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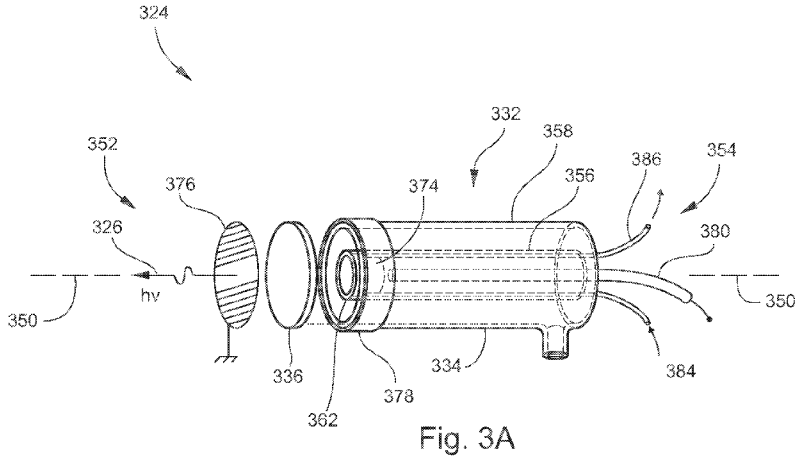


Fig. 3A

(57) Abstract: A vacuum ultraviolet (VUV) photon source includes a body, a VUV window, electrodes disposed on the body outside an interior thereof, and a dielectric barrier between the electrodes. A method for generating VUV photons includes generating a dielectric barrier discharge (DBD) in an interior of a photon source by applying a periodic voltage between a first electrode and a second electrode separated by a dielectric barrier, wherein the DBD produces excimers from a gas in a gap between the electrodes, and transmitting VUV photons through a window of the photon source.

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VACUUM ULTRAVIOLET PHOTON SOURCE, IONIZATION APPARATUS, AND RELATED METHODS

RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Patent Application Serial No. 61/738,605, filed December 18, 2012, titled "VACUUM ULTRAVIOLET PHOTON SOURCE, IONIZATION APPARATUS, AND RELATED METHODS;" and U.S. Patent Application Serial No. 13,796,292, filed March 12, 2013, titled "VACUUM ULTRAVIOLET PHOTON SOURCE, IONIZATION APPARATUS, AND RELATED METHODS;" the contents of which are incorporated by reference herein in their entireties.

TECHNICAL FIELD

[0002] The present invention relates generally to generating vacuum ultraviolet (VUV) photons, which may be utilized, for example, for photo-ionization of neutral molecules. Photo-ionization may be implemented, for example, in conjunction with mass spectrometry (MS).

BACKGROUND

[0003] A mass spectrometry (MS) system in general includes an ionization apparatus (or ion source) for ionizing components of a sample of interest, a mass analyzer for separating the ions based on their differing mass-to-charge ratios (or m/z ratios, or more simply "masses"), an ion detector for counting the separated ions, and electronics for processing output signals from the ion detector as needed to produce a user-interpretable mass spectrum. Typically, the mass spectrum is a series of peaks indicative of the relative abundances of detected ions as a function of their m/z ratios. The mass spectrum may be utilized to determine the molecular structures of components of the sample, thereby enabling the sample to be qualitatively and quantitatively characterized. In certain "hyphenated" or "hybrid" systems, the sample supplied to the ionization apparatus may first be subjected to a form of analytical separation. For example, in a liquid chromatography-mass spectrometry (LC-MS) system or a gas chromatography-mass spectrometry (GC-MS) system, the output of the LC or GC column may be transferred into the ion source through appropriate interface hardware.

[0004] The type of ionization apparatus deployed in the system depends on many factors. Examples of ionization techniques implemented by different types of ionization apparatuses include photo-ionization (PI), electrospray ionization (ESI), chemical ionization (CI), field ionization (FI), electron ionization (EI), laser desorption ionization (LDI), and matrix-assisted laser desorption ionization (MALDI). Some of these techniques are effective at or near atmospheric pressure and others are effective at vacuum pressure, while some may be adapted for implementation in either regime.

[0005] Ultraviolet (UV) PI is becoming recognized for its ability to ionize many chemical species, both polar and non-polar, with reduced ion suppression and retention of high sensitivity and dynamic range, as compared for example to widely used ESI. With the appropriate choice of photon wavelength (energy), efficient analyte ionization and low levels of undesired ionization of common LC solvents can be achieved simultaneously. Common UV PI sources, however, use a low internal-pressure gas discharge lamp, e.g. krypton (10.2 eV), in an atmospheric pressure ionization chamber. These sources are limited in their use mainly by low-intensity radiation (photon flux), ambient optical absorption of the UV flux, and unwanted ion chemistry in the high-pressure environment.

[0006] Therefore, there is a need for PI sources capable of producing higher photon flux levels and ionization efficiency with minimal ionization of non-analytical molecules, and which are effective for providing the advantages of UV PI in both low-pressure and high-pressure environments.

SUMMARY

[0007] To address the foregoing problems, in whole or in part, and/or other problems that may have been observed by persons skilled in the art, the present disclosure provides methods, processes, systems, apparatus, instruments, and/or devices, as described by way of example in implementations set forth below.

[0008] According to one embodiment, a vacuum ultraviolet (VUV) photon source includes: a body enclosing an interior and comprising a VUV window; a first electrode disposed on the body outside the interior; a dielectric barrier; and a second electrode disposed on the dielectric barrier outside the interior, and separated from the first electrode by a gap in the interior, wherein the dielectric barrier is disposed between the first electrode and the second electrode.

[0009] According to another embodiment, a photo-ionization (PI) apparatus includes: a chamber comprising a sample inlet and an ion outlet; and a VUV photon source disposed in the chamber.

[0010] According to another embodiment, a mass spectrometry (MS) system includes: a PI apparatus; and a mass analyzer communicating with the PI apparatus.

[0011] According to another embodiment, a method for generating vacuum ultraviolet (VUV) photons includes: generating a dielectric barrier discharge (DBD) in an interior of a photon source by applying a periodic voltage between a first electrode and a second electrode, wherein the first electrode and the second electrode are disposed outside the interior and are separated by a dielectric barrier and a gap in the interior, and wherein the DBD produces excimers from a gas in the gap; and transmitting VUV photons emitted from the excimers through a window of the photon source.

[0012] According to another embodiment, a method for ionizing a sample includes: introducing the sample into a chamber; and exposing the sample to VUV photons by generating the VUV photons according to any of the methods disclosed herein, wherein the VUV photons are transmitted into the chamber from the window.

[0013] According to another embodiment, a method for analyzing a sample includes: ionizing the sample according to any of the methods disclosed herein to produce ions; and transmitting the ions into a mass analyzer.

[0014] Other devices, apparatus, systems, methods, features and advantages of the invention will be or will become apparent to one with skill in the art upon examination of the following figures and detailed description. It is intended that all such additional systems, methods, features and advantages be included within this description, be within the scope of the invention, and be protected by the accompanying claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015] The invention can be better understood by referring to the following figures. The components in the figures are not necessarily to scale, emphasis instead being placed upon illustrating the principles of the invention. In the figures, like reference numerals designate corresponding parts throughout the different views.

[0016] Figure 1 is a schematic view of an example of a mass spectrometry (MS) system according to one embodiment.

[0017] Figure 2 is a schematic view of an example of a photo-ionization (PI) apparatus according to some embodiments.

[0018] Figure 3A is a perspective view of an example of a vacuum ultraviolet (VUV) photon source according to one embodiment.

[0019] Figure 3B is a cross-sectional side view of the VUV photon source illustrated in Figure 3A.

[0020] Figure 4 is a perspective view of an example of a VUV photon source according to another embodiment.

[0021] Figure 5 is a perspective view of an example of a VUV photon source according to another embodiment.

[0022] Figure 6 is a schematic view of an example of a PI apparatus according to other embodiments.

[0023] Figure 7 is a schematic view of an example of a PI apparatus according to other embodiments.

DETAILED DESCRIPTION

[0024] Figure 1 is a schematic view of an example of a mass spectrometry (MS) system **100** according to one embodiment. The MS system **100** generally includes a sample source **102**, an ionization apparatus (or ion source) **104**, a mass spectrometer (MS) **106**, and a vacuum system for maintaining the interior of the MS **106** (and in some embodiments the interior of the ionization apparatus **104**) at controlled, sub-atmospheric pressure levels. The vacuum system is schematically depicted by vacuum lines **108** and **110** leading from the ionization apparatus **104** and MS **106**, respectively. The vacuum lines **108** and **110** are schematically representative of one or more vacuum-generating pumps and associated plumbing and other components appreciated by persons skilled in the art. The structure and operation of various types of sample sources, ionization apparatuses, MSs, and associated components are generally understood by persons skilled in the art, and thus will be described only briefly as necessary for understanding the presently disclosed subject matter. In practice, the ionization apparatus **104** may be

integrated with the MS **106** or otherwise considered as the front end or inlet of the MS **106**, and thus in some embodiments may be considered as a component of the MS **106**.

[0025] The sample source **102** may be any device or system for supplying a sample to be analyzed to the ionization apparatus **104**. The sample may be provided in a liquid- or gas-phase form that flows from the sample source **102** into the ionization apparatus **104**, or in a solid form in which case the sample source **102** may be a sample support structure or sample probe that is loaded into or mounted in the ionization apparatus **104**. In hyphenated systems such as liquid chromatography-mass spectrometry (LC-MS) or gas chromatography-mass spectrometry (GC-MS) systems, the sample source **102** may be an LC or GC system, in which case an analytical column of the LC or GC system is interfaced with the ionization apparatus **104** through suitable hardware. The pressure in the sample source **102** (or the pressure outside the outer structure of the ionization apparatus **104**) is typically around atmospheric pressure (around 760 Torr) or at a somewhat sub-atmospheric pressure.

[0026] Generally, the ionization apparatus **104** is configured for producing analyte ions from a sample provided by the sample source **102** and directing the as-produced ions into the MS **106**. In embodiments described herein, the ionization apparatus **104** is a photo-ionization (PI) apparatus (or PI source). The ionization apparatus **104** may generally include an ionization chamber that receives or supports the sample, and a PI device configured for generating photons that irradiate the sample to effect ionization. In embodiments described herein the PI device is a vacuum ultraviolet (VUV) photon source (or VUV photon lamp), as described further below by way of examples. For purposes of the present disclosure, the wavelength at which VUV photons propagate is generally taken to be 200 nm or lower. The internal pressure of the ionization apparatus **104** may generally range from 0 to 1000 Torr. Thus, in some embodiments the ionization apparatus **104** may be utilized for atmospheric pressure photo-ionization (APPI). In other embodiments, the internal pressure of the ionization apparatus **104** is maintained by the vacuum system at an intermediate, sub-atmospheric pressure that is lower than the pressure of the sample source **102** (or the ambient pressure outside the ionization apparatus **104**) but is higher than the vacuum pressure inside the MS **106**, particularly the mass analyzing region of the MS **106**. In some embodiments, the pressure of the ionization apparatus **104** ranges from 0.01 to 100 Torr. In other embodiments, the pressure of the ionization apparatus **104** ranges from 0.05

to 50 Torr. In other embodiments, the pressure of the ionization apparatus **104** ranges from 0.1 to 10 Torr.

