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(54) Title: ARGON RECYCLING SYSTEM FOR AN INDUCTIVELY COUPLED PLASMA MASS SPECTROMETER

(57) Abstract: Certain configurations of systems and methods which can recycle argon used in an inductively coupled plasma mass spectrometer are described. In some configurations, the system may comprise two or more separate stages each of which can remove impurities from a fluid stream comprising the argon. In some instances, substantially pure argon is recovered using the systems and methods, and the substantially pure argon can be reused in the inductively coupled plasma mass spectrometer.

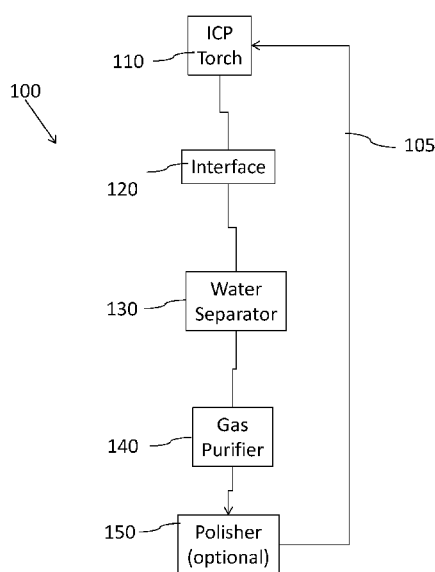


FIG. 1A

TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW,
KM, ML, MR, NE, SN, TD, TG).

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**ARGON RECYCLING SYSTEM FOR AN
INDUCTIVELY COUPLED PLASMA MASS SPECTROMETER**

[0001] TECHNOLOGICAL FIELD

[0002] This application is directed to systems and methods of recycling argon used in an inductively coupled plasma mass spectrometer.

[0003] BACKGROUND

[0004] Inductively coupled plasma mass spectrometry (ICP-MS) involves the use of an inductively coupled plasma to ionize analytes in a sample. Argon gas is used to sustain the inductively coupled plasma. The total argon gas flow rates can be 30 liters per minute or more.

[0005] SUMMARY

[0006] Certain illustrative configurations are directed to methods and systems which can recycle argon used in an inductively coupled plasma mass spectrometer. In some examples, the system may comprise two or more different stages which can be used to separate/purify argon from other species present in a fluid stream such as a gas stream. As noted herein, additional stages can also be included and/or it may be possible to omit one or more stages depending on the exact components present in an argon fluid stream exiting an inductively coupled plasma torch.

[0007] In one aspect, a method comprises collecting a fluid flow exiting from an inductively coupled plasma torch using an interface fluidically coupled to the inductively coupled plasma torch. The method may also comprise providing the collected fluid flow to a cooled, permeable support, e.g., one comprising an open cell metal foam or mesh, to remove water from the collected fluid flow to provide a substantially water free fluid flow. The method may also comprise providing the substantially water free fluid flow to a thermally active titanium open cell porous medium to remove gaseous impurities to provide a substantially pure argon flow. The method may also comprise providing the substantially pure argon flow to a metal foam

comprising single-walled carbon nanotubes to remove residual impurities from the substantially pure argon flow and provide substantially pure argon gas.

[0008] In certain embodiments, the method comprises providing the substantially pure argon gas back to an inlet of the inductively coupled plasma. In other examples, the method comprises symmetrically collecting the exiting fluid flow by isolating output from the inductively coupled plasma torch from surrounding air and without disturbing flow of an inductively coupled plasma sustained within the inductively coupled plasma torch. In some examples, the method comprises cooling the permeable support using a thermoelectric cooler. In certain instances, the method comprises heating the permeable support to liquefy cooled water to permit draining of the liquid water. In other examples, the method comprises heating the thermally active open cell titanium porous medium with an electric heater to thermally activate the open cell titanium porous medium. In certain embodiments, the method comprises configuring the single-walled carbon nanotubes to be present on a permeable support such as, for example, a metal foam or a metal mesh. In some instances, the method comprises controlling the temperature of the permeable support comprising the single-walled carbon nanotubes. In other examples, the method comprises filtering particulate material from the collected fluid flow prior to providing the collected fluid flow to the water separator. In certain embodiments, the method comprises filtering particulate material from the substantially water free fluid flow prior to providing the substantially water free fluid flow to the gas purifier. In some instances, the method comprises filtering particulate material from the substantially pure argon prior to providing the substantially pure argon flow to the polisher. In some examples, the method comprises configuring the gas purifier with a bypass line configured to bypass the polisher. In certain embodiments, the method comprises fluidically coupling a second polisher to the polisher. In certain instances, the method comprises collecting and storing the substantially pure argon. In some embodiments, the method comprises configuring the interface with a plurality of individual output ports.

[0009] In another aspect, recycling system configured to purify argon used in an inductively coupled plasma mass spectrometer is described. In some examples, the recycling system comprises an interface configured to fluidically couple to an inductively coupled plasma torch and receive fluid comprising argon exiting from the inductively coupled plasma torch, a water separator fluidically coupled to the interface, the water separator comprising a permeable support such as, for example, a metal foam or a metal mesh configured to be cooled and to remove water from the fluid comprising the argon received by the interface, a gas purifier device fluidically coupled to the water separator, the gas purifier comprising a titanium metal open cell porous medium configured to remove gaseous impurities from fluid comprising the argon, and a polisher fluidically coupled to the gas purifier device, the polisher comprising single-walled carbon nanotubes configured to remove residual impurities from the fluid flow comprising the argon to provide substantially pure argon gas.

[0010] In certain embodiments, the system comprise a fluid line configured to provide fluidic coupling between the polisher and the inductively coupled plasma torch to provide the substantially pure argon gas back to the inductively coupled plasma torch. In some examples, the interface is configured to isolate output from the torch from surrounding air to provide for symmetrical collection of the fluid comprising the argon without disturbing flow of the inductively coupled plasma. In other examples, the interface comprises a sliding dynamic seal. In certain embodiments, the interface comprises a plurality of channels. In some examples, the water separator comprises a thermoelectric cooler thermally coupled to the permeable support to cool the permeable support and freeze water vapor present within the flow comprising the argon. In certain instances, the water separator comprises a drain to remove liquid water from the gas purifier. In some examples, the gas purifier comprises the titanium metal open cell porous medium within a sealed nickel-chromium module. In other examples, the gas purifier comprises a heating device to thermally activate surfaces of the titanium metal open cell porous medium within the sealed nickel-chromium module. In some embodiments, the titanium metal open cell

porous medium is further configured to filter particulate matter in the fluid comprising the argon. In some examples, the polisher comprises a metal foam comprising the single-walled carbon nanotubes. In certain embodiments, the system may comprise a collector configured to receive argon from the polisher and store the argon. In other examples, the system may comprise a second polisher fluidically coupled to the polisher. In some examples, the water separator comprises a plurality of individual compartments comprising the permeable support. In other examples, the gas purifier comprises a plurality of individual compartments comprising the titanium metal open cell porous medium.

[0011] In an additional aspect, an inductively coupled mass spectrometer comprises an inductively coupled plasma torch, a mass analyzer fluidically coupled to the inductively coupled plasma torch and configured to receive ions from the inductively coupled plasma torch, an interface fluidically coupled to the inductively coupled plasma torch and configured to permit passage of ions to the mass analyzer and to collect fluid comprising argon exiting from the inductively coupled plasma torch, a water separator fluidically coupled to the interface, the water separator comprising a permeable support such as, for example, a metal foam or a metal mesh configured to be cooled and to remove water from the fluid comprising the argon received by the interface, a gas purifier device fluidically coupled to the water separator, the gas purifier comprising a thermally active titanium metal open cell porous medium configured to remove gaseous impurities from fluid comprising the argon, and a polisher fluidically coupled to the gas purifier device, the polisher comprising single-walled carbon nanotubes configured to remove residual impurities from the fluid flow comprising the argon to provide substantially pure argon gas.

[0012] In certain embodiments, the mass spectrometer further comprises a fluid line configured to provide fluidic coupling between the polisher and the inductively coupled plasma torch to provide the substantially pure argon gas back to the inductively coupled plasma torch. In some examples, the interface is configured to isolate output from the torch from surrounding air to

provide for symmetrical collection of the fluid comprising the argon without disturbing flow of the inductively coupled plasma. In other examples, the interface comprises a sliding dynamic seal. In some embodiments, the interface comprises a plurality of channels. In other examples, the water separator comprises a thermoelectric cooler thermally coupled to the permeable support to cool the permeable support and freeze water vapor present within the flow comprising the argon. In some instances, the water separator comprises a drain to remove liquid water from the gas purifier. In other examples, the gas purifier comprises a thermally active titanium metal open cell porous medium within a sealed nickel-chromium module. In some embodiments, the gas purifier comprises a heating device to thermally activate surfaces of the titanium metal open cell porous medium. In certain examples, the titanium metal open cell porous medium powder is further configured to filter particulate matter in the fluid comprising the argon. In other examples, the polisher comprises a permeable support, e.g., a metal foam or metal mesh, comprising the single-walled carbon nanotubes. In some instances, a collector configured to receive argon from the polisher and store the argon can be present. In some embodiments, the mass analyzer is selected from the group consisting of a quadrupole assembly, a magnetic sector analyzer and an ion trap. In other examples, the mass spectrometer may comprise a detector fluidically coupled to the mass analyzer, e.g., an electron multiplier, a Faraday cup, a scintillation plate and a multi-channel plate. In certain instances, the water separator comprises a plurality of individual compartments comprising the permeable support. In some examples, the gas purifier comprises a plurality of individual compartments comprising the titanium metal open cell porous medium. In another configuration, the mass spectrometer comprises a sample introduction device configured to provide sample to the inductively coupled plasma torch. In some instances, the sample introduction device comprises a nebulizer. In some examples, the mass analyzer comprises a double or triple quadrupole assembly and the detector comprises an electron multiplier.

[0013] In an additional aspect, an interface configured to collect a fluid flow comprising argon exiting an inductively coupled plasma while permitting passage of ions from the plasma to a mass analyzer, the interface comprising a seal and a quartz bonnet to prevent arcing between the plasma and the interface is disclosed.

[0014] In another aspect, a method of recycling argon used in an inductively coupled plasma comprises collecting argon in a fluid flow exiting the plasma, and cooling the collected argon in the fluid flow using a cooling jacket configured to cool an inductively coupled plasma torch.

[0015] Additional aspects, examples, embodiments and configurations are described further below.

