

produced, can be oriented maximize the production of ions near nose piece 25 opening 28 to optimize performance. Charged liquid droplets produced in the Electrospray or pneumatic nebulization assisted Electrospray process evaporate to form ions in Electrospray chamber 30 aided by heated countercurrent drying gas 27 flowing through endplate nose-piece opening 28. A portion of the ions formed in ES chamber 30 are directed into capillary bore 23 where they are swept into vacuum by the gas flow through capillary bore 23. Charged droplet evaporation can also occur during the transfer of partially evaporated Electrosprayed charged droplets into vacuum through capillary bore 23. Capillary 21 can be heated to aid in the charged droplet evaporation process. A detailed description of the invention is given below using the cross sections diagrams shown in FIGS. 2 and 3.

[0037] FIG. 2 is a top view diagram of an Electrospray ion source 1 showing dual tip ES probe assembly 5. FIG. 3 is a side view of ES source 1 shown in FIG. 1 configured with dual off axis probe assembly 2 and 5. ES source 1, is operated by applying electrical potentials to cylindrical electrode 20, endplate electrode 26 and capillary entrance electrode 40 while maintaining all ES electrode tips at ground potential. Heated counter current drying gas flow 41 is directed to flow through endplate heater 42 and into ES source chamber 30 through endplate nosepiece 25 opening 28. The orifice into vacuum as shown in FIGS. 1 and 2 is a dielectric capillary tube 24 with entrance orifice 48. The potential of an ion being swept through dielectric capillary tube inner bore 23 into vacuum is described in U.S. Pat. No. 4,542,293. To produce positive ions, negative kilovolt potentials are applied to cylindrical electrode 20, endplate electrode 26 with attached electrode nosepiece 25 and capillary entrance electrode 40. Typically, for generating positive ions, -4,000,-3,500 and -3,000 Volts are applied to capillary entrance 40, endplate 26 and cylindrical electrode 20 respectively during Electrospray operation and ES probe assemblies 2 and 5 with ES tips 3, 4, 6 and 7 remain at ground potential. To produce negative ions, the polarity of the electrical potentials applied to electrodes 20, 26 and 40 are reversed while ES probe tips 3, 4, 6 and 7 remain at ground potential. Alternatively, if a nozzle, thin plate orifice or conductive metal capillaries are used as orifices into vacuum, kilovolt potentials can be applied to ES probe tips 3, 4, 6 and 7 with lower potentials applied to cylindrical electrode 20, endplate electrode 26 and the orifice into vacuum during operation. Alternatively, heated capillaries, nozzles or thin plate orifices can be configured as the orifice into vacuum operating with or without counter current drying gas during ES or APCI ionization.

[0038] Referring to FIG. 2, when the appropriate potentials are applied to elements 6, 7, 20, 26 and 40 in ES source chamber 30, charged liquid droplets are produced from the unassisted Electrospraying or Electrospraying with pneumatic nebulization assist of separate solutions delivered to ES tips 6 and 7. In the embodiment shown in FIG. 2, the position of ES tips 6 and 7 are fixed relative to each other during Electrospray operation. Alternatively, ES probe assembly can be configured to allow adjustment of the relative positions of tips 6 and 7. The charged droplets Electrosprayed from each solution exiting from ES tips 6 and 7 are driven by the electric field against the counter current drying gas flow 27. As the charged droplets evaporate, ions are formed from the components originally in the

solutions delivered through tips 6 and 7, and mix in region 43. A portion of the mixture of ions in region 43 is swept into vacuum through the capillary bore 23 are directed into mass analyzer and detector 45, located in vacuum region 46, where they are mass analyzed. If a heated capillary is configured as an orifice into vacuum with or without counter current drying gas, a mixture of partially evaporated charged droplets sprayed from ES tips 6 and 7 are swept into the heated capillary orifice. Charged droplet evaporation and the production of a mixture of ions can occur in the capillary when Electrosprayed charged droplets are not completely evaporated in atmospheric pressure chamber 30 prior to being swept into the capillary orifice. The resulting ions produced from a mixture of charged droplets produced from two Electrosprayed solutions in the heated capillary will form an ion mixture in the capillary and in vacuum. Ions formed from multiple solutions can also be mixed and stored in ion traps in vacuum. Three dimensional ion traps and multipole ion guides operated in two dimensional trapping mode can hold mixtures of ions which are trapped simultaneously or sequentially from multiple solutions sprayed in one API source. Mass analysis of the ion mixtures is then conducted using mass analyzer and detector assembly 45.

[0039] For example, the multiple ES probe API source embodiment shown in FIG. 1 can be interfaced to a multipole ion guide Time-Of-Flight mass analyzer where the multipole ion guide is operated in two dimensional trapping mode as described in U.S. Pat. No. 5,689,111. Ions formed from spraying a solution from ES probe 7 can initially be trapped by a multipole ion guide operated in two dimensional trapping mode. The solution flow to ES probe 7 can then be turned off and a different solution flow through ES probe 6 turned on forming ions which are also trapped in the same multipole ion guide operating as a two dimensional trap. The ion mixture formed in this manner can be trapped for a period of time to promote ion-ion interactions or ion-molecule interactions and/or reactions with added neutral background gas. The resulting trapped ion mixture can then be released from the multipole ion guide trap and mass analyzed in the Time-Of-Flight mass analyzer. Alternatively, MS/MSⁿ experiments can be conducted on the trapped ion population as is described in U.S. patent application Ser. No. 08/694,542. Two different sample solutions can be sprayed from ES probe tips 6 and 7 independently or simultaneously during ES source operation. As described above, when two solutions are Electrosprayed, with or without pneumatic nebulization assist, simultaneously from ES probe tips 6 and 7, ions resulting from the two separate sprays mix in region 43. A portion of the ion mixture is swept into vacuum through capillary bore 23 and subsequently mass to charge analyzed. Using this embodiment of the invention, the sample solution from ES probe tip 6 has a minimum effect on the ions produced from the sample solution sprayed from ES probe tip 7. Chemical components in the sample solutions delivered from independent solution sources through ES probe tips 6 and 7 do not mix in solution prior to spraying. Charged droplets and ions of the same polarity are produced when Electrospraying from ES probe tips 6 and 7. Charged droplets and ions of like polarity have minimal chemical interaction during evaporation in ES chamber 30 due to charge repulsion so minimal distortion of the individual ion population produced from each solution occurs prior to entry into vacuum. Compounds of known molecular weight, referred to as calibration compounds, can be added