[0027] The MS **106** may generally include a mass analyzer **112** and an ion detector **114** enclosed in a housing **116**. The vacuum line **110** maintains the interior of the mass analyzer **112** at very low (vacuum) pressure. In some embodiments, the mass analyzer **112** pressure ranges from 10^{-4} to 10^{-9} Torr. The vacuum line **110** may also remove any residual non-analytical neutral molecules from the MS **106**. The mass analyzer **112** may be any device configured for separating, sorting or filtering analyte ions on the basis of their respective m/z ratios. Examples of mass analyzers include, but are not limited to, multipole electrode structures (e.g., quadrupole mass filters, ion traps, etc.), time-of-flight (TOF) analyzers, and ion cyclotron resonance (ICR) traps. The mass analyzer **112** may include a system of more than one mass analyzer, particularly when ion fragmentation analysis is desired. As examples, the mass analyzer **112** may be a tandem MS or MS^n system, as appreciated by persons skilled in the art. As another example, the mass analyzer **112** may include a mass filter followed by a collision cell, which in turn is followed by a mass filter (e.g., a triple-quad or QQQ system) or a TOF device (e.g., a qTOF system). In other embodiments another type of analytical separation instrument, such as an ion mobility spectrometer (IMS), may be substituted for the MS **106** (in which case an IMS drift tube may be substituted for the mass analyzer **112**) or operate in tandem with the MS **106** to provide an additional dimension to the analysis. The ion detector **114** may be any device configured for collecting and measuring the flux (or current) of mass-discriminated ions outputted from the mass analyzer **112**. Examples of ion detectors **114** include, but are not limited to, electron multipliers, photomultipliers, and Faraday cups.

[0028] Figure 1 schematically depicts the ionization apparatus **104** as including a sample inlet **118** for introducing a sample into the ionization apparatus **104** and an ion outlet **120** for transferring an ion beam into the MS **106**. The sample inlet **118** may be a conduit for introducing a fluid sample, or a sealable door for introducing a solid sample. The ion outlet **120** may be any component or combination of components configured for enabling the analyte ions to be transferred into the mass analyzer **112** with minimal or no loss of ions, with minimal non-analytical components such as neutral species, and without breaking the vacuum of the MS **106**. The ion outlet **120** may, for example, include one or more of the following, as appreciated by

persons skilled in the art: capillary, orifice, ion optics, skimmer plate, ion guide, ion funnel, ion slicer, aperture, etc.

[0029] Figure 2 is a schematic view of an example of a PI apparatus **204** according to some embodiments. The PI apparatus **204** may include an ionization chamber **222**; a sample inlet **218**, an ion outlet **220** and vacuum line **210** communicating with the ionization chamber **222**; and a VUV photon source **224** positioned to direct VUV photons **226** toward a sample **228** in the ionization chamber **222** to produce analyte ions **230**. The VUV photon source **224** may include a body **232** that is sealed or sealable in a fluid-tight manner. The body **232** encloses an interior that may be filled with a plasma-forming gas. The body **232** may include a main portion (or dielectric portion) **234** that is composed of a dielectric material such as, for example, a glass (e.g., fused silica or quartz). The body **232** may also include a VUV window **236** attached to the main portion **234** in a fluid-tight manner. The VUV window **236** may be attached to the main portion **234** by any means resulting in a fluid-tight interface, such as by an adhesive or bond layer. A non-limiting example of an adhesive or bond layer is glass frit material, where bonding is activated by an appropriate thermal treatment. The VUV window **236** may be composed of a material that transmits VUV photons with high efficiency. As an example of high efficiency transmission in the present context, the VUV window **236** may transmit 80% or greater of VUV photons incident on its inside surface. The VUV window **236** may, for example, be composed of magnesium fluoride (MgF_2), calcium fluoride (CaF_2), or lithium fluoride (LiF). The VUV window **236** may be cut along a crystallographic orientation that maximizes VUV photon transmission through its lattice and/or aids in matching the thermal expansion coefficient of the window **236** to that of the body **232** particularly during the high-temperature process of bonding the window **236** to the body **232**. for example C-cut (cut along the c-plane) MgF_2. In some embodiments, the pressure in the body **232** is about atmospheric pressure. In some embodiments, the gas pressure in the body **232** ranges from 200 to 1500 Torr. The VUV photon source **224** may also include electrodes (not shown) disposed on the body **232**, examples of which are described below, for applying an electrical field in which the plasma-forming gas is immersed.

[0030] The PI apparatus **204** may also include an electrical power source **238** communicating with the electrodes of the VUV photon source **224**. The power source **238** may include a voltage source configured for applying a voltage to the electrodes suitable for generating plasma from

the gas in the interior of the VUV photon source **224** and maintaining the plasma in a stable manner for any desired period of time. In embodiments described herein, the voltage source is configured for applying a periodic (time-varying) voltage, which may be a sinusoidal voltage such as an alternating current (AC) voltage, or may have another type of periodic characteristic such as square wave, sawtooth, etc. A periodic voltage potential is applied between at least one electrode serving as a high-voltage electrode, and at least one other electrode spaced from the first electrode by a gap and either biased to a non-zero voltage or grounded. One or more dielectric barriers are positioned in the gap between the two electrodes. A part of the body **232** of the VUV photon source **224** may, for example, serve as the dielectric barrier. The VUV photon source **224** may be considered as a dielectric barrier discharge (DBD) excimer lamp. Application of the periodic voltage at an appropriate magnitude and frequency generates a DBD in the gap, which in turn generates plasma from the gas exposed to the DBD. The plasma is of the type that includes excimers (excited dimers) whose formation is induced by the DBD. The excimers upon relaxation (return to ground state) emit VUV photons.

[0031] It will be noted that the plasma itself remains sealed within the body **232** of the VUV photon source **224**. Only the VUV photons **226** that pass through the VUV window **236** enter the ionization chamber **222** to interact with the sample **228**. Other energetic components of the plasma (ions, electrons, metastables, etc.) remain confined within the sealed body **232**.

[0032] The plasma-forming gas may be any gas or combination of gases from which an intense, non-coherent DBD plasma containing VUV photon-emitting excimers may be generated. The plasma-forming gas may also be characterized as having a composition that includes excimer precursors. Examples of the plasma-forming gas species suitable for forming VUV photon-emitting excimers in response to excitation by a DBD include, but are not limited to, a noble gas (argon, xenon, krypton, neon, and helium), a combination or two or more noble gases, and a combination of one or more noble gases and a non-noble gas such as hydrogen. In addition, certain noble gas halides are capable of forming excimers (or "exciplexes") that emit photons in the VUV range, for example argon fluoride (ArF*, about 193 nm). In some embodiments, the VUV photon source **224** may provide high conversion efficiency (e.g., 40% or greater) of electrical energy to VUV photon flux. Prototypes of the VUV photon source **224** utilizing argon have been found to provide a flux level of at least ten times greater than that of a standard krypton gas discharge lamp of similar size. In addition, minimal photon absorption

occurs in a DBD due to electrical excitation of the argon neutrals to excimers via a three-body process and decay (radiation) to a non-absorbing ground state. In addition, as demonstrated below by detailed representative embodiments of the VUV photon source **224**, the electrodes utilized for generating the DBD may be positioned outside of the gas-filled interior. By such configuration, the electrodes are not exposed to the high-frequency, short-lived filamentary micro-discharges characterizing the DBD, thereby avoiding loss of electrode material and contamination of the gas due to plasma-induced metal sputtering. Moreover, the use of argon (10 eV) has been found to be near optimal in terms of maximizing analyte ionization and avoiding solvent ionization. However, the other gases and combinations of gases noted above may be suitable for the ionization process in many applications.

[0033] The parameters of the periodic voltage effective for generating the DBD plasma and concomitant VUV photon-emitting excimers may depend on factors such as the type of plasma-forming gas utilized and the gas pressure in the VUV photon source **224**. In some embodiments, the periodic voltage has a magnitude on the order of kilovolts (kV) and a frequency on the order of hertz (Hz) or kilohertz (kHz). In some embodiments, the periodic voltage has a magnitude ranging from 3 kV to 60 kV peak-to-peak and a frequency ranging from 50 Hz to 300 kHz.

[0034] The PI apparatus **204** may also include a cooling device or system **240** configured for cooling the high-voltage electrode and optionally other components of the VUV photon source **224** during operation. In some embodiments the cooling device or system **240** may be configured for circulating a suitable heat transfer medium (or coolant) into thermal contact with the high-voltage electrode and other components. For this purpose, the cooling device or system **240** may include one or more fluid reservoirs, pumps or other fluid moving devices, conduits, heat exchangers, and the like as appreciated by persons skilled in the art. The heat transfer medium may be a gas (e.g., air) or a liquid (e.g., water). The thermal contact made between the heat transfer medium and the high-voltage electrode may be direct contact or indirect contact. That is, the term "thermal contact" generally refers to routing the heat transfer medium into close enough proximity to the high-voltage electrode to remove heat at a rate and quantity sufficient for maintaining consistent, failure-free operation of the VUV photon source **224**. Alternatively or additionally, a passive cooling system not requiring the movement of a fluid may be utilized. For example, heat may be conducted away from the high-voltage electrode using a high thermal

conductivity rod or tube, for example aluminum nitride, which may also function as an electrical insulator for the high-voltage electrode.

[0035] The VUV photon source **224** may include one or more gas ports **242** formed through the body **232** between the interior and the ambient outside the body **232**. The gas port(s) **242** may be sealed in a fluid-tight manner by any suitable sealing component (e.g., plug) and technique to fluidly isolate the interior from the ambient and prevent gas leakage. In some embodiments, the gas port **242** may be sealed in a permanent manner. In this case, as part of the fabrication process, the body **232** may be cleaned, evacuated, and charged with a desired type of plasma-forming gas via the gas port **242**, and then the gas port **242** is sealed and remains so for the operational life of the VUV photon source **224**. In other embodiments, the gas port **242** may be re-sealable. That is, the sealing component may be removable and either reusable or replaceable with a new sealing component. In this case, the sealing component may be removed to purge the interior, after which the VUV photon source **224** may be re-charged with the same gas but to a different pressure level, or charged with a different gas or mixture of gases.

