

- b. introducing at least two solutions into said ion source through at least two probes;
  - c. introducing at least one solution comprising a known sample substance;
  - d. producing ions from at least two said solutions introduced through said at least two probes;
  - 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.
- 157.** A method according to claim 156, wherein said known sample substance contains chemical components used for mass scale calibration.
- 158.** A method according to claim 156, wherein said known chemical components from which said ions are produced result in internal mass scale calibration peaks when mass analyzed.
- 159.** A method according to claim 156, wherein at least two of said solutions are introduced into said ion source through at least one of said probes through concentric layered tubes.
- 160.** A method according to claim 159, wherein at least one of said solutions introduced into said ion source through said concentric tubes comprises a known sample substance from which said ions are produced which result in internal mass scale calibration peaks when mass analyzed.
- 161.** 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 utilizing at least two means for delivery;
  - d. delivering said at least one solution from a means which comprises but is not limited to a chemical separation system;
  - e. 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.
- 162.** A method according to claim 161, wherein at least one said solution is delivered to at least one said probe using a liquid chromatography system.
- 163.** A method according to claim 161, wherein at least two of said solutions are delivered to at least two said probes using at least two liquid chromatography systems.
- 164.** A method according to claim 161, wherein at least one said solution is delivered to at least one said probe using a capillary electrophoresis system.
- 165.** A method according to claim 161, wherein at least two of said solutions are delivered to at least two said probes using at least two capillary electrophoresis systems.
- 166.** A method according to claim 161, wherein at least one said solution is delivered to at least one said probe using a liquid pump.
- 167.** A method according to claim 161, wherein at least one said solution is delivered to at least one said probe from a solution reservoir.
- 168.** A method according to claim 161, wherein at least one said solution is delivered to at least one said probe from a pressurized solution reservoir.
- 169.** A method according to claim 161, wherein at least one said solution is delivered to at least one said probe from a liquid delivery system with an injector valve.
- 170.** A method according to claim 161, 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.
- 171.** A method according to claim 161, wherein at least one said solution is introduced into said ion source using an Electrospray microtip.
- 172.** A method according to claim 161, 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.
- 173.** 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 utilizing at least two means for delivery;
  - d. delivering said at least one solution from a means which comprises but is not limited to a chemical separation system;
  - e. 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.
- 174.** A method according to claim 173, wherein said chemical separation system is a liquid chromatography system.
- 175.** A method according to claim 173, wherein said chemical separation system is a capillary electrophoresis system.
- 176.** A method according to claim 173, wherein said chemical separation system is a capillary electrophoresis chromatography system.
- 177.** A method according to claim 173, wherein said chemical separation system is a liquid chromatography system and a electrophoresis chromatography system each supplying separate said solutions into said ion source.
- 178.** A method according to claim 173, wherein said ions are produced by using Electrospray ionization.
- 179.** A method according to claim 173, wherein said ions are produced by using Electrospray ionization with nebulization assist.
- 180.** A method according to claim 173, wherein said ions are produced by using Atmospheric Pressure Chemical Ionization.
- 181.** A method according to claim 173, wherein said ions are produced by using Electrospray ionization and Atmospheric Pressure Chemical Ionization.
- 182.** A method according to claim 173, wherein said ions are produced by using Inductively Coupled Plasma ionization.