[0016] **BRIEF DESCRIPTION OF THE SEVERAL VIEW OF THE DRAWINGS**

[0017] Certain configurations of systems and methods used to recycle argon used to sustain an inductively coupled plasma in a mass spectrometer are described below with reference to the accompanying figures in which:

[0018] FIG. 1A is a block diagram of various components of an argon recycling system, in accordance with certain examples;

[0019] FIG. 1B is an illustration of an interface fluidically coupled to a torch, in accordance with certain examples;

[0020] FIG. 2 is an illustration of an inductively coupled plasma torch, in accordance with certain examples;

[0021] FIG. 3 is an illustration of a water separator, in accordance with certain configurations;

[0022] FIG. 4 is another illustration of a water separator, in accordance with certain configurations;

[0023] FIG. 5 is an illustration of a gas purifier, in accordance with certain examples;

[0024] FIG. 6 is another illustration of a gas purifier, in accordance with certain configurations;

[0025] FIG. 7 is a block diagram of an inductively coupled plasma mass spectrometer (ICP-MS) system, in accordance with certain embodiments;

[0026] FIG. 8A, 8B, 8C and 8D are a photograph of components of a collector (FIGS. 8A, 8B and 8C) and an assembled collector coupled to a torch and a sampler cone (FIG. 8D), in accordance with certain examples;

[0027] FIG. 9 is a cross-sectional illustration of a system comprising an interface with a collector, in accordance with certain examples;

[0028] FIG. 10 is an illustration of a collector for collecting argon, in accordance with certain configurations; and

[0029] FIGS. 11A and 11B are illustrations showing a cooling jacket that can be used to collect the argon, in accordance with certain examples.

[0030] **DETAILED DESCRIPTION**

[0031] Various components are described below in connection with recycling systems that can be used with mass spectrometers that comprise an inductively coupled plasma to ionize a sample introduced into the mass spectrometer. The exact configuration of the recycling system and mass spectrometer can vary depending on the intended use of the mass spectrometer.

[0032] In certain embodiments and referring to FIG. 1A, a simplified block diagram of some components of an argon recycling system is shown. The system 100 can be used with an inductively coupled plasma (ICP) torch 110 and may comprise an interface 120 fluidically coupled to the ICP torch 110. As discussed in more detail below, the interface 120 can be configured to isolate the output from the ICP torch 110 from surrounding air and enable symmetrical collection of argon from the mass spectrometer orifice without any substantial plasma flow disturbance. The interface 120 may permit torch alignment through a dynamic seal and by using a quartz bonnet to prevent or avoid plasma-interface arcing. The dynamic seal can be configured for use without the need to use any sealants or gaskets to avoid plasma

contamination. The interface 120 can be configured to use an existing cooling jacket in an ICP-MS system to cool the collected fluid stream while the fluid stream passes through the channels of the interface 120. The design of the interface 120 permits retrofitting of existing ICP-MS systems with the interface and the other components associated with the interface to permit argon recycling.

[0033] In certain examples, the interface 120 is fluidically coupled to a water separator 130. The water separator 130 can be configured to remove water vapor from the cooled, fluid stream provided by the interface 120. Without wishing to be bound by any particular theory and referring to FIG. 2, a sample can be introduced into a torch designed to sustain an inductively coupled plasma. For example, an inductively coupled plasma device 200 is shown that comprises a torch and an induction coil 205. The ICP device 200 comprises a torch comprising an outer tube 201 and an inner tube 202. A nebulizer 203 is also shown and can be used to introduce a sample into the plasma 206. The device 200 can be used to sustain an inductively coupled plasma 206 using the gas flows shown generally by the arrows in FIG. 2. The helical induction coil 205 may be electrically coupled to a radio frequency energy source (not shown) to provide radio frequency energy to the torch to sustain the inductively coupled plasma 206 within the torch. Aqueous based sample is typically provided to the plasma 206 through the nebulizer 203, and the inductively coupled plasma 206 can vaporize and ionize analytes in the provided sample. Due to most samples being aqueous based, a large percentage of the introduced sample is water or water vapor once the sample is vaporized. Fluid exiting the ICP device 200 typically comprises a mixture of argon, ions, water vapor and other gases. The ions can be provided to a downstream mass analyzer (not shown) through one or more other interfaces which can extract ions from a central portion of the fluid stream. The remainder of the fluid stream is typically not used or goes to waste.

[0034] In certain embodiments and referring to FIG. 1B, an illustration of a torch 160 fluidically coupled to an interface comprising a quartz extension/bonnet 170 is shown. A cooling jacket

180 is showing positioned beneath the interface. The quartz extension 170 can be used to reduce or minimize air leakage between the torch 160 and the cooling jacket 180, which comprises collector ducts to collect the argon and provide it to a downstream device/stage for recycling. The quartz extension 170 can be adjusted based on the distance between the torch and a sampling orifice and/or in a x-y position (side-to-side). The interface with the extension 170 can contribute to cooling the collected argon gas. The cooling jacket 180 also keeps the quartz extension 170 cool by conducting heat to the cooling system. The collected argon may be, for example, present at a temperature below 500 Kelvin at the interface exit.

[0035] In certain examples, to recycle the argon in the exiting fluid stream, the water separator 130 may comprise a permeable support such as, for example, a metal foam or a metal mesh configured to be cooled and to remove water from the fluid comprising the argon received by the interface. Referring to FIG. 3, an illustration of the permeable support 310 within a housing 305 is shown. The open cell nature of the permeable support 310 acts to increase the available surface area for water vapor to condense. The exact porosity of the permeable support present in the water separator can vary, and in certain instances the void content of the permeable support is at least 90%, e.g., is about 90% to about 97%. In addition, the permeable support composition may vary, and illustrative metal species include, but are not limited to, nickel and alloys, copper and alloys and aluminum and alloys and meshes and foams including any of these materials. The permeable support 310 can be thermally coupled to a heating/cooling device 320, e.g., a thermoelectric cooler, to reduce the temperature of the support 310 below the freezing point of the water. As a contaminated argon stream is passed through the permeable support 310, the support 310 provides good mixing and cooling and causes the water to condense and freeze on the surface of the cooled support 310. The fluid which exits the support 310 is substantially free of water vapor. While not shown, the housing 305 may comprise a valve or drain to permit removal of water from the permeable support 310 and permit reuse of the permeable support 310 once the water is removed. For example, the permeable support can be heated during a

regeneration step using the heating/cooling device 320 to liquefy any frozen water present on the permeable support 310. The liquid water can pool or collect in the housing 305 and may be removed by opening a drain or valve. If desired, the permeable support 310 can be heated above the boiling point of the water to vaporize any water which remains within the housing 305 and provide a “dry” permeable support which can be reused. The permeable support is generally durable and can withstand heating above the vaporization temperature of water without any damage. As noted herein, the permeable support typically comprises a metal mesh or a metal foam.

[0036] In some examples, it may be desirable to split the water separator into a plurality of individual channels to increase the overall water removal capacity of the water separator. A top view of one configuration of a multi-channel water separator is shown in FIG. 4. The separator 400 comprises a plurality of individual channels each of which may comprise a permeable support as described in connection with FIG. 3. The individual channels may be thermally coupled to a common heating/cooling device or comprise their own respective heating device. The presence of multiple individual channels can increase the overall water removal capacity while minimizing space. In some instances, the individual channels can be packed together into a cartridge which can be fluidically coupled to the interface. In some examples, one of the channels may be used during a particular recycling period while the other channels remain unused. Once the used channel becomes filled to capacity, the separator 400 can be configured to use to a different channel. The previously used channel can be regenerated as discussed herein while the other channel is being used.

[0037] In certain configurations, once the water vapor has been removed from the argon fluid stream, the stream still comprises particles, ions, and gaseous contaminants. Some or all of these residual contaminants can be removed by providing the water free argon fluid to the gas purifier 140. In certain examples, the gas purifier 140 may comprise a titanium metal open cell porous medium which can be sealed within a metal module, e.g., a nickel-chromium module. Referring

to FIG. 5, a module 505 comprises the titanium metal open cell porous medium 510. The exact porosity of the titanium metal open cell porous medium present in the gas purifier 140 can vary, and in certain instances the void content of the titanium metal foam is about 25% to about 35%. The average particle size of the titanium powder may be in a range from 250 to 500 microns. The module 505 can be thermally coupled to a heating device 520 which can be used to thermally activate the titanium metal open cell porous medium 510. For example, the heating device 520 can be heated to 700 deg. Celsius or more to activate the titanium surface. Trace gas impurities such as, for example, oxygen, nitrogen, hydrogen, hydrocarbons, etc. can bind to the titanium surface and eventually diffuse into and become trapped in the microstructure of the foam 510. The argon is generally inert and does not bind to any substantial degree to the titanium surface. The foam 510 can also act as a filter to remove any particulate matter which still may be present. The foam 510 can permit gas flow in either or both directions. Similar to the water separator, the gas purifier stage can be split into a plurality of individual channels as shown in the purifier 600 of FIG. 6. Any one or more of the channels can be used at a time. The fluid which exits the foam 510 generally is free of other gases and may be suitable for reuse, e.g., it can be provided back to the inductively coupled plasma torch 110 or can be collected and stored for reuse at a later time.

[0038] In certain configurations, it may be desirable to remove any trace impurities from the flow exiting the gas purifier by providing the flow to a polisher 150. The polisher 150 can generally clean up any residual contaminants to provide substantially pure argon gas. In some examples, the polisher 150 may comprise single wall carbon nanotubes (SW-CNTs) which can separate any residual contaminant gases from the argon. The SW-CNTs can be deposited on a permeable support, e.g., a metal mesh or a metal foam, to increase the overall surface area comprising SW-CNTs. While not wishing to be bound by any particular purity value, the argon exiting the polisher 150 can be substantially pure and free from other materials, such as water, particles, oxygen, nitrogen, hydrocarbons, etc., and may be at least 99.9% pure, 99.99% pure or

even 99.9999% pure, for example. In some instances, the polisher may be omitted and argon gas exiting the gas purifier may be sufficiently pure without further treatment or processing. In such cases, a bypass line can be present to remove the polisher 150 from fluidic coupling with the gas purifier 140.

[0039] In certain examples, the substantially pure argon which exits the polisher 150 can be provided back to the inductively coupled plasma torch through a fluid line 105 (see FIG. 1), or it may be stored, collected or otherwise maintained separately from argon introduced into the ICP torch 110. In some examples, at least 70%, e.g., 75-80%, of the initial argon introduced into the ICP torch 110 can be recovered using the recycling systems described herein. The recovered argon can be pre-mixed with argon from other sources or can be reintroduced back into the ICP torch 110 in a closed loop fashion where the introduced argon is continuously recycled back to the front end of the ICP torch 110. If argon becomes depleted or lost due to the recycling process or due to the analyses process, then new argon can be introduced into the system to raise the argon level/flow rate back to a desired level.