[0036] In other embodiments, the PI apparatus **204** may also include a gas transport system (or gas handling system) **244** that communicates with one or more gas ports **242** in a fluid-tight manner via one or more gas lines **246** (e.g., conduits, tubing, etc.). The gas transport system **244** may be configured for alternately filling and purging the VUV photon source **224**, or for circulating a plasma-forming gas through the VUV photon source **224** (for example, by utilizing two or more gas ports **242** and respective gas lines **246**). Circulating the gas may be useful, for example, for removing from the photon source's interior residual contaminants or contaminants outgassing from the photon source's materials, or for removing heat from the lamp during operation. For these purposes, the gas transport system **244** may include one or more gas reservoirs, pumps or other fluid moving devices, conduits, flow controllers, pressure transducers and the like as appreciated by persons skilled in the art. The gas transport system **244** may, for example, be configured for enabling selection of different types of gases and gas mixtures for use as the plasma-forming gas in the VUV photon source **224**. The gas transport system **244** may be fluidly isolated from the ambient such that when it is in open communication with the body's interior the VUV photon source **224** remains fluidly isolated from the ambient. The gas transport system **244** may include an ON/OFF valve in the gas line **246** that is closed when the gas transport system **244** is not in use.

[0037] As illustrated in Figure 2, in some embodiments the VUV photon source **224** may extend partially into the ionization chamber **222**, such as through a vacuum-tight feed-through structure in a wall of the ionization chamber **222**, so that at least the VUV window **236** is disposed in the ionization chamber. Thus, in low-pressure ionization implementations, a portion of the VUV photon source **224** including the VUV window **236** is exposed to vacuum and the remaining portion is exposed to atmospheric pressure. It will be understood that the respective orientations of the sample inlet **218**, ion outlet **220** and VUV photon source **224** are illustrated in Figure 2 by example only, and that many other orientations are possible.

[0038] Figure 3A is a perspective view and Figure 3B is a cross-sectional side view of an example of a VUV photon source **324** according to one embodiment. The VUV photon source **324** includes a body **332** that includes a main portion **334** and a VUV window **336**. The main portion **334** is composed of a dielectric material and the VUV window **336** is composed of a VUV-transmitting material, as described above. At least a portion of the body **332** is shaped as a hollow cylinder to define an interior that in practice is filled with a plasma-forming gas. The main portion **334** extends along a longitudinal axis **350** between a first end **352** and a second end **354**. In the present embodiment, the VUV window **336** is disk-shaped and oriented perpendicularly to the longitudinal axis **350**. The VUV window **336** is attached to the main portion **334** at the first end **352**, and may be considered as defining or forming a part of the first end **352**.

[0039] Also in the present embodiment the main portion **334** includes an inner section **356** and an outer section **358**, both of which may be cylindrical. The inner section **356** coaxially surrounds the longitudinal axis **350** and the outer section **358** coaxially surrounds the inner section **356**, thereby forming an axially elongated interior having an annular cross-section (i.e., an annular interior space). The outer section **358** extends between the first end **352** and the second end **354**. The inner section **356** includes a closed first end **362** and an open second end **364**, such that the inner section **356** surrounds a cylindrical space that is outside the interior. The first end **362** of the inner section **356** is axially spaced from the VUV window **336**, thereby defining a cylindrical interior space adjacent to the annular interior space. The second end **364** of the inner section **356** may be axially coextensive with the second end **354** of the outer section **358**, with an annular wall **366** of the body **332** adjoining the inner section **356** and outer section **358** at this location. The annular wall **366** may be part of the inner section **356**, part of the outer

section **358**, or a separate part. The VUV window **336** may be hermetically sealed to the main portion **334**, and separate parts of the main portion **334** may be hermetically sealed together, using glass frit material. One or more gas ports **342** may be formed through the thickness of the outer section **358**, and may be sealable as described above.

[0040] The VUV photon source **324** also includes a first electrode **372** and a second electrode **374**, both of which may be disposed on locations of the body **332** outside the interior and thus isolated from the electrical discharges and energetic plasma components generated in the interior. The first electrode **372** and second electrode **374** may be composed of any highly electrically conductive materials suitable for the voltages contemplated, such as various metals and metal alloys (e.g., brass, copper, oxygen-free copper, etc.). Generally, the first electrode **372** and second electrode **374** are separated (spaced from each other) by a gap in the interior, and at least one solid dielectric barrier is positioned between the first electrode **372** and second electrode **374**. In the present embodiment, the first electrode **372** includes an axial electrode section **376** disposed on the VUV window **336** and a radial electrode section **378** disposed on the outer section **358**. The second electrode **374** is disposed on the first end **362** of the inner section **356** in the cylindrical space surrounded by the inner section **356**. The axial electrode section **376** and the second electrode **374** are spaced from each other along the longitudinal axis **350**. Thus, the VUV window **336** and the inner section **356** serve as dielectric barriers between the axial electrode section **376** and the second electrode **374**. The radial electrode section **378** and the second electrode **374** are spaced from each other along a direction radial to the longitudinal axis **350**. Thus, the inner section **356** and outer section **358** serve as dielectric barriers between the radial electrode section **378** and the second electrode **374**.

[0041] The first electrode **372** may be grounded or biased to a non-zero voltage, and the second electrode **374** may serve as the high-voltage electrode. As schematically shown, an insulated high-voltage lead wire **380** runs through the cylindrical space surrounded by the inner section **356** to place the second electrode **374** in signal communication with a high-voltage power source **338**. A portion of the cylindrical space occupied by the second electrode **374** and its connection with the lead wire **380** may be filled with an electrical insulator **382** such as a high-voltage potting compound to prevent unwanted discharges from the second electrode **374**. One or more conduits **384** and **386** may extend into the cylindrical space for circulating a heat

transfer medium. The conduits **384** and **386** may be part of a cooling system **240** (Figure 2) as described above.

[0042] To maximize transmission of VUV photons through the VUV window **336**, the axial electrode section **376** of the first electrode **372** may have a highly open structure. As one example, 80% or greater of the total surface area occupied by the axial electrode section **376** on the VUV window **336** may be open (i.e., devoid of electrode material). The axial electrode section **376** may, for example, be structured as a mesh or grid formed by a plurality of parallel wires running in one or more directions. The axial electrode section **376** may be fabricated by any suitable technique, and may be secured to the VUV window **336** by any suitable technique. The radial electrode section **378** may be a contiguous band or layer of metallization extending around the perimeter of the outer section **358**. The axial electrode section **376** and radial electrode section **378** may or may not be electrically interconnected to each other; in either case, they are both in signal communication with the power circuitry in a configuration appropriate for generating a DBD in the photon source's interior.

[0043] In some embodiments, the axial electrode section **376** may be formed by a metallization process in which a two-dimensional grid is patterned directly onto the VUV window **336**. This process may ensure intimate contact between the metal grid and the VUV window **336** without any gaps. Otherwise, electrical discharges could occur in gaps between the VUV window **336** and the grid and damage the VUV window **336**. The metallization process may entail deposition of a thin film directly on the VUV window **336**. Several deposition techniques may be suitable, one non-limiting example being electron beam (e-beam) evaporation. The thin film may be formed as a composite or intermetallic such as, for example, by depositing 100 nm Ti to promote adhesion followed by 300 nm Au. As a further example, the radial electrode section **378** may be structured as 100 nm Ti/ 100 nm Pt/ 300 nm Au, where the platinum (Pt) is added for solderability. Prior to depositing the electrode materials, the target surfaces may be prepared as needed to according to known techniques, such as cleaning with a solvent and/or oxygen plasma, etc.

[0044] In operation, a periodic voltage potential is applied between the first electrode **372** and second electrode **374**, generating a DBD as schematically depicted in Figure 3B by filamentary micro-discharges **384**. The gas exposed to the DBD forms plasma containing short-lived excimers that emit VUV photons. As illustrated, the spatial orientation of the micro-

discharges **384** may have axial and/or radial components, as the voltage potential is applied across both the axial gap between the axial electrode section **376** and the second electrode **374** and the radial gap between the radial electrode section **378** and the second electrode **374**. Initially, the micro-discharges may occur predominantly in the axial direction. As power is increased and the dielectric material between the axial electrode section **376** and the second electrode **374** becomes saturated, micro-discharges around the corners and radial micro-discharges may occur. This may increase the formation of excimers and resulting emission of VUV photons. Ultimately, VUV photons **326** are transmitted through the VUV window **336** predominantly in the axial direction.

[0045] In other embodiments, the radial electrode section **378** may be structured as a mesh or grid and the section of the body **332** covered by the radial electrode section **378** may be composed of a VUV-transmitting material. In such embodiments, VUV photons may be emitted from the VUV photon source **324** in radial directions as well as axial directions.

[0046] Figure 4 is a perspective view of an example of a VUV photon source **424** according to another embodiment. The VUV photon source includes a body **432** that includes a first end **452**, a second end **454**, an inner section **456**, a VUV window **436**, and one or more sealable gas ports (not shown). The body **432** may be generally similar to that described above and illustrated in Figures 3A and 3B, except that the VUV window **436** is an outer cylindrical section coaxially surrounding the inner section **456** and extending along a longitudinal axis **450** between the first end and **452** second end **454**. The other body components may be composed of a glass or other dielectric material. The VUV photon source **424** also includes a first electrode **472** and a second electrode **474** (high-voltage electrode) disposed on locations of the body **432** outside the interior. The first electrode **472** is disposed on the first end **452**, and the second electrode **474** is disposed on the inner section **456** in the cylindrical space surrounded by the inner section **456**. Thus, the first electrode **472** and second electrode **474** are separated by an axial gap in the interior. The first end **452** of the body **432** and the end of the inner section **456** on which the second electrode **474** is disposed serve as dielectric barriers between the first electrode **472** and the second electrode **474**.

[0047] The VUV photon source **424** may include power circuitry and provisions for cooling as generally described above and illustrated in Figures 3A and 3B. The operation of the VUV photon source **424** may be generally similar to that described above and illustrated in Figures 3A

and 3B. In the present embodiment, however, the micro-discharges of the DBD have a predominantly axial orientation (between the axially spaced first electrode **472** and second electrode **474**), and the VUV photons are transmitted through the VUV window **436** predominantly in radial directions.

[0048] Figure 5 is a perspective view of an example of a VUV photon source **524** according to another embodiment. The VUV photon source **524** includes a body **532** that includes a first end at which a VUV window **536** is located, a second end **554**, a main portion **534** extending along a longitudinal axis **550** between the VUV window **536** and the second end **554**, and one or more sealable gas ports (not shown). The body **532** may be generally similar to that described above and illustrated in Figures 3A and 3B, except that the main portion **554** includes one cylindrical section with no inner section. Excepting the VUV window **536**, the body components may be composed of a glass or other dielectric material. The VUV photon source **524** also includes a first electrode **572** and a second electrode **574** (high-voltage electrode) disposed on locations of the body **532** outside the interior. The first electrode **572** is disposed on the VUV window **536** and may be a mesh or grid as described above, and the second electrode **574** is disposed on the second end **554**. Thus, the first electrode **572** and second electrode **574** are separated by an axial gap in the interior. The VUV window **536** and the second end **554** serve as dielectric barriers between the first electrode **572** and the second electrode **574**.

