

solutions sprayed vaporized and ionized through APCI probe **360**. The positive ions produced in the corona discharge region surrounding the tip of corona discharge needle **370** are drawn towards the capillary **361**, end plate **375**, and corona discharge needle **365** due the applied electrical potentials. The negative ions produced in the corona discharge region surrounding the tip of corona discharge needle **365** are drawn towards corona discharge needle **370** due to the applied electrical potentials. The positive and negative ions interact and react at atmospheric pressure in region **371**. The positive and negative ion interaction at atmospheric pressure will result in the neutralization of some the positive and negative ions, however, some positive ions after reacting can be re-ionized and subsequently drawn towards nose piece **375** and capillary **361** by the applied electrical potentials. Positive ions are swept into vacuum through the bore of capillary where they are mass analyzed by a mass spectrometer located in vacuum region **374**. A higher number of positive solvent ions may be introduced from a higher solution flow rate through APCI probe assembly **366** compared with the solution flow rate delivered to APCI probe assembly **360**. The higher abundance of positive solvent ions ion in mixing region **371** will increase the efficiency of re-ionization of positive ions after a neutralization reaction with a negative ion. Reversing voltage polarities in API source, will allow negative ions to be produced from solution delivered to APCI probe assembly **366** and positive ions to be produced from solution delivered to APCI probe assembly **360**. A portion of the reacted negative ion population will be swept into vacuum and mass to charge analyzed.

[0086] Variations of APCI probe locations can be configured to achieve multiple sample ion-ion interaction from different solutions sprayed from multiple APCI probe assemblies. More than two APCI probes can be configured in an API source positioned at angles $\phi_1 \dots_i$ ranging from 0 to 180 degrees and rotation angles $\theta_1 \dots_i$ ranging from 0 to 360 degrees. Selected neutral gas composition can be added to nebulizer or counter current drying gas study ion-neutral reactions in relation to ion-ion interactions.

[0087] An embodiment of an API source configured with three APCI probe assemblies positioned to facilitate the study of ion-ion interactions at atmospheric pressure is shown in FIG. 18. APCI probe assembly **380** is positioned at angles $\phi_{380}=90^\circ$ and, $\theta_{380}=270^\circ$ with electrical potentials applied relative to grid **381** to produce negative ions in the corona discharge region surrounding the tip of corona discharge needle **392**. A second APCI probe assembly **382** is positioned at angles $\phi_{382}=90^\circ$ and $\theta_{382}=90^\circ$ with electrical potentials applied relative to grid **384** to produce negative ions. A third APCI probe assembly **385** is positioned at angles $\phi=0$ and $\theta=0$ with electrical potentials applied relative to grid **390** to produce positive ions. The positive and negative ions produced from APCI probe assemblies **380**, **382** and **385** pass through grids **381**, **384** and **390** respectively and interact at atmospheric pressure. Two grids **381** and **384** are positioned between APCI probe assembly **385** and the entrance of capillary **386**. Interaction between ions of opposite polarity results in the cause the neutralization of the positive and negative ions, however, the positive sample and solvent ions supplied from APCI probe assembly **385** can re-ionize reacted product molecules. The newly formed ion will be drawn towards nose piece **389** and capillary **386** by the applied electric fields. Ions swept through the bore of

capillary **386** into vacuum are mass analyzed with a mass spectrometer and ion detector. The applied voltage polarities can be switched to enable the mass analysis of a negative reacted ion population. One or more APCI probes assemblies configured in the embodiment shown in FIG. 18 can be removed or replaced with Electrospray probe assemblies. API sources configured with multiple APCI probe assemblies can be used to study a range of ion-ion interactions and reactions.

[0088] Multiple ES and APCI inlet probe configurations as diagrammed in FIGS. 1, 2, 3, 5, 6, 8, 9, 11, 14, 16, 17 and 18 show individual solution delivery systems connected to each inlet probe tip. alternatively, multiple sample delivery systems can be switched directed to supply solution to an individual inlet probe tip. The combination of multiple sample inlet lines and multiple nebulizers can be configured in a single API source assembly. Several combinations of multiple probe tip positions can be configured by one skilled in the art and the invention is not limited to those multiple ES and APCI probe embodiments specifically described herein.

[0089] Having described this invention with respect to specific embodiments, it is to be understood that the description is not meant as a limitation since further modifications and variations may be apparent or may suggest themselves to those skilled in the art. It is intended that the present application cover all such modifications and variations as fall within the scope of the appended claims.

[0090] References Cited:

[0091] The following references are referred to in this document, the disclosures of which are hereby incorporated herein by reference:

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