[0040] In certain configurations, the recycling systems described herein can be used in an inductively coupled plasma mass spectrometer (ICP-MS). Referring to FIG. 7, a block diagram of one configuration of an ICP-MS system is shown. The system 700 comprises a sample introduction device 705 fluidically coupled to an ICP torch 710. The ICP torch 710 is fluidically coupled to a mass analyzer 720 through an interface 715. The interface 715 can be configured to isolate the output from the torch 710 from surrounding air and enable symmetrical collection of argon from the mass-spectrometer orifice without plasma flow disturbance. The interface 715 may permit torch alignment through a dynamic seal and by using a quartz bonnet to prevent or avoid plasma-interface arcing. The dynamic seal can be configured for use without the need to use any sealants or gaskets to avoid plasma contamination. The interface 715 can be configured to use an existing cooling jacket in the ICP-MS system 700 to cool the collected argon while passing through the channels of the interface 715. The design of the interface 715 permits

retrofitting of existing ICP-MS systems with the interface and the other components associated with the interface to permit argon recycling. The interface 715 is also configured to permit passage of ions produced by the ICP torch 710 to the downstream mass analyzer 720. The mass analyzer 720 is fluidically coupled to a detector 730 which can detect ions selected by the mass analyzer 720. The system 700 also comprises a water separator 740 fluidically coupled to the interface 715, a gas purifier 750 fluidically coupled to the water separator 740, and a polisher 760 fluidically coupled to the gas purifier 750. The interface 715, water purifier 740, gas purifier 750 and polisher 760 may each be configured as described herein. The sample introduction device 705, ICP torch 710, the mass analyzer 720 and the detector 730 may be operated at reduced pressures using one or more vacuum pumps. In certain examples, however, only the mass analyzer 720 and the detector 730 may be operated at reduced pressures.

[0041] In certain instances, the sample introduction device 705 may take the form of a sample inlet system that can receive sample while permitting the components to remain under vacuum. The sample introduction device 705 can be configured as batch inlet, a direct probe inlet, a chromatographic inlet or other sample introduction systems. In some embodiments, the sample introduction device 705 may be an injector, a nebulizer or other suitable devices that may deliver liquid samples to the ICP torch 710. As noted herein, the liquid sample typically comprises 50% or more water which can be removed from the argon stream using the water separator 740.

[0042] In certain examples, the mass analyzer 720 may take numerous forms depending generally on the sample nature, desired resolution, etc. For example, the mass analyzer can be a scanning mass analyzer, a magnetic sector analyzer (e.g., for use in single and double-focusing MS devices), a quadrupole mass analyzer, an ion trap analyzer (e.g., cyclotrons, quadrupole ion traps, orbitraps), time-of-flight analyzers (e.g., matrix-assisted laser desorbed ionization time of flight analyzers), and other suitable mass analyzers that may separate species with different mass-to-charge ratios. In some embodiments, the mass analyzer may be coupled to another mass analyzer which may be the same or may be different. For example, a double quadrupole device

or a triple quadrupole device can be used as, or part of, a mass analyzer. If desired, the mass analyzer 720 may also include ions traps or other components that can assist in selecting ions with a desired mass-to-charge ratio from other ions present in the sample. The mass analyzer 720 can be scanned such that ions with different mass-to-charge ratios are provide to the detector 730 in real time. In some examples, the detector 730 may comprise an electron multiplier, Faraday cup, multi-channel plate or other detectors commonly used in mass spectrometers, e.g., scintillation detectors, time of flight devices, etc. The system 700 is typically electrically coupled to a processor (not shown) which includes a microprocessor and/or computer and suitable software for analysis of samples introduced into the system 700. One or more databases may be accessed by the processor for determination of the chemical identity of species introduced into system 700. If desired, the processor may also control flow of fluid comprising argon through the water separator 740, the gas purifier 750 and/or the polisher 760. For example, one or more valves can be present between any of the stages 740, 750, 760, and the valves can be controlled by the processor to permit fluid to flow or not between the various stages 740, 750, and 760. Further, the processor can be used to control the temperature of any associated heating/cooling devices which are present in the stages 740, 750, and 760. Other suitable additional devices known in the art may also be used with the MS system 700 including, but not limited to, autosamplers, such as AS-90plus and AS-93plus autosamplers commercially available from PerkinElmer Health Sciences, Inc. If desired, argon which exits the polisher 760 may be provided back to the ICP torch 710 through a fluid line 702. Alternatively, argon which exits the polisher 760 may be collected and stored for use at a later time or with a different system or other device.

[0043] In certain examples, the systems described herein can be used in processes to collect and purify argon from a fluid stream comprising the argon and other contaminants. For example, the interfaces described herein can be used to collect a fluid flow exiting from an inductively coupled plasma torch using an interface that is fluidically coupled to the inductively coupled

plasma torch. The collected fluid comprising argon, water and other contaminants can be cooled and provided to a cooled, permeable support to remove water from the collected fluid flow to provide a substantially water free fluid flow. The substantially free water fluid flow comprising argon and other contaminants can be provided to a thermally active open cell titanium porous medium to remove gaseous impurities to provide a substantially pure argon flow, which may be contaminant free or may comprise residual gaseous contaminants. Solid particles present in the substantially water free fluid flow may also be filtered out using the thermally active open cell porous medium. The substantially pure argon flow can be provided to a metal foam comprising single-walled carbon nanotubes to remove residual gaseous impurities from the substantially pure argon flow and provide substantially pure argon gas. In some examples, the substantially pure argon gas back to an inlet of the inductively coupled plasma. For example, the argon gas can be provided directly to an ICP torch or can be mixed with commercially pure argon with the mixture being provided to the ICP torch. As noted herein, the interface can be used to symmetrically collect the exiting fluid flow by isolating output from the inductively coupled plasma torch from surrounding air and without disturbing flow of an inductively coupled plasma sustained within the inductively coupled plasma torch. This permits a mass analyzer to continue to receive ions while the recycling system is in the process of recycling the argon gas.

[0044] In certain examples, as noted herein, any one or more of the components can be heated and/or cooled to provide a desired temperature effect. For example, cooling the permeable support using a thermoelectric cooler can be performed such that the surfaces of the permeable support are colder than the freezing point of the water vapor. In some examples, the surfaces may be at least 5 degrees, 10 degrees, 20 degrees or even 25 degrees colder than the freezing point of the water, which may vary slightly due to pressure variations in the system. The permeable support can also be heated to remove frozen water from the surfaces. In some instances, heating may be a multi-stage process where the frozen water is first liquefied, the liquid water is then removed, e.g., through a drain or valve, and then any residual water vapor

can be removed by heating the permeable support above the vaporization temperature of the water, e.g., at least 5 degrees, 10 degrees, 20 degrees or even 25 degrees above the vaporization temperature, to dry the open cell metal foam. An inert gas, e.g., nitrogen, can be passed through the permeable support during heating to assist in removal of any residual water vapor and increase the water retention capacity of the water separator prior to re-use. In some instances, one or more fluid lines may couple the water separator to the interface to permit fluid to flow between the two devices. One or more valves can be present in the fluid line to control fluid movement if desired.

[0045] In some examples, the gas purifier can be heated to thermally activate the titanium metal open cell porous medium which is present. Heating can be performed using a heating device associated with or thermally coupled to a module comprising the titanium metal open cell porous medium, or in some instances, the entire module can be placed in an oven similar to a chromatography oven to control the temperature of the gas purifier. As noted herein, the gas purifier can be configured such that fluid flow may occur from either end of the gas purifier without any unwanted removal of particulate matter which may be filtered out by the gas purifier. In some instances, one or more fluid lines may couple the gas purifier to the water separator to permit fluid to flow between the two devices. One or more valves can be present in the fluid line to control fluid movement if desired.

[0046] In some examples, the polisher can be designed to remove residual gaseous impurities by exposing the fluid stream to single-walled carbon nanotubes disposed on an permeable support such as, for example, an open cell metal foam which may be the same or different than the open permeable support of the water separator. For example, an open cell metal foam or metal mesh provides a support for carbon nanotubes with large the available surface area. If desired, the temperature of the polisher can also be controlled using a heating/cooling device or by placing the polisher in a temperature controlled environment, e.g., within an oven.

[0047] In certain configurations, one or more filters comprising a filtration medium can be present between any one or more of the stages described herein. For example, charcoal filters, paper filters, sand filters, screen filters or the like can be present between any two or more of the stages described herein. In some examples, a filter is present between the interface and the water evaporator. In other examples, a filter is present between the water evaporator and the gas purifier. In other instances, a filter is present between the gas purifier and the polisher. Where a return line is present between the polisher and the ICP torch, a filter can be present in the return line if desired. Where a filter is present, the filter is typically used to remove particulate matter from the fluid stream.

[0048] In certain instances, the systems described herein may comprise additional stages or devices which can be used. For example, two gas purifier stages positioned in series or in parallel can be used. Similarly, two or more water separators in series or in parallel may be present. If desired, two or more polishers can also be present. Where two or more similar stages are present, the particular materials present can be the same or can be different in the different stages. For example, two water separators can be present with different metals present in the permeable supports. If desired, the interface can be configured with a plurality of individual outlet ports to split the fluid flow collected from the ICP torch to many different individual recycling systems to provide simultaneous parallel recycling of the fluid stream comprising the argon.

[0049] In certain embodiments, the various stages of the recycling systems described herein can be packaged in the form of a kit which may comprise one or more modules. Any one or more of the modules can be used in combination with other modules as desired to permit retrofitting of ICP-MS systems with the recycling system modules described herein. For example, in one kit configuration, the kit may comprise an interface and instructions for using the interface in an ICP-MS system to recycle argon. In another configuration, the kit may comprise an interface, water separator and instructions for using the interface and water separator with an ICP-MS

system to recycle argon. In additional configurations, the kit may comprise an interface, water separator, a gas purifier and instructions for using the interface, water separator and gas purifier with an ICP-MS system to recycle argon. In other configurations, the kit may comprise an interface, water separator, a gas purifier, a polisher and instructions for using the interface, water separator, gas purifier, and polisher with an ICP-MS system to recycle argon. In some instances, the kit may further comprise an ICP torch which can be pre-configured with an interface which can be used with a recycling system and/or a mass analyzer. Additional components can also be present in the kit as desired.

[0050] Certain specific examples are described below to facilitate a better understanding of the technology described herein.

[0051] Example 1

[0052] Referring to FIGS. 8A-8D and 9, an argon collector was assembled by placing a quartz extension between a torch and a sampler cone. FIGS. 8A-8D are photographs of the system, and a cross-sectional view is shown in FIG. 9. Referring to FIG. 8A a torch extension 810 is shown. Referring to FIG. 8B, a torch housing 820 is shown. A cooling jacket 830 comprising collector ducts 832 is shown in FIG. 8C. An assembly is shown in FIG. 8D which includes the components of FIGS. 8A-8C along with a torch 850 and a sampler cone 840. Referring to FIG. 9, a mounting plate 910, spring-loaded guides 920, a Teflon holder 930 and quartz collector 940 are shown. Component 950 was added to provide the collector ducts to the cooling jacket.

[0053] Referring to FIG. 10, the quartz collector 940 is shown as providing a snug fit over the Teflon holder. The quartz collector 940 slides over the torch 905 but does not contact the outer surfaces of the torch 905. The collector 940 is spring-loaded from the guides 920 to seal against the collector ducts. The cooling jacket of the system included the collector ducts which were used to collect argon exiting from the torch 905 and through the quartz collector 940. Argon exiting the torch enters into the quartz extension and then enters into the collector ducts of the

cooling jacket. The collected argon may then be provided from the collector ducts to a water separator stage, gas purifier stage and an optional polisher stage, as described herein, to recycle the argon.

