transmission reaches a maximum at a jet disturber voltage of 165 V and decreases rapidly when the voltage either increases or decreases. At approximately 40 V difference from the optimum ion transmission voltage, maximum ion transmission suppression was observed. Specifically, the base peak percentage of the ion intensity decreased from 45% to approximately 2% (I_{max}/I increases from 1 to ~26).

The DC potential applied to each ion funnel plate was derived from a linear resistor chain, resulting in a constant DC gradient across the ion funnel. The DC potential at each funnel plate can be easily calculated using

$$V_p = DC^+ - (L_p/L)(DC^+ - DC^-)$$

where V_p is the DC potential on the funnel plate measured at distance L_p from the first ion funnel plate, L is the total length of the ion funnel (100 mm), and DC^+ and DC^- are the DC potentials at the first and last ion funnel plates, respectively. From the DC potential settings (FIG. 4), the DC potential of the ion funnel plate next to the jet disrupter, 20 mm from the first ion funnel plate, was calculated to be

168.8 V. This indicates that the ion funnel provides optimum ion transmission when the jet disturber voltage was approximately equal to the DC potential at its neighboring ion funnel plate. This conclusion was further confirmed by theoretical simulations (discussed below) in which the potential difference between the jet disturber and the neighboring ion funnel plate was defined as the DC offset of the jet disturber.

Because the jet disturber was mounted in a dual-inlet funnel electrode and the spacing of RF ion funnel plates at the jet disturber location increased significantly from 1 to 3 mm, it was important to determine whether the ion transmission modulation in the jet disrupter channel also affected ion transmission in the main channel of the ion funnel. FIG. 5 shows the mass spectral regions for each ion species at both maximum ion transmission (FIG. 5a) and ion suppression (FIG. 5b) jet disturber voltages. The ion intensities for each corresponding peak, shown in spectra FIG. 5 clearly indicate that the main channel ion transmission is essentially constant, but the intensity of reserpine (m/z) 609.2 ions in the jet disturber channel is changed by a factor of at least 25 between optimum ion transmission jet disturber voltage, FIG. 5a, and maximum ion suppression jet disturber voltage, FIG. 5b.

The shift of the reserpine peak in FIG. 5b is due to the chemical noise from the main channel electrospray. As verified experimentally, no mass shift was observed for the reserpine peak at the maximum ion suppression jet disturber voltage if the main channel electrospray of the Agilent ESI tuning mix was turned off. This implies an even better ion transmission modulation efficiency in the jet disturber channel. FIG. 5 clearly indicates negligible "cross talk" in ion transmission between the dual channels of the ion funnel. As discussed in the summary of the invention, a second jet disturber can be installed in the main channel of the ion funnel if independent modulations of ion transmission in both channels is desired.

To ensure that effective ion transmission modulation can be achieved over a broad m/z range, the dual channel interface was further evaluated by switching the sample solutions. As shown in both FIG. 6 and Table 1, similar ion transmission modulation efficiency was achieved for all peaks in the Agilent ESI tuning mix. The data listed in Table 1 further indicates that ion intensity modulation by a factor of 28 to 35 for all the m/z ions can be obtained when the jet disturber voltage is at optimum ion transmission and maximum ion suppression conditions, respectively.

TABLE 1

Effective Ion Transmission Modulation and Optimum Jet Disturber Voltages for Different m/z Ions					
m/Z	I_{max}/I	optimum V_{jd}	m/z	I_{max}/I	optimum V_{jd} (V)
322	30	165.9	1522	35.2	158.3
622	29.5	165.9	2122	29.7	158.3
922	28.9	165.9	609b	1.1 b	

(Ion funnel voltage settings: DC^+ , 201.5 V; DC^- , 35 V; RF, 70 V_{p-p}, 500 KHz; DC_{cap} , 218.9 V; temp, 150° C.; main channel electrospray, reserpine (1 ng/uL); jet disturber channel electrospray: Agilent ESI tuning mix; infusion rate: 2 uL/min. b Indicating the constant ion transmission for reserpine ions in the main channel of the ion funnel during the ion transmission modulation in the jet disturber ion channel of the ion funnel.)

The ion transmission in the main ion funnel channel for the reserpine ion still remains independent of the ion modu-