[0021] **FIG. 7***b* is a mass spectrum of a calibration solution containing Tri-Tyrosine and Hexa-Tyrosine

[0022] Electrosprayed with pneumatic nebulization assist from a second ES probe positioned near the ES source centerline.

[0023] **FIG. 7***c* is a mass spectrum of the sample and calibration solutions Electrosprayed simultaneously into the ES chamber from an off-axis ES probe and an ES probe positioned near the ES source centerline respectively.

[0024] **FIG. 8** is a diagram of an Electrospray source configured with three independent Electrospray probes with two off-axis ES probes connected to two LC separation systems.

[0025] **FIG. 9** is a diagram of an Atmospheric Pressure Chemical Ionization source with two independent sample inlet probes configured with one probe angled off-axis to the APCI source centerline and one probe aligned with the APCI source centerline.

[0026] **FIG. 10** contains mass spectra of sample and calibration solutions sprayed separately from individual APCI inlet probes and a mass spectrum of sample and calibration solutions sprayed simultaneously in a dual inlet probe APCI source configured as shown in **FIG. 9**.

[0027] **FIG. 11** is a diagram of an Atmospheric Pressure Chemical Ionization source configured with two APCI sample inlet pneumatic nebulization tips oriented to spray in a substantially parallel direction.

[0028] **FIG. 12** is a cross section diagram of a two layer Electrospray probe tip.

[0029] **FIG. 13** is a cross section diagram of a three layer Electrospray tip.

[0030] **FIG. 14** is a diagram of an Atmospheric Pressure Ion Source configured with Electrospray probe assembly and an Atmospheric Pressure Chemical Ionization probe assembly.

[0031] **FIG. 15** is a series of mass spectrum acquired separately and simultaneously from different sample solutions delivered to the Electrospray and APCI probes configured as shown in **FIG. 14**.

[0032] **FIG. 16** is a diagram of an Electrospray ion source comprising two Electrospray probes which are configured to produce Electrospray ions of opposite polarity.

[0033] **FIG. 17** is a diagram of an APCI source comprising two APCI probe and vaporizer assemblies which are configured to produce ions of opposite polarity.

[0034] **FIG. 18** is a diagram of an APCI source comprising three APCI probe and vaporizer assemblies which are configured to produce a mixture of positive and negative ions simultaneously.

DESCRIPTION OF THE INVENTION

[0035] One embodiment of the invention, as diagrammed in **FIG. 1**, comprises an Electrospray ion source which includes multiple Electrospray solution inlet probes. The Electrospray ion source is interfaced to amass spectrometer which is configured in vacuum chamber **31**. Individual Electrospray probe assemblies can be configured in the Electrospray ion source atmospheric pressure chamber **30** where solution is sprayed from individual probe tips at flow rates ranging from below 25 nL/min to above 1 mL/min. The spraying of a solution from an Electro spray tip may or may not include nebulization assist. Electrospray source assembly **1** includes two ES probe sets **2** and **5** each configured with dual ES tips. ES dual probe assembly **2** comprises two Electrospray tips **3** and **4** configured with pneumatic nebulization assist. Each ES tip **3** and **4** is supplied solution independently through delivery lines **9** and **10** respectively. ES sprayer tips **3** and **4** are located off center line or axis **24** of ES source **1** as defined by the centerline of capillary **21** orifice **23** into vacuum. A second ES dual probe assembly **5** is comprises two parallel ES tips **6** and **7** which are configured with pneumatic nebulization assist. Solution is independently supplied to ES tips **6** and **7** through solution delivery lines **14** and **15** respectively during ES operation. ES probe tips **6** and **7** are positioned near centerline **24** of ES source **1**. Each ES dual probe assembly is configured to provide gas flow concentrically at tips **3**, **4**, **6** and **7** through gas supply lines **11**, **8**, **12** and **13** respectively. The gas flow to each ES probe tip can be controlled individually or collectively to allow ES operation with pneumatic nebulization assist or to provide gas such as oxygen or sulfur hexaflouride (SF_6) at an ES tip to suppress corona discharge during positive or negative Electrospray ion production. In the embodiment shown, solutions can be Electrosprayed from ES tips **3**, **4**, **5** and **6** individually or simultaneously or with combinations of simultaneous spraying from individual ES probe tips during Electrospray operation. A portion of the ions produced from the solutions Electrosprayed into ES chamber **30** are transported into vacuum through bore **23** in capillary **21** where they are mass to charge analyzed by a mass spectrometer and detector.

[0036] In the embodiment shown in **FIG. 1**, the axis of ES tips **3** and **4** are positioned to be approximately parallel in dual tip ES probe assembly **2**. The position of ES probe assembly **2** can be adjusted in the x direction and rotationally, effectively moving ES tips **3** and **4** in the y direction. The position of ES probe tips **3** and **4** can be locked in place after adjustment with locking screw **16**. The x and y ES tip position adjustment sets location and direction of the spray produced from probe tips **3** and **4** relative to centerline **24** of ES source **1**. As will be explained in more detail below, the position adjustment allows optimization of the ion mixture delivered to vacuum when Electrospraying simultaneously from ES probe tips **2** and **3** over a wide range of liquid flow rates and solution chemistries. Similarly, the x and rotational or y positions ES tips **6** and **7** can be adjusted by moving ES probe assembly **5** and locking the position in place with locking screw **19**. The x and y ES probe tip position adjustment, relative to ES source axis **24** and capillary orifice **23**, allows optimization of performance when spraying sample solutions from ES probe tips **6** and **7** individually or simultaneously. As is diagrammed in **FIG. 6**, ES probe assemblies **2** and **5** may alternatively be configured to include full x-y-z tip position adjustment. Depending on the initial ES dual probe assembly mounting position and the range of tip position adjustment, the orientation of the ES probe tip axis may be configured to extend over a range of angles from 0 to greater than 90 degrees relative to the x-z ES source plane. Zero degrees is defined as the z axis pointing into bore **23** of capillary **21**. An ES probe tip axis, and consequently the centerline of an Electrospray plume