[0054] FIGS. 11A and 11B show the cooling jacket in more detail. The cooling jacket 1100 included a cut-out 1110 for the plasma viewport. Duct channels 1150 were present and used for symmetric pumping. An O-ring seal 1160 was present to prevent air entry into the system. Tubing was welded into hole 1170 to connect the cooling jacket 1100 to a pump. The hole 1180 was for a connecting channel and was plugged.

[0055] The cooling jacket 1100 can be used in combination with a total argon flow rate of about 17.2 Liters/minute. Based on pump efficiency and pressures, around 12-14 Liters/minute of the argon could be collected. In one measurement, around 70-80% of the total argon input could be captured and recycled using the cooling jacket.

[0056] When introducing elements of the examples disclosed herein, the articles "a," "an," "the" and "said" are intended to mean that there are one or more of the elements. The terms "comprising," "including" and "having" are intended to be open-ended and mean that there may be additional elements other than the listed elements. It will be recognized by the person of ordinary skill in the art, given the benefit of this disclosure, that various components of the examples can be interchanged or substituted with various components in other examples.

[0057] Although certain aspects, examples and embodiments have been described above, it will be recognized by the person of ordinary skill in the art, given the benefit of this disclosure, that additions, substitutions, modifications, and alterations of the disclosed illustrative aspects, examples and embodiments are possible.

CLAIMS

1. A method comprising:

collecting a fluid flow exiting from an inductively coupled plasma torch using an interface fluidically coupled to the inductively coupled plasma torch;

providing the collected fluid flow to a cooled, permeable support configured to remove water from the collected fluid flow to provide a substantially water free fluid flow;

providing the substantially water free fluid flow to a thermally active open cell titanium porous medium to remove gaseous impurities to provide a substantially pure argon flow; and

providing the substantially pure argon flow to a metal foam comprising single-walled carbon nanotubes to remove residual impurities from the substantially pure argon flow and provide substantially pure argon gas.

2. The method of claim 1, further comprising providing the substantially pure argon gas back to an inlet of the inductively coupled plasma.

3. The method of claim 1, further comprising symmetrically collecting the exiting fluid flow by isolating output from the inductively coupled plasma torch from surrounding air and without disturbing flow of an inductively coupled plasma sustained within the inductively coupled plasma torch.

4. The method of claim 3, further comprising cooling the permeable support using a thermoelectric cooler.

5. The method of claim 4, further comprising heating the permeable support to liquefy cooled water to permit draining of the liquid water.

6. The method of claim 4, further comprising heating the thermally active open cell titanium porous medium with an electric heater to thermally activate the open cell titanium porous medium.
7. The method of claim 6, further comprising configuring the single-walled carbon nanotubes to be present on an open cell metal foam.
8. The method of claim 7, further comprising controlling the temperature of the open cell metal foam comprising the single-walled carbon nanotubes
9. The method of claim 7, further comprising filtering particulate material from the collected fluid flow prior to providing the collected fluid flow to the water separator.
10. The method of claim 7, further comprising filtering particulate material from the substantially water free fluid flow prior to providing the substantially water free fluid flow to the gas purifier.
11. The method of claim 7, further comprising filtering particulate material from the substantially pure argon prior to providing the substantially pure argon flow to the polisher.
12. The method of claim 7, further comprising configuring the gas purifier with a bypass line configured to bypass the polisher.
13. The method of claim 7, further comprising fluidically coupling a second polisher to the polisher.

14. The method of claim 7, further comprising collecting and storing the substantially pure argon.

15. The method of claim 7, further comprising configuring the interface with a plurality of individual output ports.

16. A recycling system configured to purify argon used in an inductively coupled plasma mass spectrometer, the recycling system comprising:

an interface configured to fluidically couple to an inductively coupled plasma torch and receive fluid comprising argon exiting from the inductively coupled plasma torch;

a water separator fluidically coupled to the interface, the water separator comprising an permeable support configured to be cooled and to remove water from the fluid comprising the argon received by the interface;

a gas purifier device fluidically coupled to the water separator, the gas purifier comprising a titanium metal open cell porous medium configured to remove gaseous impurities from fluid comprising the argon; and

a polisher fluidically coupled to the gas purifier device, the polisher comprising single-walled carbon nanotubes configured to remove residual impurities from the fluid flow comprising the argon to provide substantially pure argon gas.

17. The system of claim 16, further comprising a fluid line configured to provide fluidic coupling between the polisher and the inductively coupled plasma torch to provide the substantially pure argon gas back to the inductively coupled plasma torch.

18. The system of claim 16, in which the interface is configured to isolate output from the torch from surrounding air to provide for symmetrical collection of the fluid comprising the argon without disturbing flow of the inductively coupled plasma.
19. The system of claim 18, in which the interface comprises a sliding dynamic seal.
20. The system of claim 19, in which the interface comprises a plurality of channels.
21. The system of claim 18, in which the water separator comprises a thermoelectric cooler thermally coupled to the open cell metal foam or mesh to cool the open cell metal foam or mesh and freeze water vapor present within the flow comprising the argon.
22. The system of claim 21, in which the water separator comprises a drain to remove liquid water from the gas purifier.
23. The system of claim 21, in which the gas purifier comprises the titanium metal open cell porous medium within a sealed nickel-chromium module.
24. The system of claim 23, in which the gas purifier comprises a heating device to thermally activate surfaces of the titanium metal open cell porous medium within the sealed nickel-chromium module.
25. The system of claim 24, in which the titanium metal open cell porous medium is further configured to filter particulate matter in the fluid comprising the argon.

26. The system of claim 24, in which the polisher comprises a metal foam comprising the single-walled carbon nanotubes.
27. The system of claim 24, further comprising a collector configured to receive argon from the polisher and store the argon.
28. The system of claim 43, further comprising a second polisher fluidically coupled to the polisher.
29. The system of claim 16, in which the water separator comprises a plurality of individual compartments comprising the permeable support.
30. The system of claim 16, in which the gas purifier comprises a plurality of individual compartments comprising the titanium metal open cell porous medium.
31. An inductively coupled mass spectrometer comprising:
- an inductively coupled plasma torch;
 - a mass analyzer fluidically coupled to the inductively coupled plasma torch and configured to receive ions from the inductively coupled plasma torch;
 - an interface fluidically coupled to the inductively coupled plasma torch and configured to permit passage of ions to the mass analyzer and to collect fluid comprising argon exiting from the inductively coupled plasma torch;
 - a water separator fluidically coupled to the interface, the water separator comprising a permeable support configured to be cooled and to remove water from the fluid comprising the argon received by the interface;

a gas purifier device fluidically coupled to the water separator, the gas purifier comprising a thermally active titanium metal open cell porous medium configured to remove gaseous impurities from fluid comprising the argon; and

a polisher fluidically coupled to the gas purifier device, the polisher comprising single-walled carbon nanotubes configured to remove residual impurities from the fluid flow comprising the argon to provide substantially pure argon gas.

32. The mass spectrometer of claim 31, further comprising a fluid line configured to provide fluidic coupling between the polisher and the inductively coupled plasma torch to provide the substantially pure argon gas back to the inductively coupled plasma torch.

33. The mass spectrometer of claim 31, in which the interface is configured to isolate output from the torch from surrounding air to provide for symmetrical collection of the fluid comprising the argon without disturbing flow of the inductively coupled plasma.

34. The mass spectrometer of claim 33, in which the interface comprises a sliding dynamic seal.

35. The mass spectrometer of claim 34, in which the interface comprises a plurality of channels.

36. The mass spectrometer of claim 33, in which the water separator comprises a thermoelectric cooler thermally coupled to the open cell metal foam to cool the open cell metal foam and freeze water vapor present within the flow comprising the argon.

37. The mass spectrometer of claim 36, in which the water separator comprises a drain to remove liquid water from the gas purifier.

38. The mass spectrometer of claim 36, in which the gas purifier comprises a thermally active titanium metal open cell porous medium within a sealed nickel-chromium module.
39. The mass spectrometer of claim 38, in which the gas purifier comprises a heating device to thermally activate surfaces of the titanium metal open cell porous medium.
40. The mass spectrometer of claim 39, in which the titanium metal open cell porous medium is further configured to filter particulate matter in the fluid comprising the argon.
41. The mass spectrometer of claim 39, in which the polisher comprises a metal foam comprising the single-walled carbon nanotubes.
42. The mass spectrometer of claim 39, further comprising a collector configured to receive argon from the polisher and store the argon.
43. The mass spectrometer of claim 39, in which the mass analyzer is selected from the group consisting of a quadrupole assembly, a magnetic sector analyzer and an ion trap.
44. The mass spectrometer of claim 43, further comprising a detector fluidically coupled to the mass analyzer.
45. The mass spectrometer of claim 44, in which the detector is selected from the group consisting of an electron multiplier, a Faraday cup, a scintillation plate and a multi-channel plate.
46. The mass spectrometer of claim 44, in which the water separator comprises a plurality of individual compartments comprising the permeable support.

47. The mass spectrometer of claim 44, in which the gas purifier comprises a plurality of individual compartments comprising the titanium metal open cell porous medium.

48. The mass spectrometer of claim 41, further comprising a sample introduction device configured to provide sample to the inductively coupled plasma torch.

49. The mass spectrometer of claim 41, in which the sample introduction device comprises a nebulizer.

50. The mass spectrometer of claim 44, in which the mass analyzer comprises a double or triple quadrupole assembly and the detector comprises an electron multiplier.

51. An interface configured to collect a fluid flow comprising argon exiting an inductively coupled plasma while permitting passage of ions from the plasma to a mass analyzer, the interface comprising a seal and a quartz bonnet to prevent arcing between the plasma and the interface.

52. A method of recycling argon used in an inductively coupled plasma, the method comprising:
collecting argon in a fluid flow exiting the plasma; and
cooling the collected argon in the fluid flow using a cooling jacket configured to cool an inductively coupled plasma torch.

