Depending on the analytical application, solution introduction tube **72** or **80** can be configured as a Capillary Electrophoresis column, a microbore packed capillary column, or an open bore tube of either dielectric or conductive material. Single, two and three layer ES probe tips which are configured in off-axis positions or positioned near the API source centerline are commercially available. An off-axis probe position is typically used for higher liquid flow rate applications in Electrospray ion sources. The present invention embodies the configuration of multiple ES probes with single, double or triple layer tips in an API source with the ability to conduct individual or simultaneous spraying of solution from two or more probe tips with or without nebulization assist. Multiple probe tip positions can be fixed during API operation allowing sequential or simultaneous spraying from multiple tips without the need to adjust probe location and allowing rapid, efficient and unattended switching of solution spraying from variety of inlet probes.

[**0047**] **FIG. 5** shows an alternative embodiment of the invention. Electrospray source **114** is configured with ES probe assembly **90** comprised of six ES tips **91** through **96** with individual liquid supply lines **101** through **106** respectively. Position adjuster **97** can be used to move ES probe assembly **90** such that any ES tip can be located near ES source centerline **115**. Gas line **98** supplies nebulization gas to ES probe tips **91** through **96**. Alternatively, ES probe assembly **90** can be configured such that each ES tip **91** through **96** is configured with an individual nebulization gas supply each of which can be independently turned on and off. In the embodiment diagrammed in **FIG. 5** ES tips **95** and **92** can be supplied with individual calibration solutions while separate sample solutions are supplied to ES tips **91**, **93**, **94** and **96**. With this arrangement, mass spectra acquired from the Electrospraying of any sample solution can have internal standard peaks added by turning on the nearest adjacent ES tip supplied with calibration solution. In the embodiment shown in **FIG. 5**, several sample solutions can be rapidly analyzed with little or no cross contamination which can occur when multiple samples are delivered to the ES source sequentially through the same ES probe tip. After acquiring MS data from a sample solution spraying from ES tip **96** simultaneously with a calibration solution spraying from ES probe tip **95**, ES probe assembly **98** can be translated using adjuster **97** such that ES tip **94** is positioned near ES source centerline **115**. ES tip **95** can be used to spray calibration solution simultaneously with the Electrospraying of a sample solution from ES tip **94** to provide internal standard peaks in the acquired sample solution mass spectrum. Further ES probe assembly translation can be used to position ES tip **92** near ES source centerline **115** to selectively spray calibration solution during sample solution Electrospraying from either tips **91** or **93**. The linear ES tip configuration of ES probe **90** can be extrapolated into a two dimensional array of tips with automatic x and y position translators. Also, flow-through ES tips can be replaced by pre-loaded microtips. Alternatively, all tips of ES probe assembly **90** can be used to spray sample solutions and a single off axis ES probe can used to Electrospray calibration solution when it is desirable acquire a external standard calibration mass spectrum or to add an internal standard to the acquired sample solution mass spectra. Kilovolt potentials can be applied to ES source elements **110**, **111** and **112** to initiate Electrospray with ES probe assembly **90** operated at ground potential. Alternatively, kilovolt electrical potentials can be applied to ES probe tips **91** through **96** during Electrospray operation. ES source **114** can be configured with heated counter current drying gas to aid in the evaporation of the Electrospray produced charged droplets sprayed sequentially or simultaneously from one, two or more ES tips.

[**0048**] The ES probe tip positions can either be fixed with respect to each other and the ES source capillary entrance or the tip positions can be adjustable. As is shown in **FIG. 1**, ES tip positions **3** and **4** are fixed relative to each other but, as a set, movable in the x direction and rotationally around the ES probe **2** mounting block rotational axis. An alternative to the invention is shown in **FIG. 6** where ES probe assemblies **120** and **122** include full x, y and z position adjustments for ES tips **121** and **123** respectively. ES probe assembly **122** is positioned parallel to ES source **130** centerline **131**. The angle of ES probe tip **123** axis **124** relative to ES source centerline **130** is equal to zero degrees, $\phi_1=0°$. Sample bearing solution can be introduced into liquid delivery tube **129** of ES probe assembly **122** or into entrance tube **132** of ES probe assembly **120** with independent liquid delivery systems. In this manner, different samples or mixture of samples and/or solvents can be sprayed simultaneously or individually. Liquid delivery systems may include but are not limited to, liquid pumps with or without auto injectors, separation systems such as liquid chromatography or capillary electrophoresis, syringe pumps, pressure vessels, gravity feed vessels or solution reservoirs. During ES source operation, the spray produced from each ES probe can be initiated by turning on the liquid flow using a solution delivery system. With the appropriate solution reservoir configuration, pneumatic nebulization gas flow can also be used to initiate Electrospray. When nebulization assist is not used, the Electrospray from either ES tip **121** or **123** can be turned on by increasing the voltage applied to an ES tip relative to the voltage applied to ES source electrodes **140**,**141** and **142**. For example, if the voltages applied to capillary entrance electrode **140**, endplate and nosepiece **141** and cylindrical electrode **142** are set at −500, 0 and +500 V respectively, the Electrospray from ES tip **121** can be initiated by increasing the voltage applied to ES tip **121** to +5,000 V. The Electrospray from ES tip **121** can be stopped by setting the potential applied to ES tip **121** to 0 V. Electrospray from ES tip **123** would remain off with an appropriate voltage (approximately 0V) applied to ES tip **123** such that the electric field at ES tip **123** is effectively neutral. Electrospray from ES tip **123** can be turned on by applying +5,000 V to ES tip **123**. Nebulization gas supplied to ES tips **121** and **123** through gas delivery lines **136** and **128** respectively can be turned on when kilovolt potentials are applied to the ES tips to aid in the Electrospray charged droplet formation process. The nebulization gas flow to an individual ES tip can be turned off when the appropriate voltage is applied to the ES tip to shut off the Electrospray. Switching voltage and nebulization gas would allow rapid turning on and off of the Electrospray at an ES tip even if the sample bearing solution continued to flow through the tip for a period of time. Alternatively, as was shown in **FIG. 2** where a reservoir is used as a solution source, the liquid flow to ES probe tip **123** or **121** can be controlled by turning the nebulization gas flow on or off. When the nebulization gas flow is turned on, the venturi effect at the ES probe tip pulls solution from the reservoir to the ES probe tip where it is nebulized. In the case where Electrospray is sustained by