

is to turn off the nebulizing gas through the appropriate ES probe tip and change the electrical potentials applied to the ES probe tip during LC column reconditioning. The electrical potential should be switched or changed to a value which prevents unassisted Electrospray from occurring from the ES probe tip during LC column reconditioning. Solution exiting the ES probe tip from the LC column being reconditioned would then drip off and flow out the ES source chamber drain. As an example of this method, consider an LC gradient run Electrosprayed with nebulization assist through ES probe tip 175 while LC column 198 is being reconditioned with solution flowing through ES probe tip 173. In this example, switching valves 191 and 199 have been eliminated and LC columns 198 and 188 are connected directly to or are incorporated into ES probe assemblies 172 and 170 respectively. Nebulization gas flow to ES probe tip 173 is turned off during the LC column reconditioning and any ions produced from unassisted Electrospray of the liquid emerging from ES probe tip 173 may be prevented from effectively entering mixing region 182 by the opposing nebulizing gas flow from ES probe assembly 172. Unassisted Electrospray from ES probe tip 173 can be prevented by applying a potential to ES probe tip 173 which is effectively equal to the local electric field potential collectively formed by the electrical potentials applied to ES source cylindrical lens 162, endplate 165 and capillary entrance electrode 204. Liquid flowing through LC column 198 which emerges at ES probe tip 173 will drip off into ES source chamber 161 without contributing ions into mixing region 182. Similarly, the nebulizing gas flow can be turned off and the electrical potential applied to ES probe tip 175 can be changed to prevent unassisted Electrospray when liquid is flowing from LC column 188 through ES probe tip 175 during reconditioning.

[0067] Additional analytical apparatus configurations are possible with combinations of multiple LC, CEC and/or CE separation systems configured in series or in parallel supplying solution to multiple ES probes. As an example, a capillary column or micro bore column can be configured in LC system 194 while and LC system 184 is configured with a standard 4.6 mm inner diameter LC column. ES probe assembly 175 can be configured with the capillary LC column incorporated as part of the ES probe assembly to minimize dead volume while ES probe assembly 170 is configured to accommodate the higher liquid flow rates delivered from larger bore column 198. The location of probe tips 175 and 173 can be positioned to optimize performance for specific and different liquid flow rates spraying from each ES probe tip. A system may also be configured with fast flow injection analysis using injector valves 186 and 196 and manual or auto injectors 187 and 197 in alternating sequence. This alternating sample injection sequence operating mode increases the rate at which samples can be mass analyzed by reducing the relatively slow injection rate cycle time of currently available auto injectors. An "open access" system can be configured with LC, CE and/or flow injection analysis to allow the conducting of multiple LC-MS, CE-MS or flow injection MS analysis with a single ES-MS detector system where no hardware reconfiguration is required.

[0068] More than three ES probe assemblies, each with different or similar configurations, can be mounted in ES chamber 160. Each ES probe assembly can be configured to accommodate different separation systems or sample injec-

tors. One ES probe assembly may interface to an LC system, another to a CE or CEC system, another to an auto injector inlet and yet another to a calibration sample delivery system. Using multiple ES probe assembly configurations, an ES-MS or an ES-MS/MS<sup>n</sup> system can be configured for a wider range of automation sample analysis techniques. Several widely diverse sample analysis techniques can be performed in sequence or simultaneously with a single mass analyzer in an automated and unattended manner. Mass analyzers are generally more expensive as detectors than separation systems, consequently, the configuration of multiple ES probes in one ES source allows cost effective operation with multiple separation systems connected to a single API mass analyzer detector. Multiple ES probe assembly configurations can also save downtime due to component setup time by allowing simple switching from one analytical method to another.

[0069] Another embodiment of the invention is the configuration of an Atmospheric Pressure Chemical Ionization (APCI) source with multiple sample solution inlet probes or nebulizers interfaced to a mass analyzer. Each sample inlet probe can spray solution independently of other sample inlets either separately or simultaneously during APCI operation. APCI inlet probes or nebulizers can be configured to accommodate solution flow rates ranging from below 500 nL/min to above 2 mL/min. The invention includes configuring at least two APCI inlet probes with fixed or adjustable positions which independently spray solutions into a common vaporizer during APCI source operation. Solutions are delivered to the multiple APCI inlet probes configured with pneumatic nebulization through different liquid lines fed by individual liquid delivery systems. Different samples, mixture of samples and/or solutions can be sprayed simultaneously through multiple APCI inlet probes. The liquid delivery systems include but are not limited to liquid chromatography pumps, capillary electrophoresis separation systems, syringe pumps, gravity feed vessels, pressurized vessels, and/or aspiration feed vessels. Auto injectors and/or manual injection valves may be connected to one or more APCI inlet probe nebulizers for sample or calibration solution introduction. Similar to the operation of multiple ES probes in one ES source, multiple APCI nebulizers configured in one APCI source allow the introduction of multiple samples simultaneously or sequentially with different compositions and different liquid flow rates. A calibration solution can be introduced into an APCI source through one inlet probe with a sample solution introduced independently through a second inlet probe. Both calibration and sample solutions flows can be sprayed simultaneously without mixing chemical components in solution. The resulting sprayed droplet mixture is transferred into the APCI vaporizer. Ions are produced from the vaporized mixture in the corona discharge region of the APCI source. A portion of the ions produced from the vapor mixture are swept into vacuum where they are mass analyzed. The acquired mass spectrum of the ion mixture contains peaks of ions produced from compounds present in each sample and calibration solution. The calibration peaks create an internal standard used for calculating the m/z assignments of sample related peaks. Simultaneously spraying from separate sample and calibration solutions allows the acquisition of mass spectra with internal standard peaks without mixing sample and calibration solutions prior to solution nebulization. The multiple inlet probe spraying prevents contamination of sample solu-