**183**. A method according to claim 173, wherein at least one said solution is delivered to at least one said probe from a liquid delivery system with an injector valve.

**184**. A method according to claim 173, wherein at least two of said solution are delivered to at least two of said probe from at least two liquid delivery systems each with an injector valve.

**185**. A method according to claim 173, wherein at least one of said solutions is delivered into said ion source using at least one liquid delivery system with an injector valve and at least one of said solutions is delivered into said ion source using at least one liquid chromatography system.

**186**. A method for analyzing chemical species comprising:

a. utilizing an ion source operating substantially at atmospheric pressure, at least two probes configured in said ion source, and a mass analyzer;

b. introducing at least two solutions into said ion source through at least two probes;

c. delivering said at least two solutions to at least two probes from at least two means each comprising but not limited to a chemical separation systems;

d. producing ions from at least two said solutions introduced through said at least two probes; and

f. mass analyzing said ions produced with said mass analyzer.

**187**. A method according to claim 186, wherein said chemical separation system is a liquid chromatography system.

**188**. A method according to claim 186, wherein said chemical separation system is a capillary electrophoresis system.

**189**. A method according to claim 186, wherein said chemical separation system is a capillary electrophoresis chromatography system.

**190**. A method according to claim 186, wherein said chemical separation system is a liquid chromatography system and a electrophoresis chromatography system each supplying separate said solutions into said ion source.

**191**. A method according to claim 186, wherein said ions are produced by using Electrospray ionization.

**192**. A method according to claim 186, wherein said ions are produced by using Electrospray ionization with nebulization assist.

**193**. A method according to claim 186, wherein said ions are produced by using Atmospheric Pressure Chemical Ionization.

**194**. A method according to claim 186, wherein said ions are produced by using Electrospray ionization and Atmospheric Pressure Chemical Ionization.

**195**. A method according to claim 186, wherein said ions are produced by using Inductively Coupled Plasma ionization.

**196**. A method for acquiring mass spectra containing an internal calibration standard comprising;

a. utilizing an ion source operating substantially at atmospheric pressure, at least two probes configured in said ion source, and a mass analyzer;

b. introducing at least two separate solutions into said ion source simultaneously;

c. introducing at least one said solution comprising a known sample substance;

d. producing ions from at least two said solutions introduced into said ion source;

e. producing ions from at said least one solution comprising a known sample substance;

f. mixing said ions produced; and

g. mass analyzing said mixture of ions produced with said mass analyzer.

h. using at least one of said mass spectral peaks which result from said ions produced from said known sample substance as a calibration reference in the mass spectra acquired from said mass analysis.

**197**. A method according to claim 196, wherein at least two of said solutions are introduced into said ion source through at least one of said probes through concentric layered tubes.

**198**. A method according to claim 196, wherein said ions are produced using Electrospray ionization.

**199**. A method according to claim 196, wherein said ions are produced using Electrospray ionization with nebulization assist.

**200**. A method according to claim 196, wherein said ions are produced using Atmospheric Pressure Chemical Ionization.

**201**. A method according to claim 196, wherein said ions are produced using both Electrospray and Atmospheric Pressure Chemical ionization.

**202**. A method according to claim 196, wherein said ions are produced using Inductively Coupled Plasma ionization.

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