

82 pmol/ul of reserpine in a 1:1 methanol:water with 0.015% formic acid solution sprayed from APCI probe **283** at a liquid flow rate of 200 ul/min. Mass spectrum **320** contains peak **321** of the protonated molecular ion of reserpine. Solution flow to ES probe tip **296** was turned off during the acquisition of APCI-MS generated mass spectrum **320**. Mass spectrum **322** shown in **FIG. 15B** was acquired with Electrospray ionization of 10 pmol/ul of cytochrome C in a 1:1 methanol:water, 0.1% acetic acid solution spraying from ES tip **296** with pneumatic nebulization assist at a liquid flow rate of 10 ul/min. Mass spectrum **322** contains primarily the Electrosprayed multiply charged peaks **323** of cytochrome C. Solution flow to APCI inlet probe **283** was turned off during the acquisition of ES-MS spectrum **322**. Mass spectrum **324** shown in **FIG. 15C** was acquired from the same cytochrome C solution Electrosprayed into API source **282** with pneumatic nebulization assist. During the acquisition of mass spectrum **324**, containing peaks **325** of Electrospray generated multiply charged cytochrome C ions, the nebulizing gas was supplied to APCI inlet probe **283** with the vaporizer **287** heater turned on but with no high voltage applied to corona discharge needle **288** and no reserpine solution flowing to APCI inlet probe **283**. Mass spectrum **326** shown in **FIG. 15D** was acquired with the same conditions as mass spectrum **324** with high voltage applied to corona discharge needle **288** and the same reserpine solution as above sprayed from APCI inlet probe **283**. Both peak **327** of the protonated molecular ion of reserpine and peaks **328** of multiply charged protonated cytochrome C ions appear in mass spectrum **326** acquired with simultaneous ES and APCI ion production occurring in API source assembly **282**. Mass spectra **320**, **322**, **324** and **326** were acquired sequentially with no position adjustment of API source **282** hardware. Rapid switching between individual or simultaneous ES and APCI operating modes with combination source **282** shown in **FIG. 14**.

[0081] An API source with multiple ES or APCI probes or combinations of ES and APCI probes can be configured to allow the study of ion-ion interactions at atmospheric pressure. Many of the combination and multiple inlet probe API source configurations shown above can be operated using methods and techniques that will allow the study of gas phase ion-ion interactions at atmospheric pressure. Alternative embodiments of multiple inlet probe API sources configured specifically to allow the simultaneous production of opposite polarity ions will be described below. One embodiment of a multiple ES probe API source configured for studying ion-ion interactions at atmospheric pressure is diagrammed in **FIG. 16**. ES probe assembly **340** is configured with ES probe tip **344** located near axis **341** of API source **342** ($\phi_{340}=0^\circ$) spaced a distance of Z_{344} from API source nosepiece **347**. Solution is Electrosprayed from ES probe tip **344** with pneumatic nebulization assist. The polarity of the Electrosprayed ions produced is determined by the relative potentials set on the electrostatic elements comprising API source **342**. For purposes of discussion assume that the API source potentials and gas flows applied are set to produce positive ions from solutions Electrosprayed from ES probe tip **344**.

[0082] A second ES probe assembly **345** is mounted with ES probe tip **346** positioned at a distance along API source axis **341**, Z_{346} , from API source nosepiece **347** and radially, r_{346} , from API source axis **341**. The angle of the spraying axis of ES probe tip **346** is positioned approximately at 110

degrees ($\phi_{346}=110^\circ$) relative to API source centerline **341**. The voltage applied to ES probe tip **346** is set such that negatively charged liquid droplets are produced from solution Electrosprayed from ES probe tip **346** with pneumatic nebulization assist. The positive and negative ions produced from the positive and negative charged liquid droplets Electrosprayed from ES probe tips **344** and **346** respectively mix and interact in region **348** of API source **342**. This positive and negative ion-ion interaction at atmospheric pressure will cause the neutralization of some but not all of the mixed ion population. A portion of the resulting positive ion population will be driven to capillary entrance **349** by the electric fields present. A portion of the positive ions which enter capillary orifice **349** are swept through capillary bore **350** into vacuum and subsequently mass to charge analyzed with a mass spectrometer and detector. Reversing voltage polarities in API source **342**, will cause negative ions to be produced from solution Electrosprayed from ES probe tip **344** and positive ions to be produced from solution Electrosprayed from ES probe tip **346**. With polarities reversed, negative product ions will be move toward capillary entrance orifice **349**, be swept into vacuum through capillary bore **350** and subsequently mass to charge analyzed.

[0083] Several geometries of ES probes can be configured to achieve multiple sample ion-ion interaction from different solutions Electrosprayed from multiple ES probe assemblies. More than two ES probes can be configured in an API source positioned at angles, $\phi_1 \dots \phi_i$ ranging from 0 to 180 degrees and rotation angles $\theta_1 \dots \theta_i$ ranging from 0 to 360 degrees. Selected neutral gas composition can be added to nebulizer or counter current drying gas to study ion-neutral reactions in relation to ion-ion interactions. Unlike the opposite polarity ion-ion interactive studies conducted in partial vacuum reported by Smith et. al., the embodiment of the invention described allows the production of ES ions in one API source chamber with ion-ion interaction conducted in higher ion and gas densities at atmospheric pressure.

[0084] An embodiment of an API source configured with a dual APCI vaporizer, corona discharge needle and probe assembly is diagrammed in **FIG. 17**. One APCI probe assembly **366** is positioned off-axis, $\phi_{366}=90^\circ$, at a distance Z_{366} from API source nosepiece **375**. APCI probe assembly **366** comprises pneumatic nebulizer sample inlet probe assembly **367**, optional droplet separator ball **368**, vaporizer **369**, and corona discharge needle **370**. Sample solution supplied from liquid delivery system **372** is sprayed from inlet probe assembly **367**. Sprayed droplets pass around separator ball **368** and into vaporizer **369** where the droplets evaporate to form a vapor. The vapor exiting vaporizer **369** is ionized in the corona discharge region at the tip of corona discharge needle **370**. A second APCI probe assembly **360** is also positioned off-axis, $\phi_{360}=90^\circ$,

[0085] spaced a distance Z_{360} from API source nosepiece **375**. In the configuration shown dimension Z_{360} is shorter than Z_{366} . APCI probe assembly **360** comprises pneumatic nebulizer sample inlet probe assembly **362**, optional droplet separator ball **363**, vaporizer **364**, and corona discharge needle **365**. Inlet probe **362** sprays sample solution delivered from liquid delivery system **373** into APCI probe assembly **360**. For purposes of discussion, assume that the applied API source element electrical potentials and gas flows are set to produce positive ions from solutions sprayed, vaporized and ionized through APCI probe **366** and negative ions from