[0049] The VUV photon source **524** may include power circuitry and provisions for cooling as generally described above and illustrated in Figures 3A and 3B. The operation of the VUV photon source **524** may be generally similar to that described above and illustrated in Figures 3A and 3B. In the present embodiment, however, the micro-discharges of the DBD have a predominantly axial orientation as in the embodiment illustrated in Figure 4. The VUV photons are transmitted through the VUV window **536** predominantly in the axial direction as in the embodiment illustrated in Figures 3A and 3B.

[0050] In some embodiments, the VUV photon sources such as illustrated in Figures 2-5 may include one or more mirrors in the body interior configured for reflecting VUV photons, which may increase the amount of VUV photons transmitted through the VUV window. A mirror may be an inside surface of the body's structure or the surface of a component located in the body's interior. Reflection of photons may be an inherent property of the inside surface, or the result of

a surface treatment or a coating or layer applied to the inside surface such as a reflective metal surface.

[0051] In some embodiments, the VUV photon sources such as illustrated in Figures 2-5 may include a getter located in the interior space, such as a coating of appropriate composition located at one or more regions of the inside surface of the dielectric structure. The getter may be utilized for scavenging undesired components (e.g., water vapor, carbon dioxide, etc.), and/or for providing a reservoir of the plasma-forming gas via reversible adsorption.

[0052] Figures 2-5 illustrate VUV photon sources having cylindrical geometries. It will be understood that a cylindrical geometry is but one example. More generally, the VUV photon sources disclosed herein may have any geometry suitable for generating and emitting VUV photons toward a desired target such as, for example, a sample to be photo-ionized.

[0053] Figure 6 is a schematic view of an example of a PI apparatus **604** according to other embodiments. The PI apparatus **604** may include an ionization chamber **622**; a sample inlet **618**, ion outlet **620** and vacuum line **610** communicating with the ionization chamber **622**; and a VUV photon source **624** positioned to direct VUV photons **626** toward a sample in the ionization chamber **622** to produce analyte ions. As illustrated, the body of the VUV photon source **624** may be disposed completely within the ionization chamber **622**. It will be understood that Figure 6 is merely illustrative of one example of possible positions of the sample inlet **618** and VUV photon source **624**, and that other positions are possible. For example, the respective positions of the sample inlet **618** and VUV photon source **624** may be reversed to prevent a direct line-of-sight path between the the sample inlet **618** and ion outlet **620**, thus preventing un-ionized particles or neutrals from entering the MS and causing chemical noise. The PI apparatus **604** may further include an ion guide **650** positioned generally between the sample inlet **618** and the ion outlet **620**.

[0054] Generally, the ion guide **650** may have any configuration effective for collecting a large amount of analyte ions from the ionization region with high (up to 100%) efficiency, compressing or focusing ions into a narrow beam along an ion guide axis **652**, and transferring the ions into the MS with high (up to 100%) efficiency, i.e., with minimal ion loss and minimal inclusion of non-analyte species. The ion guide **650** may generally include a set of ion guide electrodes **654** arranged about the ion guide axis **652** and surrounding an interior of the ion guide **650**, an ion guide entrance **656** leading into the interior, and an ion guide exit **658** leading out

from the interior. The VUV photon source **624** (or at least the VUV window **626**) may be positioned upstream of the ion guide entrance **656**, at the ion guide entrance **656**, or inside the ion guide **650**.

[0055] The PI apparatus **604** may also include a damping gas (or collision gas) source **660**. The damping gas may be an inert gas (e.g., helium, nitrogen, argon, etc.) that reduces the kinetic energy of analyte ions ("thermalizes" or "cools" the ions) in the ion guide **650** by collisions, under conditions (pressure, ion energies) that do not induce ion fragmentation or dissociation. The damping gas may be useful for slowing down neutral analyte molecules to increase the window of time available for their ionization, assisting in producing a compressed ion beam in the ion guide **650**, and/or reducing the energy spread of the ions. The ion guide electrodes **654** may be arranged in an "open" configuration that provides multiple pathways for neutral gas/vapor species from the sample inlet to flow toward a vacuum line **610**, and for damping gas to flow through the ion guide **650** and toward the vacuum line **610**. The ion guide **650** may thus serve as a filter for material that does not contribute to the MS signal.

[0056] The ion guide electrodes **654** may be in signal communication with one or more radio frequency (RF) voltage sources and direct current (DC) sources (not shown). An RF voltage or composite RF/DC voltage is applied to at least some of the ion guide electrodes **654** at an RF voltage drive frequency and magnitude suitable for generating a periodic, two-dimensional RF confining field that repels ions of a desired m/z range (i.e., analyte ions) away from the ion guide electrodes **654**, in a manner analogous to the RF trapping field applied by a linear ion trap. Hence, the RF confining field constrains the radial component of ion motion whereby the ions are focused in an ion cloud or beam along the ion guide axis **652**. The damping gas (when employed) may assist in focusing the ions. The selection of the RF voltage drive frequency and magnitude will depend on factors such as the m/z range to be stably focused and transmitted. In some embodiments, the RF voltage drive frequency ranges from 10 kHz to 10 MHz and the voltage magnitude ranges from 10 V to 1000 V peak-to-peak.

[0057] Separately, in some embodiments a DC voltage is applied to one or more of the ion guide electrodes **654**, and/or to additional ion optics components near the ion guide entrance **656** and ion guide exit **658**, so as to generate an axial DC voltage gradient (and resulting accelerating field) sufficient to promote motion of the ions toward the ion guide exit **658** The DC voltage may be useful for preventing ion stalling that may result from the use of damping gas, and/or

preventing ion stalling or reflection (back toward the ion guide entrance **656**) that may result from the RF confining field at a small ion guide exit **658**. In some embodiments, the ion guide **650** transmits ions to the MS efficiently without the use of either a flow of damping gas or an axial DC field.

[0058] In some embodiments, the ion guide electrodes **654** have a multipole configuration in which each ion guide electrode **654** is elongated generally in a direction from the ion guide entrance **656** to the ion guide exit **658**. The ion guide electrodes **654** may be parallel with each other and circumferentially spaced from each other about the ion guide axis **652**. The electrode set may be a quadrupole arrangement (two opposing pairs of electrodes) or a higher-order multipole arrangement with additional opposing pairs of electrodes (e.g., hexapole, octopole, etc.). For clarity, only one opposing pair of ion guide electrodes **654** is shown in Figure 6. In typical implementations, the RF confining field is produced by applying RF voltages to each ion guide electrode **654** such that the RF voltage on any given ion guide electrode **654** is 180 degrees out of the phase with the RF voltage on the adjacent ion guide electrode(s) **654**. DC voltages may be applied to some or all of the ion guide electrodes **654** and/or to entrance and exit lenses as needed to control the axial motion of the ions.

[0059] In some embodiments, the ion guide electrodes **654** are configured to compress the ion beam such that the ion beam has a converging profile, i.e., the cross-sectional area of the ion beam (in the plane perpendicular to the ion guide axis) converges (reduces) in the direction of the ion guide exit **658**. By such configuration, the ion beam acceptance is defined by the ion guide entrance **656** and a final ion beam emittance smaller than the beam acceptance is defined by the ion guide exit **658** (or by a conductance-limiting aperture adjacent to the ion guide exit **658**). In some embodiments, the converging ion beam is realized by the ion guide electrodes **654** likewise having a converging profile such that the cross-sectional area of the ion guide exit **658** is less than the cross-sectional area of the ion guide entrance **654**. Examples of the foregoing include electrode configurations termed “ion funnels” as appreciated by persons skilled in the art.

[0060] Figure 7 is a schematic view of an example of a PI apparatus **704** according to other embodiments. The PI apparatus **704** may include an ionization chamber (the outer structure of which is not shown); a sample inlet **718**, ion outlet (not shown) and vacuum line (not shown) communicating with the ionization chamber; one or more ionization devices (e.g., a first ionization device **724** and a second ionization device **725**) positioned to direct energy (depicted

by example as respective beams **726** and **727**) toward a sample **728** in the ionization chamber to produce analyte ions **730**; and an ion guide **750** positioned generally between the sample inlet **718** and the ion outlet. One or more of the ionization devices **724** and **725** may be a VUV photon source as described herein. One or more of the ionization devices **724** and **725** may be a different type of ionization device such as, for example, an electron ionization (EI) device, a chemical ionization (CI) device, a field ionization (FI) device, a laser desorption ionization (LDI) device, a matrix-assisted laser desorption ionization (MALDI) device, a corona discharge device, or an atmospheric pressure ionization (API) device.

[0061] The ion guide **750** includes a plurality of ion guide electrodes **754** arranged about an ion guide axis **752**, an ion guide entrance **756**, and an ion guide exit **758** axially spaced from the ion guide entrance **756**. In operation, radial RF confining fields and axial DC acceleration fields may be generated as described elsewhere in this disclosure. In the present embodiment, the ion guide **750** includes a first section **762** of ion guide electrodes beginning at the ion guide entrance **756**, followed by a second section **764** of ion guide electrodes terminating at the ion guide exit **758**. The first section **762** may have a constant or substantially constant cross-sectional area, and in some embodiments may be a cylindrical section. The first section **762** may be useful for increasing the residence time of neutral analytes in the ion guide **750** to improve ionization yield, for enhancing removal of neutral gas/vapor species, and/or for enhancing thermalization of as-produced analyte ions **730** through increased collisions with a damping gas. The second section **764** may have a cross-sectional area that tapers (is reduced) in the direction toward the ion guide exit **758**, and in some embodiments may be a conical section. The second section **764** is thus configured for producing a converged ion beam as described above. The axial lengths of the first section **762** and second section **764** may be the same or substantially the same, or may be different.

[0062] In some embodiments, the ion guide **750** may include more than one section of ion guide electrodes of constant cross-sectional area, and/or more than one section of ion guide electrodes of tapering cross-sectional area. A section of constant cross-sectional area may be interposed between two sections of tapering cross-sectional area, and/or a section of tapering cross-sectional area may be interposed between two sections of constant cross-sectional area.

[0063] In the present embodiment, the sample inlet **718** is positioned just upstream of, or at, or inside of the ion guide entrance **756**, such that neutral sample components **728** are discharged

from the sample inlet **718** directly into the ion guide **750** and the ionization region is located at least partially in the ion guide **750**. In the present embodiment, the ionization devices **724** and **725** are positioned at or near the ion guide entrance **756**, but in other embodiments may be positioned in other locations. As an example, Figure 7 illustrates an alternative first ionization device **724'** and second ionization device **725'** positioned outside the ion guide **750** at intermediate points along the axial length of the ion guide **750**. Respective energy beams **726'** and **727'** from the alternative ionization devices **724'** and **725'** may be transmitted through apertures **766** and **768** formed through certain ion guide electrodes **754** or through spaces between adjacent ion guide electrodes **754**. It will be understood that in other embodiments, a single ionization device or more than two ionization devices may be provided of the same or different type.