1/11

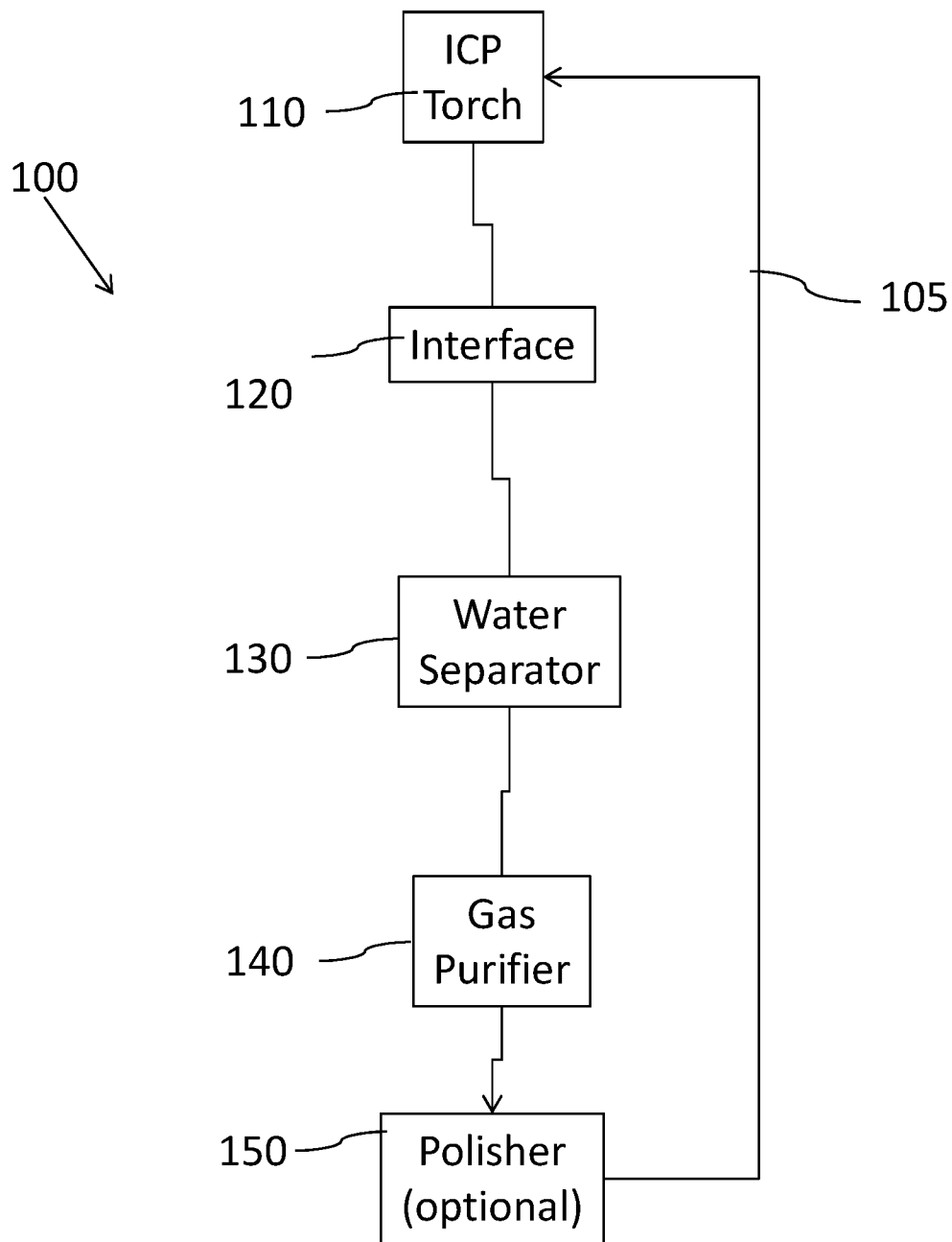


FIG. 1A

2/11

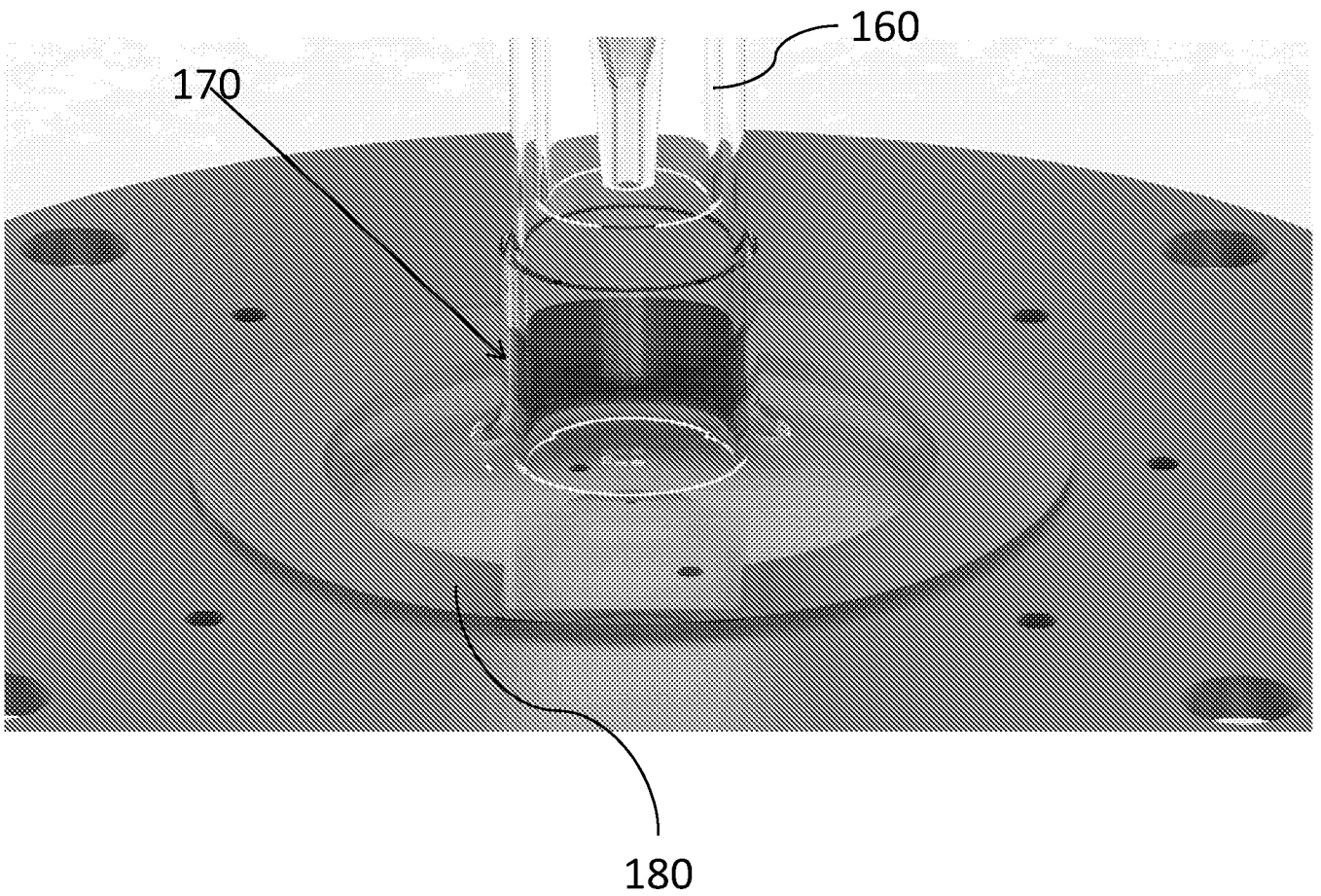


FIG. 1B

3/11

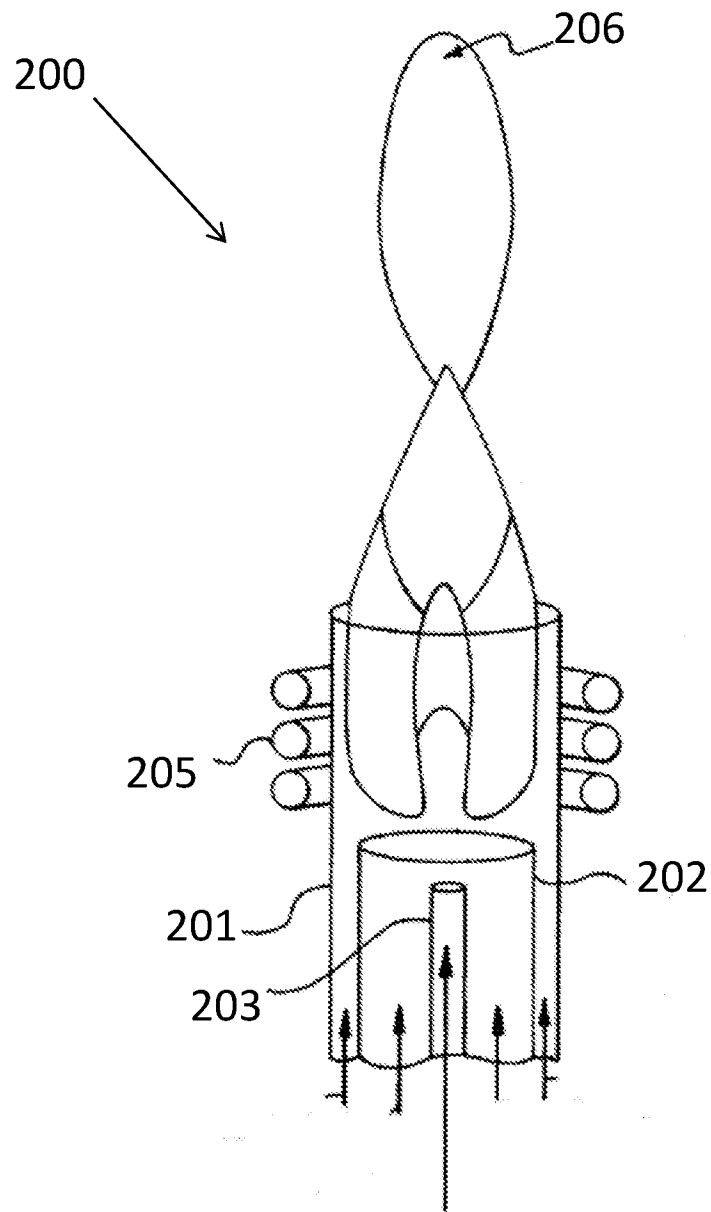


FIG. 2

4/11

