

molecular ion peak **251** of leucine enkephalin. Mass spectrum **252** of a calibration solution was acquired from a mixture of 50 pmol/ul each of tri-tyrosine and hexa-tyrosine in an solution of 80:20 water:iso-propanol, 2% propionic acid at a flow rate of 5 ul/min. The calibration solution was delivered from a solution reservoir through delivery line **236** pulled by the venturi of pneumatic nebulizer **241** configured in APCI inlet probe **214**. Mass spectrum **252** contains calibration peaks **253** and **254** of protonated tri-tyrosine and hexa-tyrosine respectively. Sample liquid flow to APCI inlet probe **213** was turned off during the acquisition of mass spectrum **252**. Mass spectrum **255** of FIG. 10 was acquired while simultaneously spraying sample and calibration solutions from APCI inlet probes **213** and **214** respectively. Solution compositions and flow rates were the same as was described above for individual spraying. Mass spectrum **255** contains internal standard peaks **256** and **258** of protonated tri-tyrosine and hexa-tyrosine respectively and sample compound peak **257** of protonated leucine enkephalin. The calibration peaks acquired as internal standards can be used to improve the calculated mass measurement of sample related peak **257**.

[0073] Electrospray ionization, an APCI source creates sample and solvent molecule vapor prior to ionization. The APCI ionization process, unlike Electrospray, requires gas phase molecule-ion charge exchange reactions. Consequently, mixing samples, via multiple inlet probe introduction, in the gas phase in an APCI source may allow enhanced opportunity to study neutral molecule and ion molecule reactions which occur in the gas phase while avoiding solution chemistry effects. Gas phase sample interaction can be avoided, if desired, by introducing sample sequentially through multiple APCI inlet probes. The nebulizer gas can remain on or be turned off when the liquid sample flow through an APCI inlet probe is turned off. The venturi effect from the nebulizing gas at the tip of an APCI inlet probe may be used to pull the sample from a reservoir to the APCI inlet probe tip. This technique avoids the need for an additional sample delivery pump. Multiple APCI probes can be fixed in position as diagrammed in FIG. 9 or can have adjustable sprayer positions relative to each other, cavity **224** or vaporizer **211**. Each APCI inlet probe is removable and a single APCI source assembly can be configured with one or more APCI inlet probes mounted in a variety of positions. It is clear to one skilled in the art that more than two APCI inlet probes can be added to APCI source **210**. Each APCI inlet probe can be configured at different angles relative to the APCI source centerline and each APCI inlet probe position can be fixed or adjustable during operation of the APCI source. APCI inlet probe tips can be configured at any position axially and radially upstream of vaporizer **211** or even configured to spray directly into corona discharge region **226**. Multiple vaporizers and corona discharge needles can also be configured into APCI source **210**. The relative radial positions of multiple APCI nebulizers spraying into a vaporizer can be set at any desired angle, radial position and tilt angle relative to the vaporizer centerline. The tips of each APCI inlet probe can be positioned to optimize nebulizer performance for a given solution flow rate and analytical application.

[0074] An alternative embodiment of the invention is diagrammed in FIG. 11 which shows a dual inlet probe APCI source with two inlet probes configured to spray in a direction parallel to the APCI source axis. APCI source

chamber **271** of APCI source **260** is configured similar to APCI source chamber **230** of APCI source **210** diagrammed in FIG. 9. APCI source **260** is configured with two pneumatic nebulization APCI inlet probes **264** and **265** which connect to liquid delivery lines **266** and **267** respectively. Nebulizer gas lines **268** and **269** supply nebulization gas separately to APCI inlet probes **264** and **265** respectively. In the embodiment shown, both APCI inlet probes **264** and **265** are configured such that axis of each pneumatic nebulizer sprayer axis is positioned to be approximately parallel with APCI vaporizer **261** axis **270**. Different solutions are sprayed individually or simultaneously from both inlet probes **264** and **265** into region **262**. A portion of the sprayed droplets pass around separator ball **263** and flow into vaporizer **261**. The sprayed liquid droplets evaporate in vaporizer **261** and ions are formed from the vapor as it passes through corona discharge region. A portion of the ions produced pass into vacuum through capillary orifice **273** and are mass to charge analyzed with a mass spectrometer and ion detector. Alternatively, APCI source **260** can be configured with more than two APCI inlet probes positioned in parallel and spraying in a direction parallel to vaporizer axis **270** into region **262**. A set of parallel APCI inlet probes positioned near and spraying parallel with vaporizer axis **270** can be configured with single or multiple off axis angled APCI inlet probes. Multiple APCI inlet probes can be connected to a variety of liquid reservoirs, delivery systems or separation systems supplying separate sample solutions and/or calibration solutions to each individual APCI inlet probe. Alternatively, the axis **270** of vaporizer **261** may be configured at an angle from axis **274** of capillary **275**. Axis **270** of vaporizer **261** and, consequently the axis of inlet probes **264** and **265** can be configured at an angle from 0 to over 120 degrees relative to axis **274** of capillary **275**. As will be shown in an alternative embodiment of the invention, off axis APCI vaporizer and inlet probe positioning allows the configuration of multiple APCI vaporizer, inlet probe and corona discharge APCI sources.

[0075] Similar to the Electrospray ionization source diagrammed in FIG. 8 with multiple ES probes, multiple separation systems can be configured to deliver sample solutions into an APCI source configured with multiple inlet probes. As described for the ES source, sample throughput can be increased using a single APCI-MS detector for multiple sample separation or inlet systems. Multiple sample inlet probes configured in an APCI source can extend the range of analytical procedures which can be automatically or manually run sequentially or simultaneously with one APCI-MS instrument. The configuration of multiple APCI inlet probes in one APCI source can also minimize the time and complexity required to reconfigure and re-optimize an APCI source for different analytical applications.

[0076] An alternative embodiment of the invention is the combination of at least one Electrospray probe with at least one Atmospheric Pressure Chemical Ionization probe and vaporizer configured in an Atmospheric Pressure Ion Source interfaced to a mass analyzer. It is desirable for some analytical applications to incorporate both ES and APCI capability in one API source. Rapid switching from ES to APCI ionization methods without the need to reconfigure the API source minimizes the time and complexity to conduct API-MS or API-MS/MSⁿ experiments with ES and APCI ion sources. The same sample can be introduced sequentially or simultaneously through both APCI and ES probes to obtain