[0064] It will be understood that Figure 7 schematically illustrates the outer profile or envelope of the interior region defined by the electrode set. In practice a number of ion guide electrodes **754**, individually addressable by voltage sources, may be spaced from each other circumferentially about the ion guide axis **752**, or axially along the ion guide axis **752**. The present disclosure encompasses various embodiments in which the ion guide electrodes **754** are configured for providing a converging ion confining region as described above.

[0065] In some embodiments, the ion guide electrodes may include a series of plate-shaped electrodes arranged transversely to the ion guide axis and axially spaced from each other, with each electrode having an aperture through which the ion guide axis passes. The aperture of the first electrode at the ion guide entrance may have the largest cross-sectional area, the aperture of the last electrode at the ion guide exit may have the smallest cross-sectional area, the apertures of one or more electrodes between the first and last electrodes may have cross-sectional areas that successively reduce from the largest to the smallest cross-sectional area. Examples of this type of ion guide are disclosed in U.S. Patent App. Pub. No. 2011/0147575, the entire contents of which are incorporated herein by reference. In other embodiments, the ion guide electrodes may include a multipole arrangement similar to that described above in conjunction with Figure 6, but with the electrodes oriented so as to converge toward each other in the direction of the ion guide exit i.e., at an angle to the ion guide axis, such that the cross-sectional area of the interior region at the ion guide entrance is greater than the cross-sectional area at the ion guide exit. Examples of this type of ion guide are disclosed in U.S. Patent No. 8,193,489, the entire contents of which

are incorporated herein by reference. In other embodiments, the ion guide electrodes may include a multipole arrangement of generally parallel electrodes, but the diameters of the electrodes are varied along the axial direction such that the cross-sectional area of the interior region at the ion guide entrance is greater than the cross-sectional area at the ion guide exit. Examples of this type of ion guide are disclosed in U.S. Patent No. 8,124,930, the entire contents of which are incorporated herein by reference. In other embodiments, the ion guide electrodes may include a longitudinal or transverse "RF carpet" arrangement with converging geometry, examples of which are disclosed in U.S. Patent App. Serial No. 13/345,392, titled "RADIO FREQUENCY (RF) ION GUIDE FOR IMPROVED PERFORMANCE IN MASS SPECTROMETERS", the entire contents of which are incorporated herein by reference.

[0066] In other embodiments, the ion guide electrodes may generally have a parallel, elongated multipole configuration as schematically shown, for example, in Figure 6. In this case, a converging ion confining region may be generated by varying the RF confining field such that it has a predominant higher-order multipole field component (e.g., a hexapole component) at the ion guide entrance and a predominant lower-order multipole field component (e.g., a quadrupole component) at the ion guide exit. This may be accomplished by applying appropriate RF voltages to the ion guide electrodes, which in some embodiments may be axially segmented to facilitate varying the RF confining field for this purpose. A fuller description of this approach and additional examples of electrode arrangements are provided in U.S. Patent No. 8,124,930, the entire contents of which are incorporated herein by reference.

[0067] EXEMPLARY EMBODIMENTS

[0068] Exemplary embodiments provided in accordance with the presently disclosed subject matter include, but are not limited to, the following:

[0069] 1. A vacuum ultraviolet (VUV) photon source, comprising: a body enclosing an interior and comprising a VUV window; a first electrode disposed on the body outside the interior; a dielectric barrier; and a second electrode disposed on the dielectric barrier outside the interior, and separated from the first electrode by a gap in the interior, wherein the dielectric barrier is disposed between the first electrode and the second electrode.

[0070] 2. The VUV photon source of embodiment 1, comprising a driver in signal communication with the second electrode and configured for applying a periodic voltage having

a magnitude ranging from 3 kV to 60 kV peak-to-peak and a frequency ranging from 50 Hz to 300 kHz.

[0071] 3. The VUV photon source of embodiment 1 or 2, comprising a driver in signal communication with the second electrode and configured for applying a periodic voltage having a magnitude and a frequency effective for generating a dielectric barrier discharge plasma from a gas in the gap, wherein the gas is selected from the group consisting of a noble gas, a combination of two or more noble gases, and a combination of a non-noble gas and one or more noble gases.

[0072] 4. The VUV photon source of any of embodiments 1-3, comprising a driver in signal communication with the second electrode and configured for applying a periodic voltage having a magnitude and a frequency effective for generating dielectric barrier discharge-induced excimers in the gap that emit photons in the VUV range.

[0073] 5. The VUV photon source of any of embodiments 1-4, wherein the body contains a gas in the gap selected from the group consisting of a noble gas, a combination of two or more noble gases, and a combination of a non-noble gas and one or more noble gases.

[0074] 6. The VUV photon source of any of embodiments 1-5, wherein the body comprises a gas port communicating with the interior and configured for fluidly isolating the interior from an environment outside the VUV photon source.

[0075] 7. The VUV photon source of embodiment 6, wherein the gas port is configured for coupling with a gas transport system fluidly isolated from the outside environment.

[0076] 8. The VUV photon source of any of embodiments 1-7, wherein the VUV window has a composition selected from the group consisting of magnesium fluoride, calcium fluoride, and lithium fluoride.

[0077] 9. The VUV photon source of any of embodiments 1-8, comprising a conduit positioned to transport a coolant into thermal contact with the second electrode.

[0078] 10. The VUV photon source of any of embodiments 1-9, wherein the body comprises an inner section coaxially disposed about a longitudinal axis and an outer section surrounding the inner section, the interior includes an annular region between the inner section and the outer section, and the inner section comprises the dielectric barrier.

[0079] 11. The VUV photon source of embodiment 10, wherein the first electrode and the second electrode are spaced from each other along the longitudinal axis.

[0080] 12. The VUV photon source of embodiment 10, wherein the first electrode is disposed on the outer section, and the first electrode and the second electrode are spaced from each other along a direction radial to the longitudinal axis.

[0081] 13. The VUV photon source of embodiment 10, wherein the first electrode comprises an axial electrode section and a radial electrode section, the axial electrode section and the second electrode are spaced from each other along the longitudinal axis, and the radial electrode section and the second electrode are spaced from each other along a direction radial to the longitudinal axis.

[0082] 14. The VUV photon source of embodiment 10, wherein the outer section comprises the VUV window.

[0083] 15. The VUV photon source of embodiment 14, wherein the first electrode and the second electrode are spaced from each other along the longitudinal axis.

[0084] 16. The VUV photon source of embodiment 10, wherein the VUV window is disposed at an axial end of the outer section.

[0085] 17. The VUV photon source of embodiment 16, wherein the first electrode is disposed on the outer section, and the first electrode and the second electrode are spaced from each other along a direction radial to the longitudinal axis.

[0086] 18. The VUV photon source of embodiment 17, wherein the first electrode comprises an axial electrode section disposed on the VUV window and a radial electrode section disposed on the outer section.

[0087] 19. The VUV photon source of any of embodiments 1-9, wherein the body comprises an axial end spaced from the dielectric barrier along a longitudinal axis.

[0088] 20. The VUV photon source of embodiment 19, wherein the axial end comprises the VUV window.

[0089] 21. The VUV photon source of any of embodiments 1-20, wherein the body comprises an inner surface configured for reflecting VUV photons.

[0090] 22. A photo-ionization (PI) apparatus, comprising: a chamber comprising a sample inlet and an ion outlet; and the VUV photon source of any of embodiments 1-21 disposed in the chamber.

[0091] 23. The PI apparatus of embodiment 22, comprising a vacuum system configured for maintaining the chamber at a pressure ranging from 0.01 to 100 Torr.

[0092] 24. The PI apparatus of embodiment 22 or 23, wherein the interior of the body contains a gas at a pressure ranging from 200 to 1500 Torr

[0093] 25. The PI apparatus of any of embodiments 22-24, wherein the chamber comprises a wall, the VUV photon source extends through the wall, and the second electrode is fluidly isolated from an interior of the chamber.

[0094] 26. The PI apparatus of any of embodiments 22-25, comprising an ion funnel in the chamber, wherein the VUV photon source is positioned to direct VUV photons at or near an entrance of the ion funnel.

[0095] 27. A mass spectrometry (MS) system, comprising: the PI apparatus of any of embodiments 22-26; and a mass analyzer communicating with the ion outlet.

[0096] 28. The MS system of embodiment 27, comprising an analytical separation device communicating with the sample inlet.

[0097] 29. A method for generating vacuum ultraviolet (VUV) photons, comprising: generating a dielectric barrier discharge (DBD) in an interior of a photon source by applying a periodic voltage between a first electrode and a second electrode, wherein the first electrode and the second electrode are disposed outside the interior and are separated by a dielectric barrier and a gap in the interior, and wherein the DBD produces excimers from a gas in the gap; and transmitting VUV photons emitted from the excimers through a window of the photon source.

[0098] 30. The method of embodiment 29, wherein the first electrode and the second electrode are spaced from each other along a longitudinal axis, the window is coaxially disposed about the longitudinal axis, the DBD has a predominantly axial orientation, and the VUV photons are transmitted through the window predominantly in a radial direction.

[0099] 31. The method of embodiment 29, wherein the first electrode and the second electrode are spaced from each other along a longitudinal axis, the first electrode is disposed on the window, the DBD has a predominantly axial orientation, and the VUV photons are transmitted through the window predominantly in an axial direction.

[00100] 32. The method of embodiment 29, wherein the first electrode comprises an axial electrode section and a radial electrode section, the axial electrode section and the second electrode are spaced from each other along a longitudinal axis, the radial electrode section is coaxially disposed about the second electrode relative to the longitudinal axis, the DBD has a

spatial orientation comprising axial and radial components, and the VUV photons are transmitted through the window predominantly in an axial direction.

[00101] 33. A method for ionizing a sample, the method comprising: introducing the sample into a chamber; and exposing the sample to VUV photons by generating the VUV photons according to the method of any of embodiments 29-32, wherein the VUV photons are transmitted into the chamber from the window.

[00102] 34. The method of embodiment 33, comprising maintaining the chamber at a pressure ranging between 0.01 and 100 Torr.

[00103] 35. The method of embodiment 33 or 34, wherein exposing the sample occurs at or near an entrance of an ion funnel, and further comprising operating the ion funnel to compress ions produced by photoionization into a converging beam.

[00104] 36. A method for analyzing a sample, the method comprising: ionizing the sample according to the method of any of embodiments 33-35 to produce ions; and transmitting the ions into a mass analyzer.

[00105] 37. The method of embodiment 36, comprising, prior to ionizing, subjecting the sample to analytical separation, and introducing the separated sample into the chamber.

[00106] 38. An analytical system, comprising:

the PI apparatus of embodiment 22; and

an analytical instrument communicating with the ion outlet.

[00107] 39. The system of embodiment 38, wherein the analytical instrument comprises an ion mobility spectrometer or an MS.