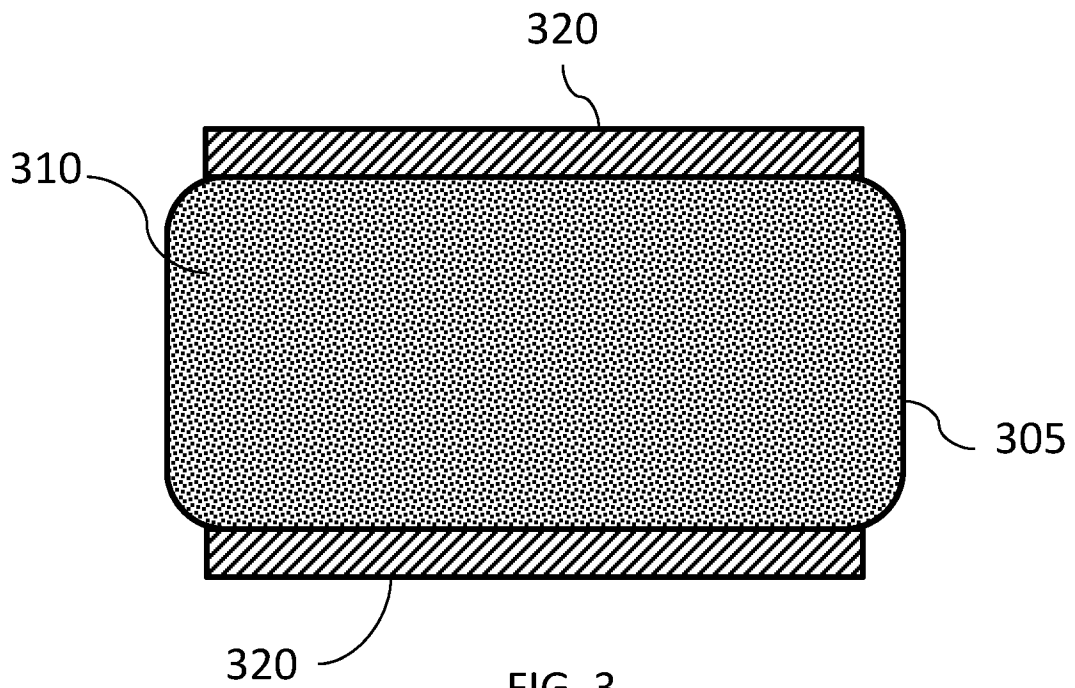


FIG. 3

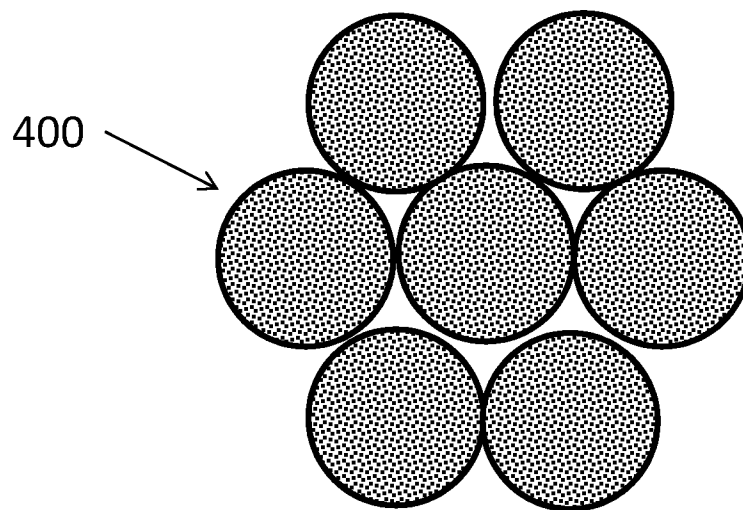
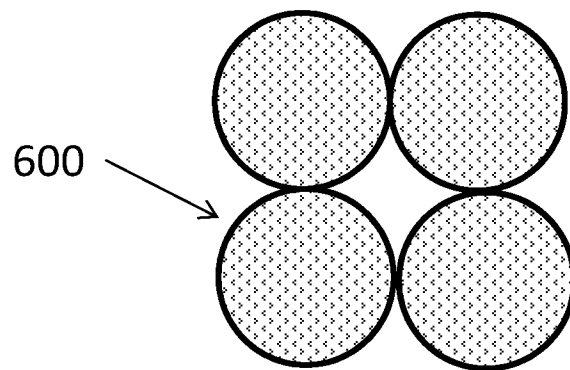
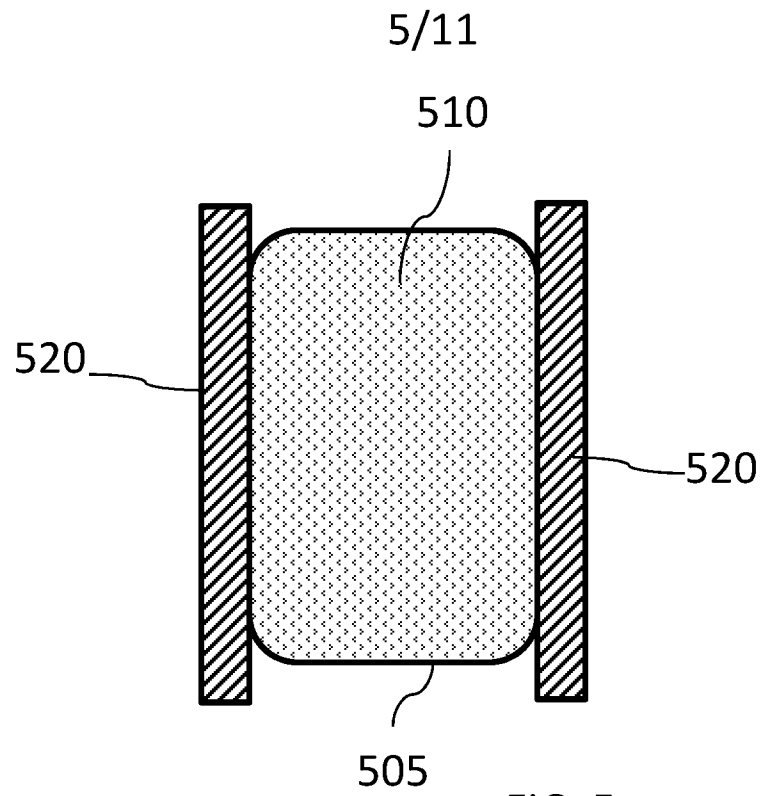


