

ing but not limited to, Time-Of-Flight (TOF), Quadrupole, Fourier Transform (FTMS), Ion Trap, Magnetic Sector or a Hybrid mass analyzer.

[0009] In one embodiment of the invention, an Electrospray ion source is configured with multiple Electrospray probes. Each probe may or may not be configured with pneumatic or ultrasonic nebulization assist and/or a second liquid layer. The multiple ES probes and each liquid layer of each ES probe may be connected to different liquid delivery systems. In this manner, different samples, mixture of samples and/or solvents can be sprayed simultaneously or individually in a variety of combinations. The liquid delivery systems include but are not limited to liquid chromatography pumps, syringe pumps, gravity feed vessels, pressurized vessels, and or aspiration feed vessels. Samples may also be introduced using auto injectors, separation systems such as liquid chromatography (LC) or capillary electrophoresis (CE), capillary electrophoresis chromatography (CEC) and/or manual injection valves connected to any or all ES probes. Multiple and independent solution introduction allows multiple samples to be analyzed simultaneously with Electrospray ionization without changing ES probe positions. The ability to introduce sample solution through one ES probe and have the option to selectively and simultaneously introduce additional secondary samples into the ES chamber through other ES probes can be used to generate mass spectra, even on-line during LC or CE separations, with internal or external calibration standards. Different sample mixtures which span a range of m/z values or sample types can be introduced through different ES probes. Depending on the unknown sample being analyzed, an optimal calibration solution can be chosen from another ES probe. For example one m/z range calibration solution can be chosen which produces singly charged ES ions when analyzing singly charged compounds and likewise multiple charged ES generated calibration ions can be produced when analyzing compounds which form multiply charged ions in Electrospray ionization. The solution flow for any secondary ES probe can be controlled independent of the solution flow to a primary ES sample solution probe without having to change or adjust any probe position, change the ES source voltages, shut off the primary sample solution flow or contaminate the solution being introduced through the primary sample solution probe. Multiple probe sets can be operated simultaneously or in sequence with other probe sets in the same API chamber. The configuration and operation of multiple ES probes can facilitate API MS detection from multiple sample sources. In particular, multiple sample probes facilitates and improves the analytical throughput of unattended automated operation of a single mass analyzer as a detector for multiple Liquid Chromatography separations systems.

[0010] In another embodiment of the invention, multiple nebulizers are configured in an Atmospheric Pressure Chemical Ionization source. Similar to ES, multiple sample solutions can be introduced into the gas phase and ionized without mixing solutions. In this APCI source embodiment, multiple nebulizers spray individual sample bearing solutions into a vaporizer where the mixture of nebulized droplets is evaporated prior to ionization in the corona discharge region. Calibration solutions can be introduced through one or more sample inlet probes independently and simultaneously with sample solution introduction through yet another inlet probe. No adjustment to probe position,

applied voltages or vaporizer temperature may be required when controlling the solution flow to multiple inlet probes. This independent sample flow control with little or no mechanical adjustment in an APCI source increases the system level analytical flexibility and sample throughput with manual or automated operation while minimizing multiple solution cross contamination. Multiple APCI and ES probes can be configured in one API source in another embodiment of the invention. The combination ES and APCI source expands the range of analytical capability of an API-MS instrument interfaced to a variety of separation systems particularly for automated operation with a variety of samples.

[0011] The use of multiple probes with API sources, including ES, APCI or ICP ionization techniques allows a more rapid introduction of samples particularly when a fast mass analyzer such as Time-Of-Flight is used. Rapid sample introduction can be limited by the cycle time of an LC, CE or CEC separation system or auto injector. Sample introduction cycle time can also be limited by the time it takes for an injected sample to travel from the injector valve to the ES or APCI probe outlet. Multiple LC, CE or CEC, auto injectors, injector valves and API probes can be configured to decrease the cycle time of sample introduction and analysis time of an API MS system.

#### DESCRIPTION OF THE FIGURES

[0012] FIG. 1 is a diagram of an Electrospray ion source configured with multiple independent Electrospray probes installed.

[0013] FIG. 2 is a diagram of the Electrospray ion source of FIG. 1 showing a cross section top view of the ES dual probe assembly positioned near the ES source centerline.

[0014] FIG. 3 is a diagram of the Electrospray ion source of FIG. 1 showing a cross section side view of a dual ES probe assembly configured off axis from the ES source centerline and an ES dual probe assembly positioned near the centerline.

[0015] FIG. 4a is a mass spectrum of a sample solution containing the doubly charged peak of Gramicidin S Electro sprayed from one tip of a dual tip off axis ES probe operating with pneumatic nebulization assist.

[0016] FIG. 4b is a mass spectrum of a calibration solution Electro sprayed with pneumatic nebulization assist from the second ES tip two of a dual tip off axis ES probe.

[0017] FIG. 4c is a mass spectrum of a sample solution Electro sprayed from tip one and a calibration solution Electro sprayed from tip two simultaneously from a dual tip off axis probe.

[0018] FIG. 5 is a diagram of a six tip ES probe array with pneumatic nebulization assist mounted near the axis to the ES source chamber centerline.

[0019] FIG. 6 is a cross section diagram of two ES probe assemblies with independent x-y-z tip position adjustment configured in an ES source.

[0020] FIG. 7a is a mass spectrum of a sample solution containing Leucine Enkephalin Electro sprayed with pneumatic nebulization assist through an off-axis ES probe assembly into the ES chamber.