[00108] In the above description, an MS system is presented as an example of an operating environment for VUV photon sources disclosed herein. It will be understood, however, that the VUV photon sources are not limited to operating in conjunction with MS systems, but instead may be utilized in any application entailing the use of VUV photons.

[00109] It will be understood that the term "in signal communication" as used herein means that two or more systems, devices, components, modules, or sub-modules are capable of communicating with each other via signals that travel over some type of signal path. The signals may be communication, power, data, or energy signals, which may communicate information, power, or energy from a first system, device, component, module, or sub-module to a second

system, device, component, module, or sub-module along a signal path between the first and second system, device, component, module, or sub-module. The signal paths may include physical, electrical, magnetic, electromagnetic, electrochemical, optical, wired, or wireless connections. The signal paths may also include additional systems, devices, components, modules, or sub-modules between the first and second system, device, component, module, or sub-module.

[00110] More generally, terms such as "communicate" and "in . . . communication with" (for example, a first component "communicates with" or "is in communication with" a second component) are used herein to indicate a structural, functional, mechanical, electrical, signal, optical, magnetic, electromagnetic, ionic or fluidic relationship between two or more components or elements. As such, the fact that one component is said to communicate with a second component is not intended to exclude the possibility that additional components may be present between, and/or operatively associated or engaged with, the first and second components.

[00111] It will be understood that various aspects or details of the invention may be changed without departing from the scope of the invention. Furthermore, the foregoing description is for the purpose of illustration only, and not for the purpose of limitation—the invention being defined by the claims.

CLAIMS

What is claimed is:

1. A vacuum ultraviolet (VUV) photon source, comprising:

a body enclosing an interior and comprising a VUV window; a first electrode disposed on the body outside the interior; a dielectric barrier; and

a second electrode disposed on the dielectric barrier outside the interior, and separated from the first electrode by a gap in the interior, wherein the dielectric barrier is disposed between the first electrode and the second electrode.

2. The VUV photon source of claim 1, comprising a driver in signal communication with the second electrode and configured for applying a periodic voltage having a magnitude and a frequency effective for generating a dielectric barrier discharge plasma from a gas in the gap, wherein the gas is selected from the group consisting of a noble gas, a combination of two or more noble gases, and a combination of a non-noble gas and one or more noble gases.

3. The VUV photon source of claim 1, wherein the body comprises a gas port communicating with the interior and configured for fluidly isolating the interior from an environment outside the VUV photon source.

4. The VUV photon source of claim 1, wherein the VUV window has a composition selected from the group consisting of magnesium fluoride, calcium fluoride, and lithium fluoride.

5. The VUV photon source of claim 1, comprising a conduit positioned to transport a coolant into thermal contact with the second electrode.

6. The VUV photon source of claim 1, wherein the body comprises an inner section coaxially disposed about a longitudinal axis and an outer section surrounding the inner section, the interior includes an annular region between the inner section and the outer section, and the inner section comprises the dielectric barrier.

7. The VUV photon source of claim 6, wherein the first electrode and the second electrode are spaced from each other along the longitudinal axis.

8. The VUV photon source of claim 6, wherein the first electrode is disposed on the outer section, and the first electrode and the second electrode are spaced from each other along a direction radial to the longitudinal axis.

9. The VUV photon source of claim 6, wherein the first electrode comprises an axial electrode section and a radial electrode section, the axial electrode section and the second electrode are spaced from each other along the longitudinal axis, and the radial electrode section and the second electrode are spaced from each other along a direction radial to the longitudinal axis.

10. The VUV photon source of claim 6, wherein the outer section comprises the VUV window.

11. The VUV photon source of claim 10, wherein the first electrode and the second electrode are spaced from each other along the longitudinal axis.

12. The VUV photon source of claim 6, wherein the VUV window is disposed at an axial end of the outer section.

13. The VUV photon source of claim 12, wherein the first electrode is disposed on the outer section, and the first electrode and the second electrode are spaced from each other along a direction radial to the longitudinal axis.

14. The VUV photon source of claim 13, wherein the first electrode comprises an axial electrode section disposed on the VUV window and a radial electrode section disposed on the outer section.

15. The VUV photon source of claim 1, wherein the body comprises an axial end spaced from the dielectric barrier along a longitudinal axis.

16. The VUV photon source of claim 15, wherein the axial end comprises the VUV window.

17. A method for generating vacuum ultraviolet (VUV) photons, comprising:

generating a dielectric barrier discharge (DBD) in an interior of a photon source by applying a periodic voltage between a first electrode and a second electrode, wherein the first electrode and the second electrode are disposed outside the interior and are separated by a dielectric barrier and a gap in the interior, and wherein the DBD produces excimers from a gas in the gap; and

transmitting VUV photons emitted from the excimers through a window of the photon source.

18. The method of claim 17, wherein the first electrode and the second electrode are spaced from each other along a longitudinal axis, the window is coaxially disposed about the longitudinal axis, the DBD has a predominantly axial orientation, and the VUV photons are transmitted through the window predominantly in a radial direction.

19. The method of claim 17, wherein the first electrode and the second electrode are spaced from each other along a longitudinal axis, the first electrode is disposed on the window, the DBD has a predominantly axial orientation, and the VUV photons are transmitted through the window predominantly in an axial direction.

20. The method of claim 17, wherein the first electrode comprises an axial electrode section and a radial electrode section, the axial electrode section and the second electrode are spaced from each other along a longitudinal axis, the radial electrode section is coaxially disposed about the second electrode relative to the longitudinal axis, the DBD has a spatial orientation comprising axial and radial components, and the VUV photons are transmitted through the window predominantly in an axial direction.