FIG. 4



6/11

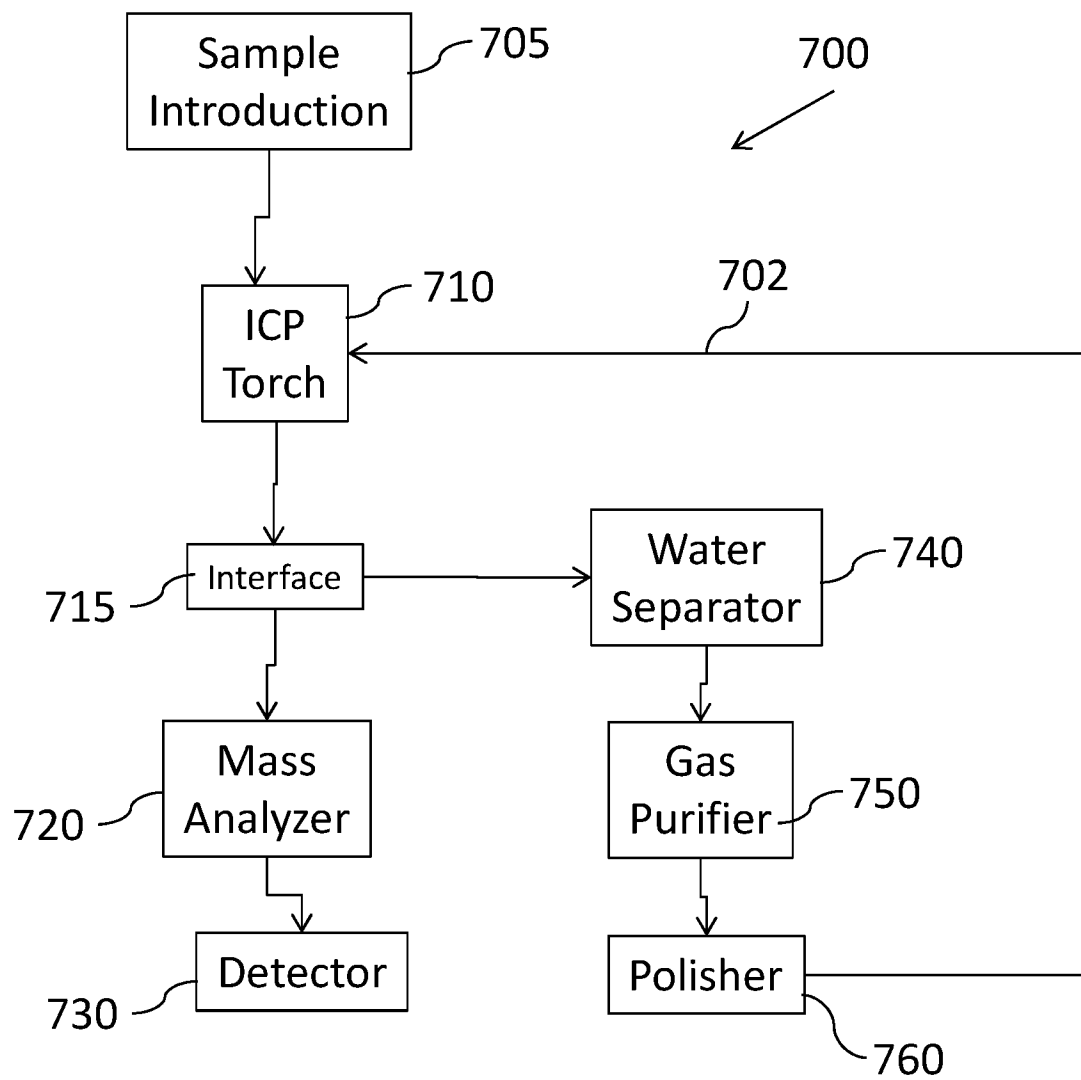


FIG. 7

7/11

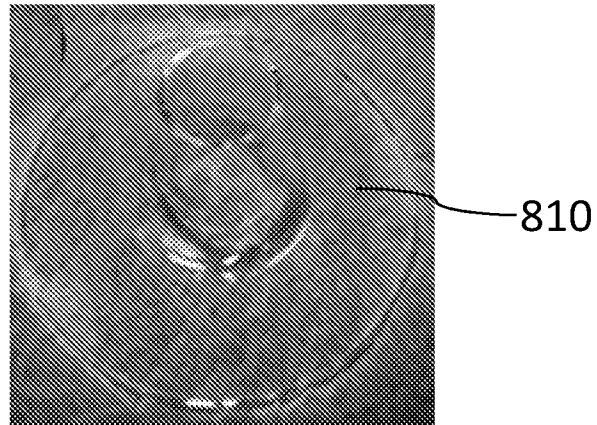


FIG. 8A

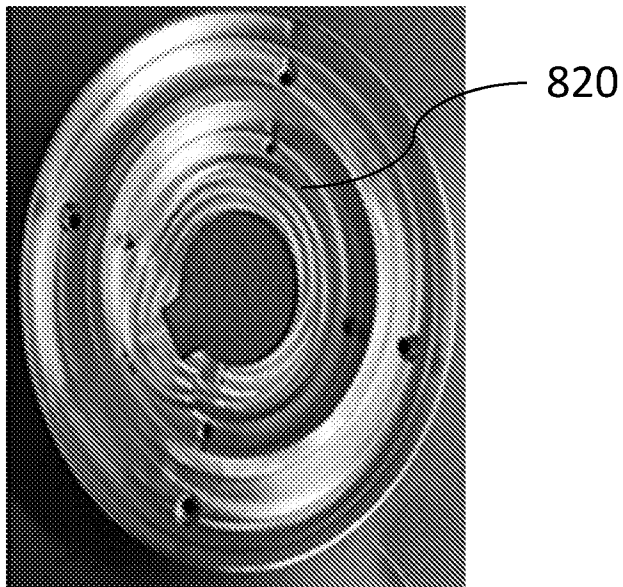


FIG. 8B

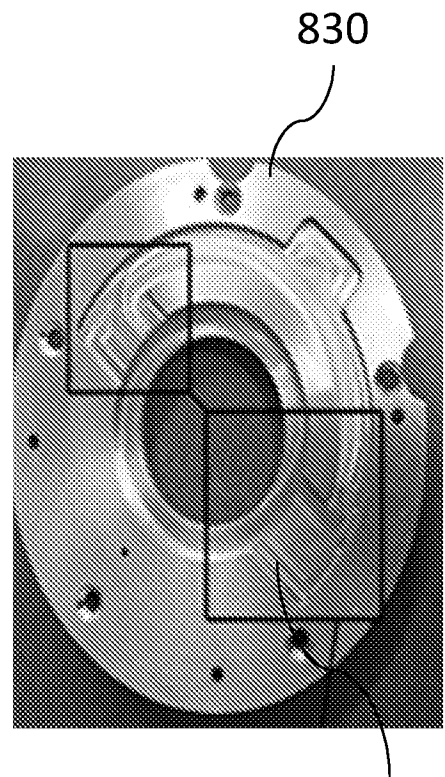


FIG. 8C

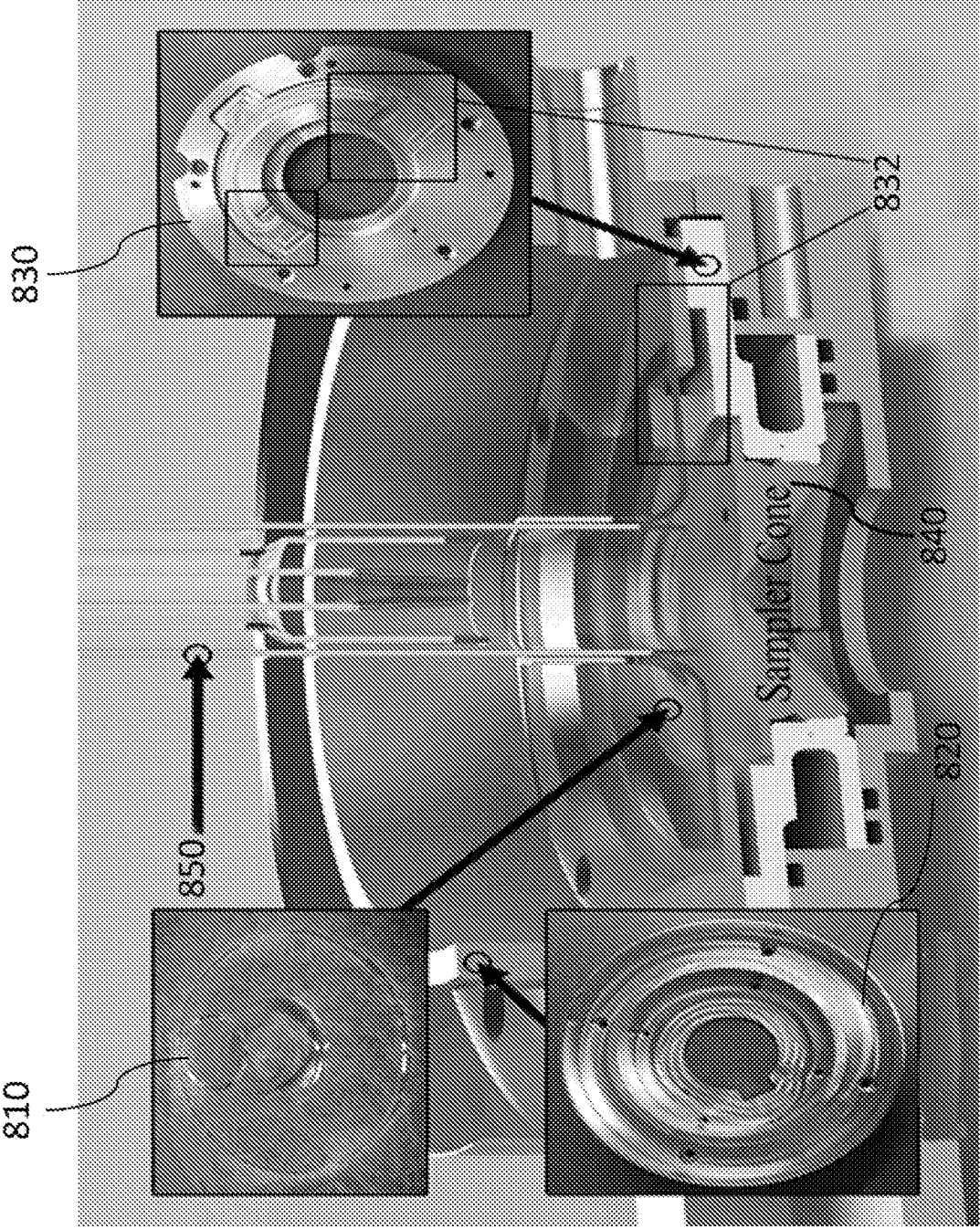
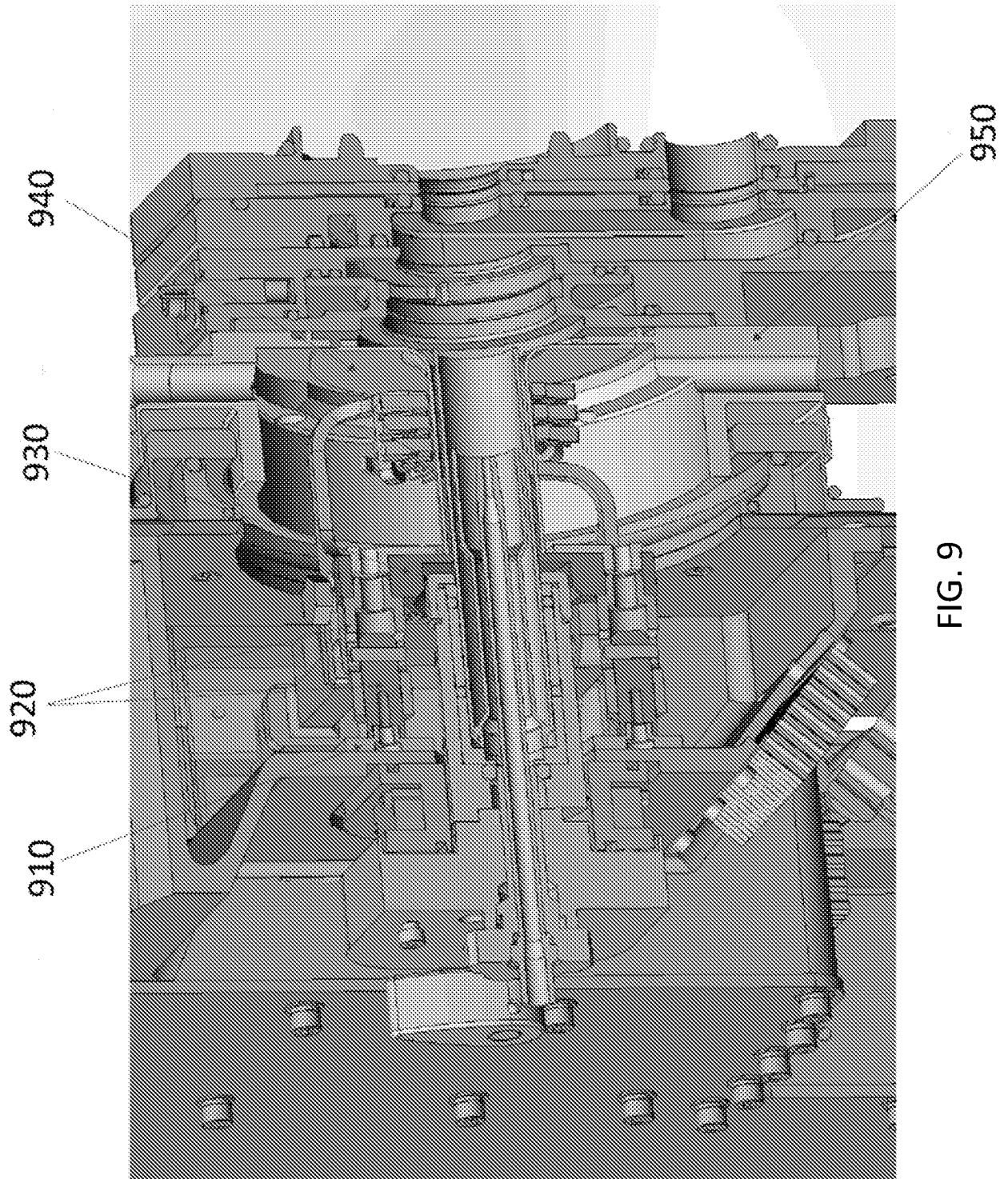


