supplying pneumatic nebulization gas flow to the ES probe, a simple and inexpensive solvent delivery system can be employed.

[0049] ES probe assembly **120** axis **137** shown in **FIG. 6** is positioned at an angle of 70 degrees, ϕ_{120}=70°, from ES source centerline **131**. ES probe assembly **120** is configured with three layer ES probe tip **121** having sample solution inlet **132**, layered flow solution inlet **138** and nebulization gas inlet **136**. A diagram cross section of ES probe tip **121** is shown in **FIG. 13**. Liquid sample enters bore **88** of first layer tube **80** through transfer line **132**. A second solution can be added through transfer line **138** into annulus **84** between tubes **80** and **81** and this solution forms a sheath liquid surrounding and mixing with the sample solution at exit end **86** in region **87**. Nebulizer or corona suppression gas can be introduced to ES probe tip **121** through gas delivery or transfer line **136** into annulus **83** between tubes **81** and **82**. Liquid layering of solutions in region **87** at the tip of three layer ES probes has been used to interface LC, CE or CEC separation systems to ES sources. When interfacing to CE, CEC or microbore LC columns, sample introduction tube **80** may actually be the CE, CEC or LC column itself. The second layer solution flow may also be used to add a calibration compounds to the sample solution exiting from tube **86** of ES probe tip **121**. The resulting mass spectrum acquired from such a mixed solution spray would contain an internal standard. The calibration solution could be started or stopped by turning on or off the liquid delivery system supplying solution through transfer line **138**. The introduction of a calibration solution in this manner avoids contaminating the original sample solution source but still necessitates mixing of solutions in region **87** prior to spraying. The calibration components in the resulting mixture may effect the Electrospray ionization efficiency of the sample compounds present thus causing peak height distortion in the acquired mass spectrum. The relative positioning of the exit ends of tubes **80** and **81** can effect the relative intensity of ion populations layered from the two solutions produced in the Electrospraying process. The layered liquid flow can also be used to introduce a different solvent system to study ion-neutral interactions in a multiple probe spray mixture. A range of solution compositions can combined in the liquid phase using the three layer probe tip assembly shown in **FIG. 13** if required in an analytical application. A four layer variation of the three layer probe shown in **FIG. 13** can be operated such that no liquid mixing occurs by separating the liquid solution layers with nebulizer or corona suppression gas. For example, a four layer probe tip embodiment can have liquid solution delivered through the innermost tube one, nebulizer gas supplied through the annulus between tubes one and two, a second liquid solution delivered through the annulus between tubes two and three and a nebulizer gas supplied through the annulus between tubes **3** and **4**. Alternatively, gas can be supplied through the innermost tube one with a liquid, gas and liquid layering. Three or more liquid solutions can be layered where some of the solutions delivered through separate layers are mixed in the liquid state as they emerge from the layered tip similar to the solution mixing shown in **FIG. 13**. Layered liquid flow allows the introduction of additional solutions through one or more Electrospray probes, and can serve as a means of interfacing ES with one or more separation systems such as CE, CEC and LC.

[0050] ES probe tip **123** is configured as a two layer probe, shown in **FIG. 12**, with calibration solution **145** supplied from reservoir **144**. With little or no pressure head or gravity feed applied, calibration solution **145** can be pulled from reservoir **144** using the venturi suction effect of the nebulizing gas applied at ES probe tip **123**. Calibration solution **144** can be sprayed from ES tip **123** when nebulization gas flow is applied through gas delivery tube **128**. Solution delivery tube **139** can be initially filled with solution by applying head pressure to reservoir **144**, by gravity feed from reservoir **144** or by turning on the nebulizing gas ES probe tip **123**. Once solution delivery tube **129** and the inner tube of ES tip **123** are filled with calibration solution, any head pressure in the attached reservoir is relieved and, with no gravity feed applied, the liquid flow through solution delivery tube **129** can be started and stopped by turning the nebulizing gas flow to ES tip **123** on and off. Calibration solution can be selectively sprayed from ES probe tip **123** individually or simultaneously with a sample solution Electrosprayed from ES probe tip **121**. Alternatively, solution can be delivered to ES probe tip **123** using a syringe pump, liquid chromatography system or other liquid delivery system. Solution flow to ES probe tip **123** can then be turned on or off by turning the solvent delivery system flow on or off.

[0051] The x-y-z and angular positions of ES probe tips **121** and **123** relative ES source axis **131** and capillary entrance **148** as shown in **FIG. 6** may be adjusted to optimize ES performance while spraying from single ES probes individually or from two ES probes simultaneously. The rotational position of ES tip **121** around ES probe assembly axis **137** is adjusted with positioning knobs **133** and **134**. The position of ES tip **121** along the axis of ES tip **121** is adjusted by turning knob **135**. Similarly, the rotational and axial position of ES tip **123** is adjusted with positioning knobs **125**, **126** and **127** respectively. ES probe tip positions may require adjustment to optimize ES performance for given liquid flow rates and solution or sample types. Once optimized for individual or simultaneous spraying, the probe positions can remain fixed during ES operation. For the embodiments shown in **FIGS. 1 and 6**, a portion of each ES probe assembly is located outside the ES source chamber housing. This allows full adjustment of x-y-z and angular position while operating the ES source to achieve optimal performance. ES probe assemblies **120** and **122** as diagrammed in **FIG. 6** also allow adjustment of the relative layered tube exit tip positions. For example, adjustment of nut **149** will move the inner tube **80** exit **86** position, as shown in **FIG. 13**, along the axis of ES probe tip **121** relative to the second and third layer tube exit positions. The relative position of innermost tube exit end **73** as shown in **FIG. 12** can be adjusted using nut **150** for optimizing the nebulizing gas performance at ES tip **123**. These ES tip adjustments allow for optimization of layered liquid flow and/or gas nebulization tube tip positions while operating the ES source. Different liquid flow rates can be delivered through ES probe tips **121** and **123** during simultaneous Electrospraying from both ES probe tips. The solution flow rate range used for ES applications extends from below 25 nanoliters per minute to over 2 milliliters per minute. For a 25 to 1,000 nanoliters per minute range of liquid flow rates, a single layer flow through or replaceable micro Electrospray probe tip can be configured to replace two layer ES probe tip **123** in ES source **130**. Unassisted Electrospray operation can be conducted from ES probe tips individually