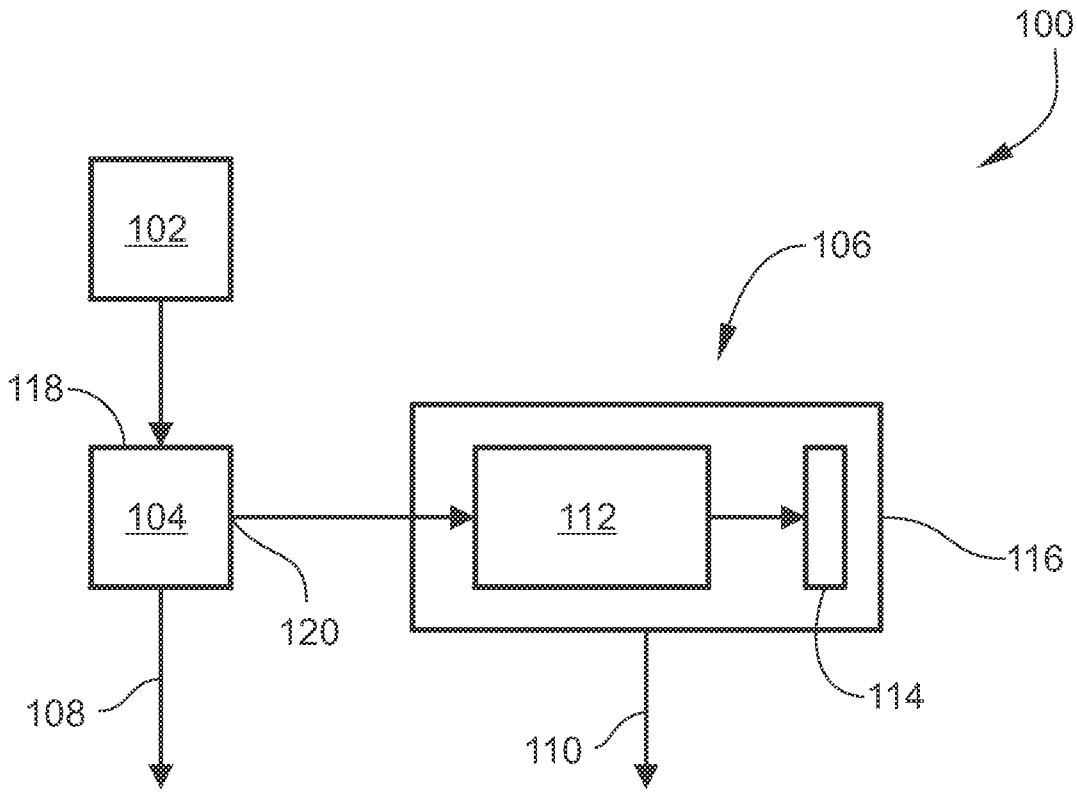


Fig. 1

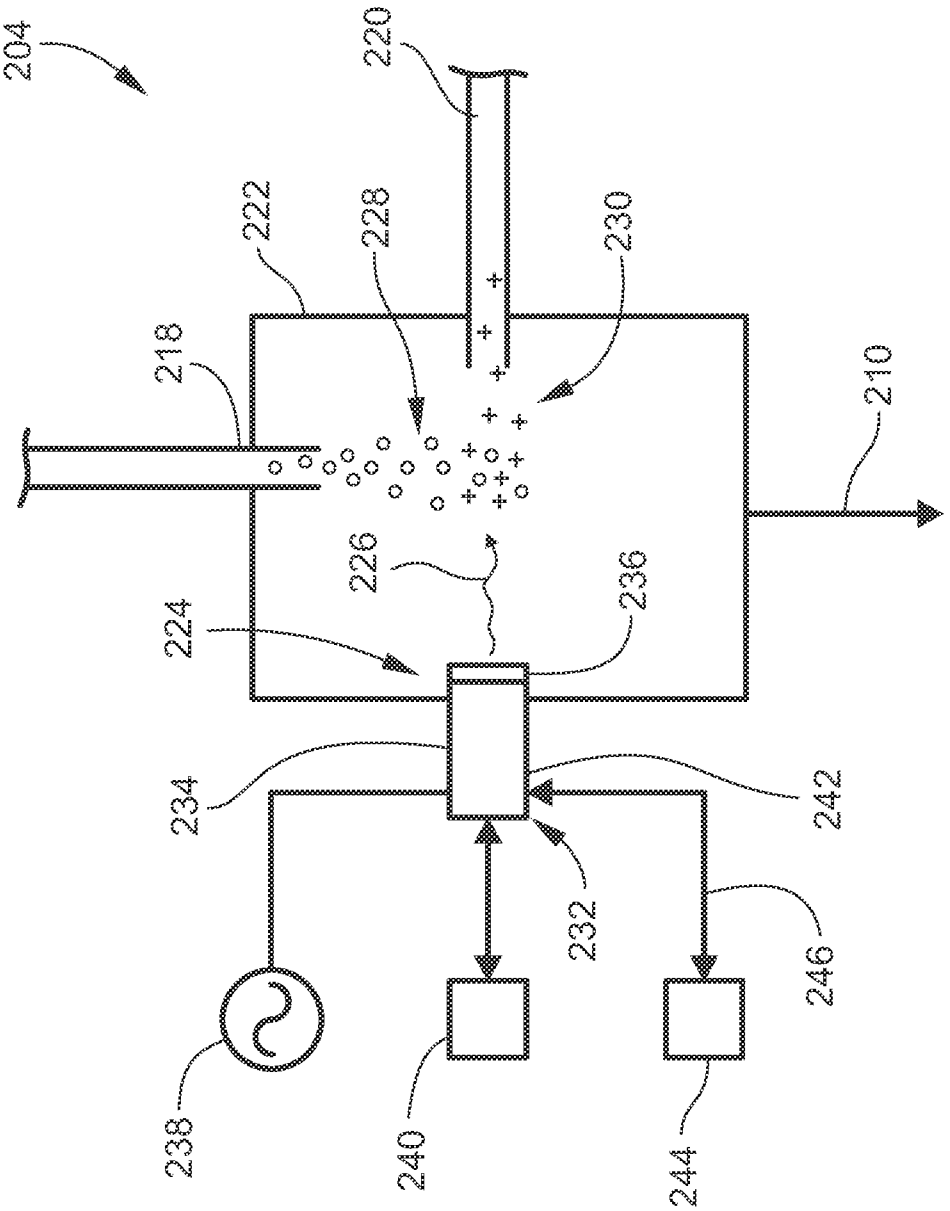

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Fig. 2

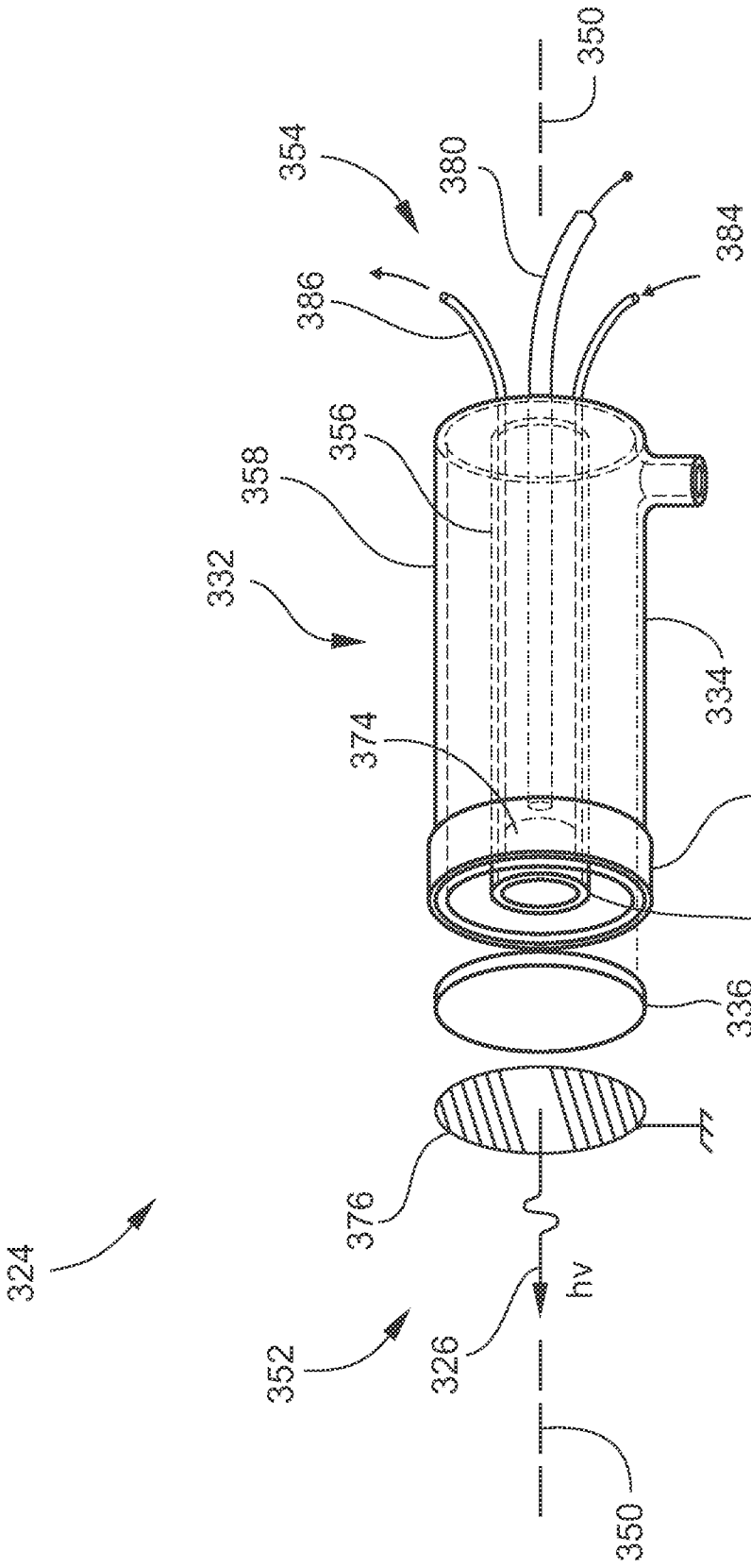

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Fig. 3A

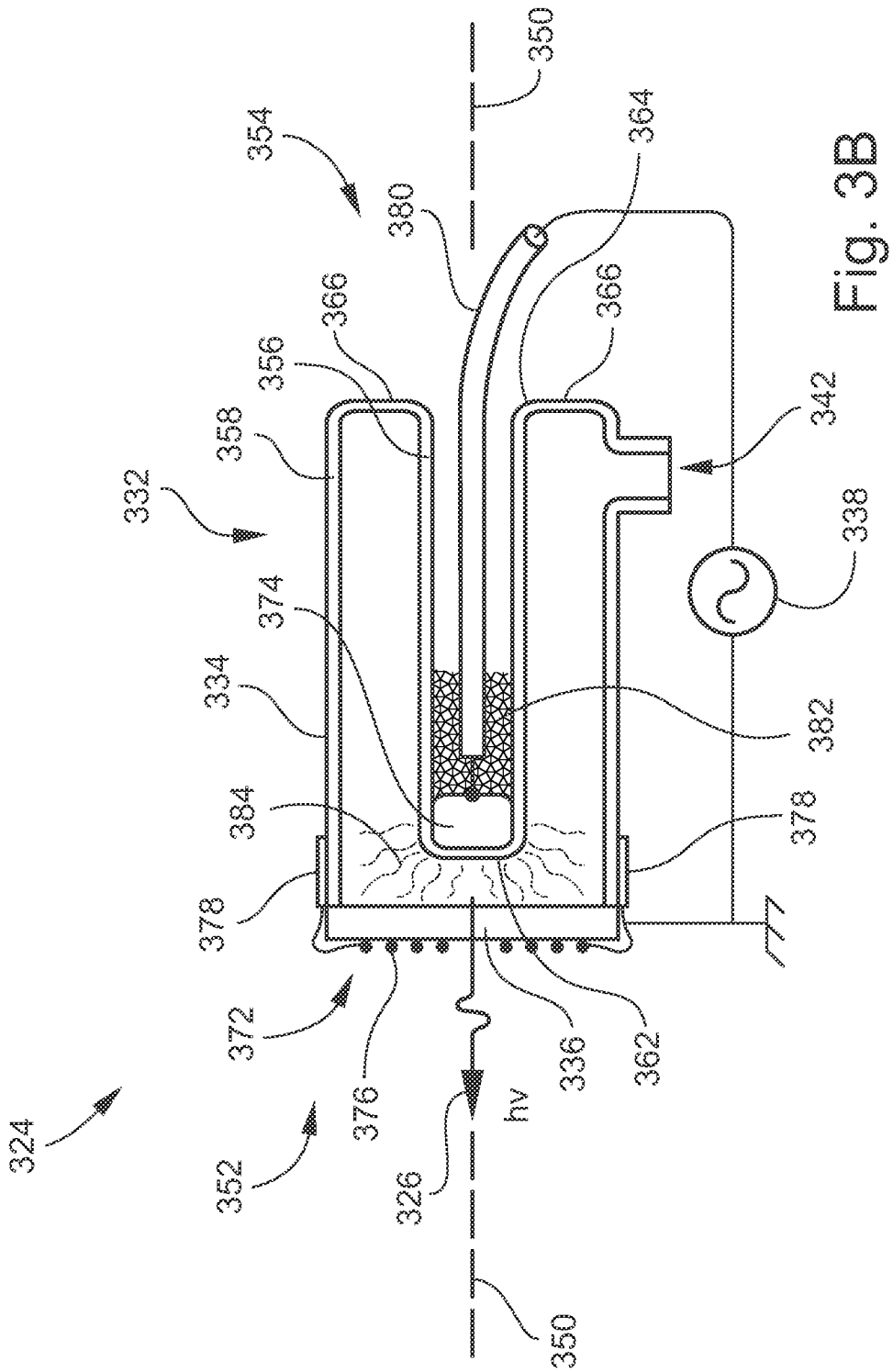

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Fig. 3B

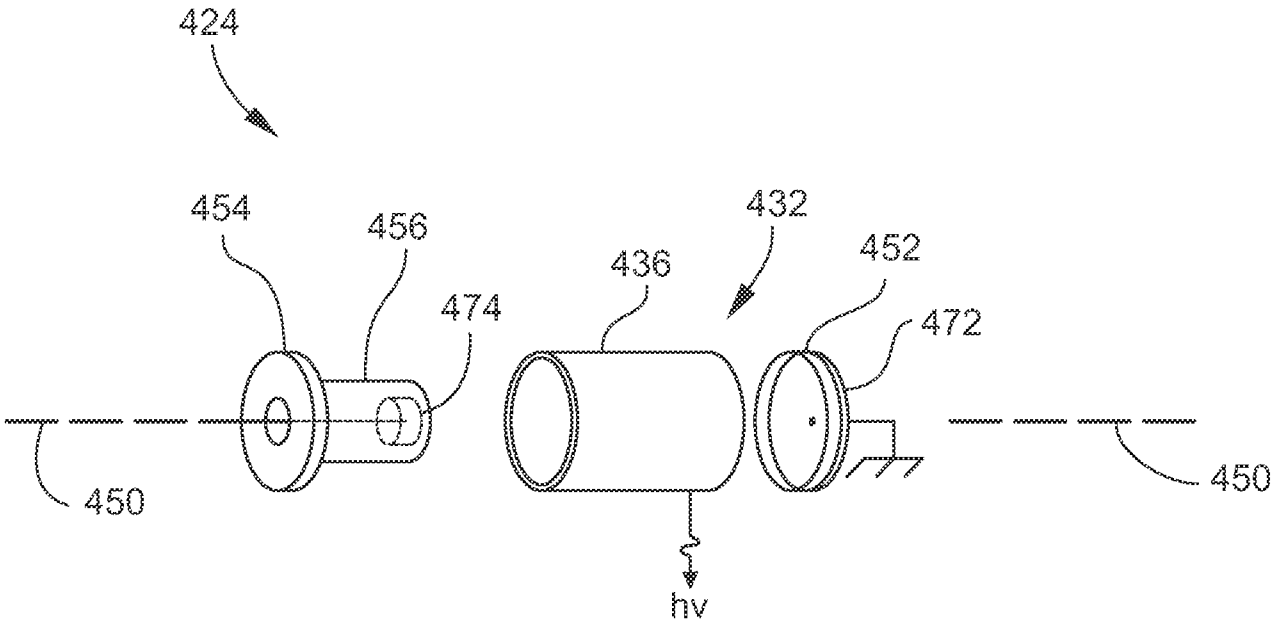

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Fig. 4

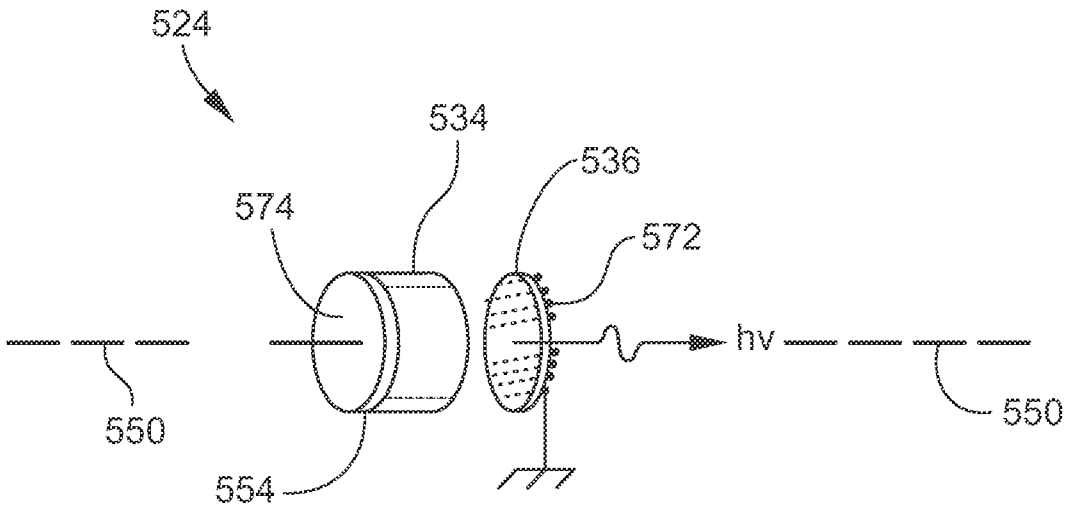

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Fig. 5

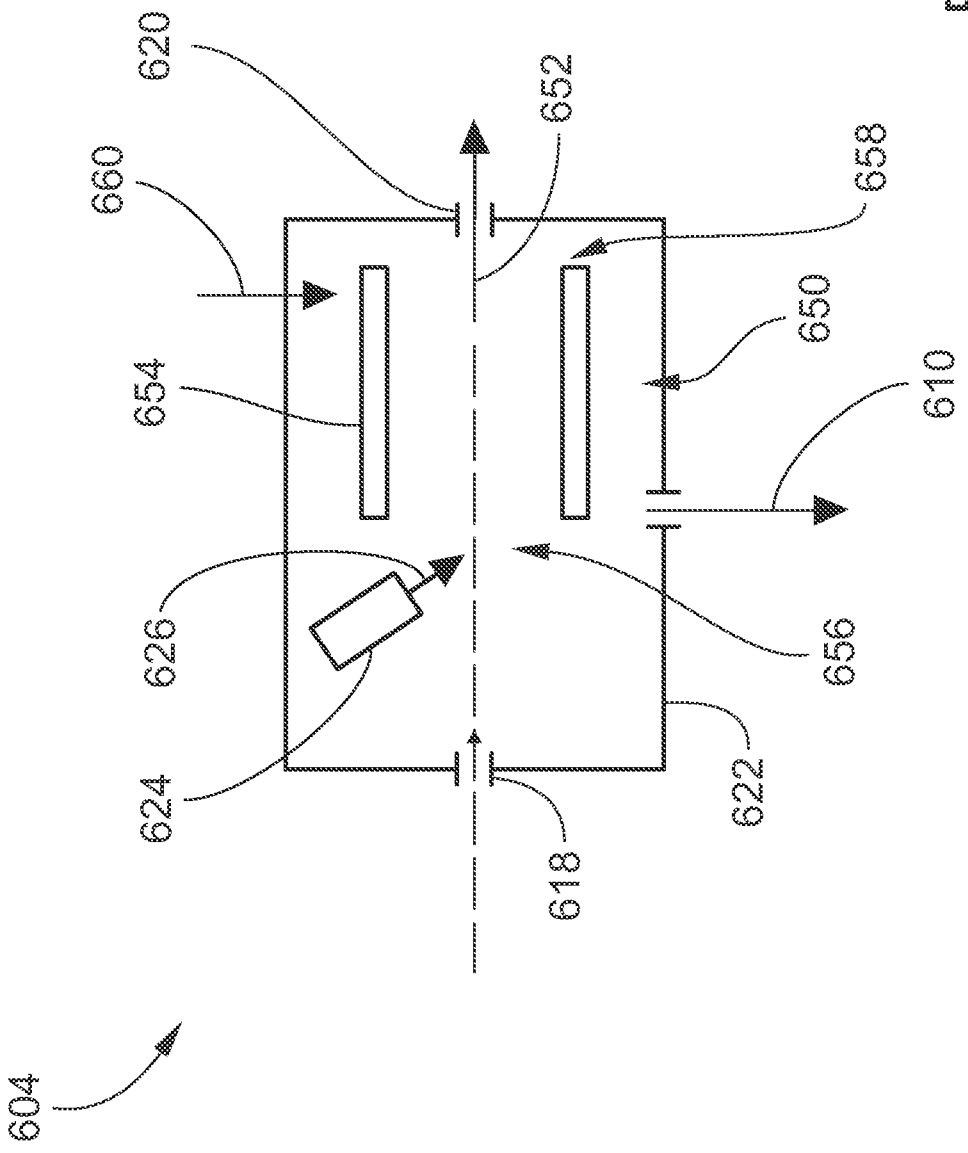


Fig. 6

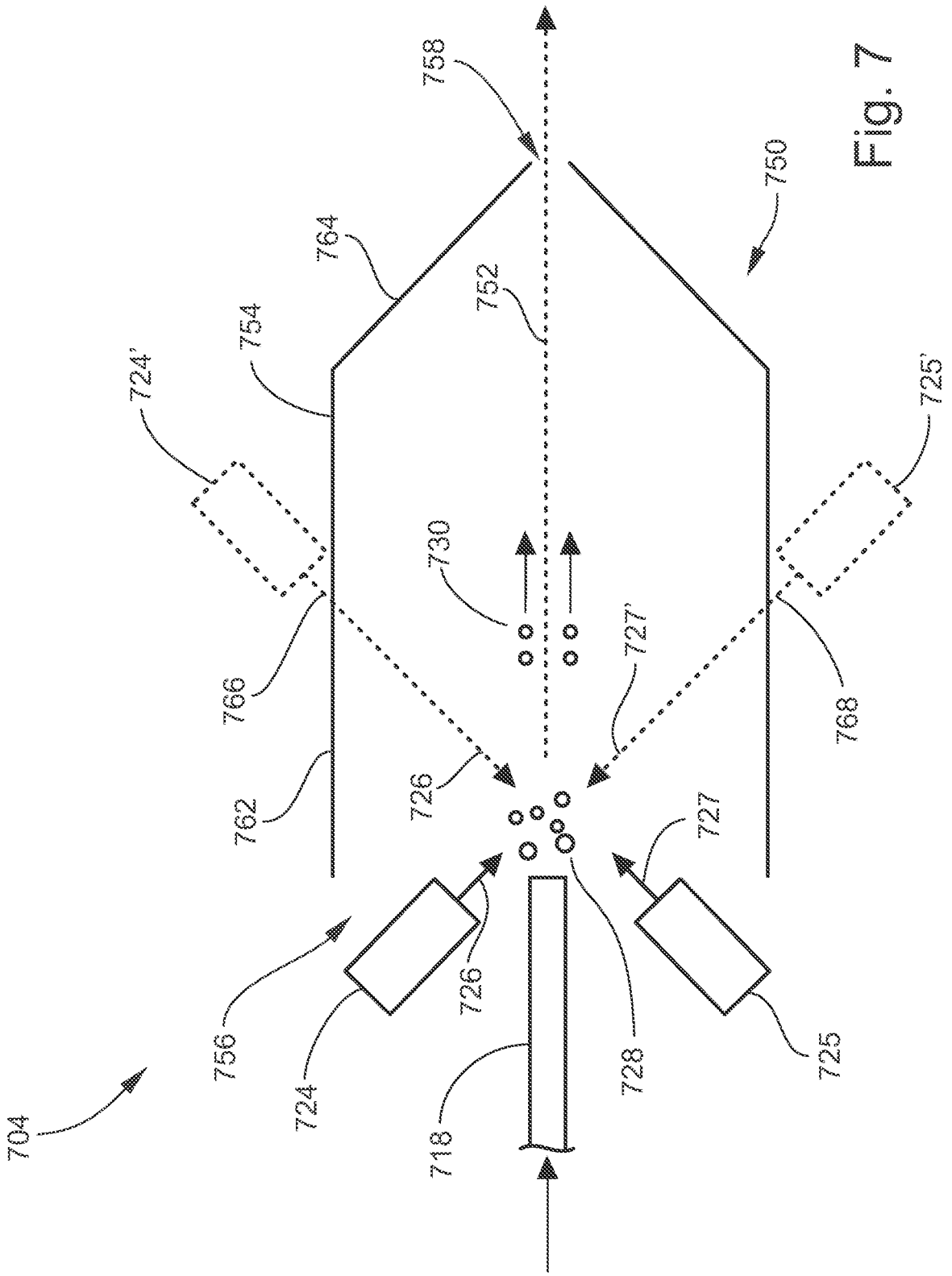

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Fig. 7

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/069720

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01J65/04 G01J3/10
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
H01J G01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP H07 220689 A (USHIO ELECTRIC INC) 18 August 1995 (1995-08-18)	1,2,6-20
Y	paragraph [0010]; figures 1,2,3	5
X	JP H08 236084 A (USHIO ELECTRIC INC) 13 September 1996 (1996-09-13)	1-4,6,8, 12,13, 15-17
Y	figures 1,4 paragraphs [0003], [0024]	5
Y	JP H09 274893 A (USHIO ELECTRIC INC) 21 October 1997 (1997-10-21) paragraphs [0002] - [0003]; figures 2-4	5
A	JP 2004 265770 A (USHIO ELECTRIC INC) 24 September 2004 (2004-09-24) paragraph [0046]	1-20

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
3 February 2014	12/02/2014

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Chevrier, Dominique

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2013/069720

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