FIG. 8D



10/11

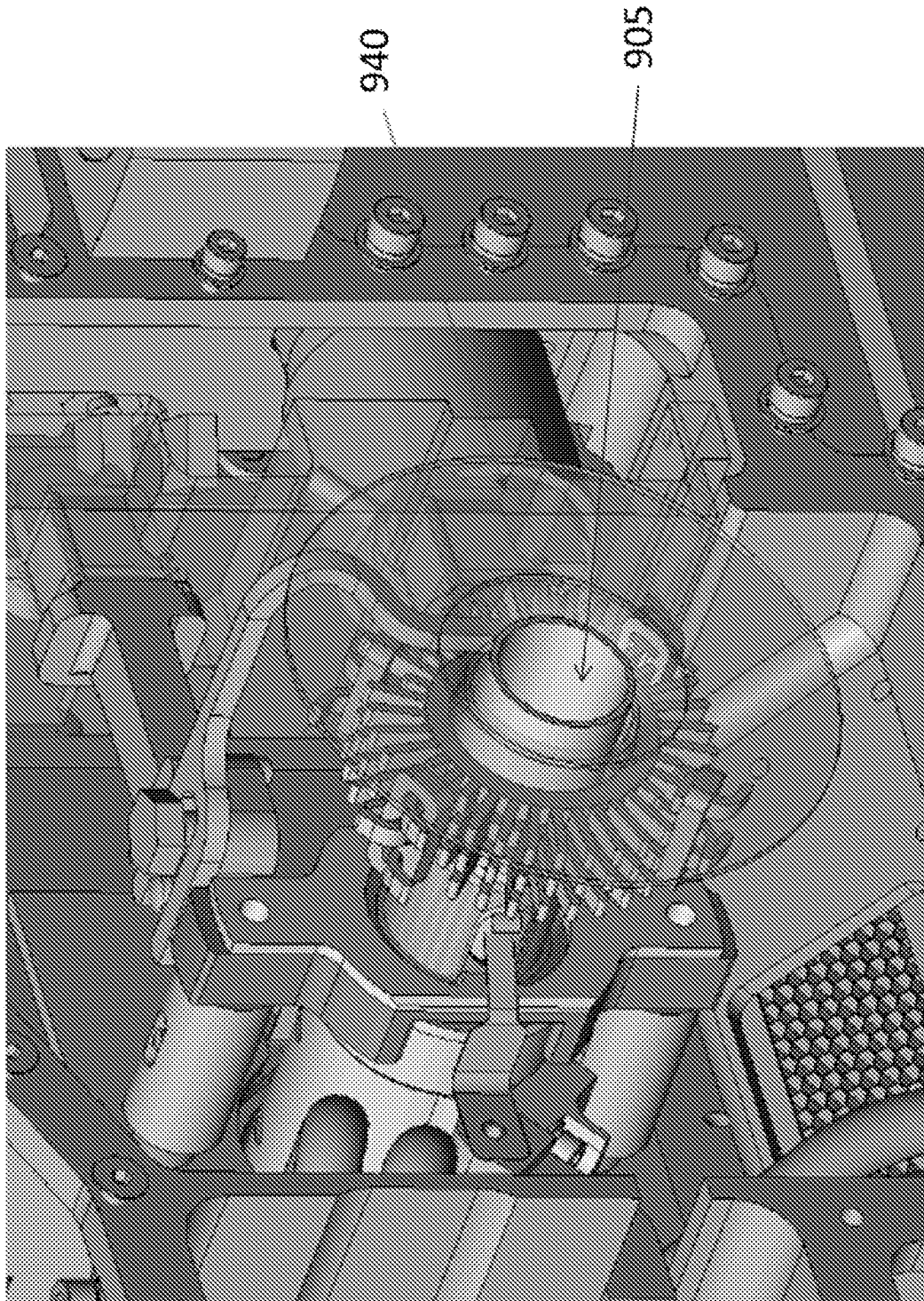


FIG. 10

11/11

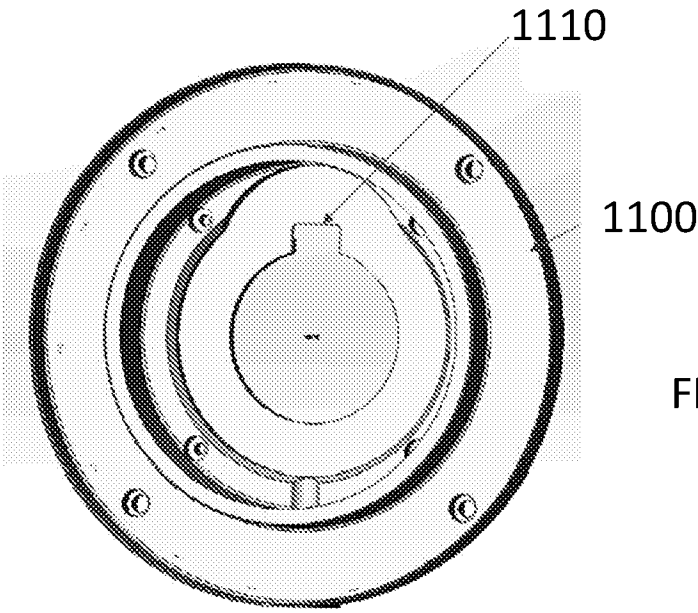


FIG. 11A

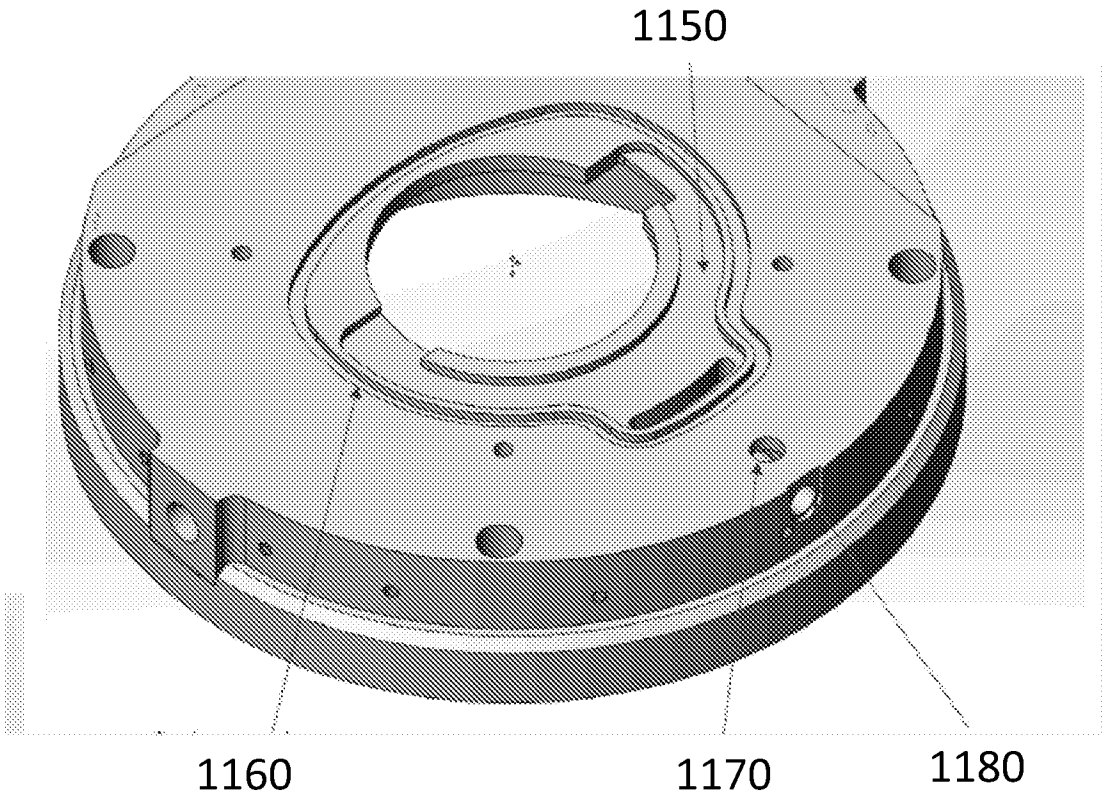


FIG. 11B

INTERNATIONAL SEARCH REPORT

International application No.

PCT/IB2018/051152

A. CLASSIFICATION OF SUBJECT MATTER

IPC: **C01B 23/00** (2006.01), **B01D 53/02** (2006.01), **H01J 49/04** (2006.01), **H01J 49/26** (2006.01)

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)

C01B 23/00, B01D 53/02, H01J 49/04, H01J 49/26 (all 2006.01)

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

Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used)

Questel-Orbit, Google Patent/Scholar (argon, plasma, metal, substrate, foam, pore, porous, nanotube, metal, substrate, gas purify+, titanium)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	Wiltse et al., Reduction of Argon Consumption to Less than 2 L min ⁻¹ by Gas recycling in Inductively Coupled Plasma Optical Emission Spectrometry, <i>Analytical Chemistry</i> , 2013 , 88, 99 7352-7357.	52 1-50
A	ML Kyle, LF Coleman, RD Pierce, JD Arntzen, Kinetics of the Titanion-Nitrogen reaction with Application to the Design of Gettering Systems, Argonne National Laboratory (ANL-7167), 1967, pp 1-34.	1-50
A	Duarte et al. Composite and Nanocomposite Metal Foams, <i>Materials</i> , 2016 , 9, 79, pp 1-34.	1-50
A	US7011760B2, 14 March 2006 (14-03-2006) WANG ET AL. Col 1, 1 49-53; col 2, 1 29-42' col 2, 56 to col 3, 1 11; col 5, 1 30 and 1 42-53; col 6, 1 1-3.	1-50
X A	US5068534A, 26 November 1991 (26-11-1991) BRADSHAW et al. Col 5, 1 24-25 and 39-40	51 1-50

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* "A" "E" "L" "O" "P"	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance earlier application or patent but published on or after the international filing date document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) document referring to an oral disclosure, use, exhibition or other means document published prior to the international filing date but later than the priority date claimed	"T" "X" "Y" "&"	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 document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone 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
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Date of the actual completion of the international search
10 May 2018 (10-05-2018)Date of mailing of the international search report
06 June 2018 (06-06-2018)Name and mailing address of the ISA/CA
Canadian Intellectual Property Office
Place du Portage I, C114 - 1st Floor, Box PCT
50 Victoria Street
Gatineau, Quebec K1A 0C9
Facsimile No.: 819-953-2476

Authorized officer

Stewart Parsons (819) 639-8528

INTERNATIONAL SEARCH REPORT

International application No.

PCT/IB2018/051152**Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of the first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claim Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claim Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claim Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Group A – Claims 1-50 are directed to a system, inductively coupled mass spectrometer and method for purifying and recycling argon from a ICP torch comprising collecting three purification steps comprising a water removal stage where the gas flow is provided to a cooled permeable support, a purification stage where the water free gas flow is provided to a heated open cell titanium porous medium to remove impurities, and a polishing stage utilizing a metal foam comprising single-wall carbon nanotubes to remove residual impurities;

Group B – Claim 51 is directed to an interface comprising a quartz bonnet and a seal; and

Group C – Claim 52 is directed to a method of recycling argon from an inductively coupled plasma by cooling collected argon using a cooling jacket.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☒ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claim Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/IB2018/051152

Patent Document Cited in Search Report	Publication Date	Patent Family Member(s)	Publication Date
US7011760B2	14 March 2006 (14-03-2006)	US2005040090A1	24 February 2005 (24-02-2005)
		AU2002367020A1	30 July 2003 (30-07-2003)
		AU2002367020B2	20 November 2008 (20-11-2008)
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		CA2470025C	21 February 2012 (21-02-2012)
		EP1465836A2	13 October 2004 (13-10-2004)
		EP2295376A2	16 March 2011 (16-03-2011)
		EP2295376A3	31 October 2012 (31-10-2012)
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		US6713519B2	30 March 2004 (30-03-2004)
		US2003116503A1	26 June 2003 (26-06-2003)
		US6824689B2	30 November 2004 (30-11-2004)
		US2004147620A1	29 July 2004 (29-07-2004)
		US7008969B2	07 March 2006 (07-03-2006)
		US2006167120A1	27 July 2006 (27-07-2006)
		US7288576B2	30 October 2007 (30-10-2007)
		WO03059813A2	24 July 2003 (24-07-2003)
		WO03059813A3	23 October 2003 (23-10-2003)
US5068534A	26 November 1991 (26-11-1991)	US5068534A	26 November 1991 (26-11-1991)
		US5068534B1	14 February 1995 (14-02-1995)
		CA1312680C	12 January 1993 (12-01-1993)
		DE68926167D1	09 May 1996 (09-05-1996)
		DE68926167T2	29 August 1996 (29-08-1996)
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		EP0436544B1	03 April 1996 (03-04-1996)
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