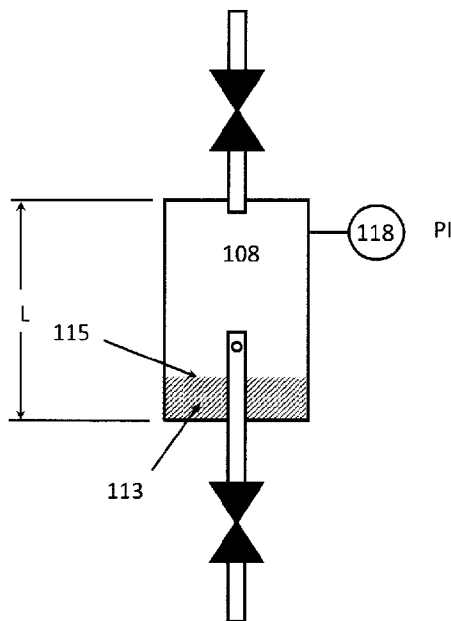




(22) Date de dépôt/Filing Date: 2017/12/27  
(41) Mise à la disp. pub./Open to Public Insp.: 2019/05/28  
(45) Date de délivrance/Issue Date: 2022/05/10  
(30) Priorité/Priority: 2017/11/28 (US15/823,777)

(51) Cl.Int./Int.Cl. *G01N 1/10* (2006.01)  
(72) Inventeur/Inventor:  
PELLERIN, JOSEPH PHILIPPE, CA  
(73) Propriétaire/Owner:  
AIR LIQUIDE CANADA, INC., CA  
(74) Agent: LEDGLEY LAW

(54) Titre : ECHANTILLONNEUR DE LIQUIDE CRYOGENIQUE  
(54) Title: CRYOGENIC LIQUID SAMPLER



(57) **Abrégé/Abstract:**

Cryogenic liquid samplers are provided to address problems of fractionation of cryogenic liquid during volatilization. The sampler includes an inner volume and a useful internal length, a cryogenic liquid inlet conduit in fluid connection with an inlet valve, a weir tube in fluid connection with the inlet valve, wherein the weir tube comprises at least one weir hole, wherein the weir tube extends a predetermined distance into the inner volume, a cryogenic liquid outlet conduit in fluid connection with inner volume and in fluid connection with an outlet valve, and a purge tube in fluid connection with the outlet valve.

### **Abstract**

Cryogenic liquid samplers are provided to address problems of fractionation of cryogenic liquid during volatilization. The sampler includes an inner volume and a useful internal length, a cryogenic liquid inlet conduit in fluid connection with an inlet valve, a weir tube in fluid connection with the inlet valve, wherein the weir tube comprises at least one weir hole, wherein the weir tube extends a predetermined distance into the inner volume, a cryogenic liquid outlet conduit in fluid connection with inner volume and in fluid connection with an outlet valve, and a purge tube in fluid connection with the outlet valve.

5

10

## CRYOGENIC LIQUID SAMPLER

### Background

5           Cryogenic liquids, for example, liquid nitrogen, oxygen and argon are employed in a number of environments and have a number of industrial and commercial applications in which the user demands high purity which necessitates accurate information as to the analytical content of trace or low level amounts of contaminating gases. Analysis is carried out on a gaseous sample of the cryogenic  
10 liquid which typically involves the use of a flash vaporizer.

          A particular difficulty arises in obtaining a gas sample which has the same molar concentration of trace contaminants as the cryogenic liquid being sampled. Thus, for example, liquid nitrogen may typically contain trace amounts of one or more of helium, hydrogen, neon, argon, oxygen, methane, carbon monoxide, carbon  
15 dioxide and water. When the temperature of the liquid nitrogen is raised, vaporization or evaporation of the nitrogen and the different contaminating gases takes place at different temperatures and thus at different points in time.

          Thus any hydrogen, helium and neon tends to vaporize before the nitrogen and any argon, oxygen, methane, carbon monoxide, carbon dioxide and water tends  
20 to vaporize after the nitrogen. In this way fractionation of the sample occurs and the analytical composition of the gas sample continuously obtained varies continuously and does not accurately represent the analytical composition of the cryogenic liquid.

          Available samplers do not fully address the problem of fractionation of the cryogenic liquid during volatilization whereby the gas sample is not a true sample of  
25 the liquid. In many cases the resulting discrepancies are not serious, however, many users are demanding liquids of ever greater purity so that it becomes increasingly necessary to be able to detect low level contaminants.

          Therefore, a need exists in the industry for a cryogenic liquid sampler that satisfies these requirements.  
30

## Summary

A cryogenic liquid sampler is provided. The sampler includes an inner volume and a useful internal length, a cryogenic liquid inlet conduit in fluid connection with an inlet valve, a weir tube in fluid connection with the inlet valve, wherein the weir tube comprises at least one weir hole, wherein the weir tube extends a predetermined distance into the inner volume, a cryogenic liquid outlet conduit in fluid connection with inner volume and in fluid connection with an outlet valve, and a purge tube in fluid connection with the outlet valve.

In accordance with an embodiment, there is provided a cryogenic liquid sampler comprising:

- a sampler vessel comprising an inner volume, an inner wall, and an internal length,
- a cryogenic liquid inlet conduit in fluid connection with an inlet valve,
- a weir tube in fluid connection with the inlet valve, wherein the weir tube comprises at least one weir hole, wherein the weir tube extends a distance (L) from the inner wall into the inner volume,
- a cryogenic liquid outlet conduit in fluid connection with inner volume and in fluid connection with an outlet valve, and
- a purge tube in fluid connection with the outlet valve.

In accordance with another embodiment, a cryogenic liquid sampler further comprises further comprising a pressure indicator in fluid connection with the inner volume.

In accordance with another embodiment, the weir tube has an outside diameter of  $D_{wt}$ , wherein the at least one weir hole has a generally circular shape and a diameter of  $D_{wh}$ , and wherein  $D_{wh} / D_{wt}$  is between about 1/4 and about 1/2.

In accordance with another embodiment, the weir tube has an outside diameter of  $D_{wt}$ , wherein the at least one weir hole has a generally rectangular shape, a height of  $H_{wh}$ , a width of  $W_{wh}$  and wherein  $H_{wh} / D_{wt}$  is between about 1/3 and about 3/4, and wherein  $W_{wh} / D_{wt}$  is between about 1/3 and about 3/4.

In accordance with another embodiment, the distance (L) from the inner wall is between about 1/4 and 1/2 of the useful internal length; further to another embodiment the predetermined distance is between about 1/4 and 1/2 of useful internal length of the inner volume.

5

In accordance with another embodiment, the sampler vessel is stainless steel.

In accordance with another embodiment, the sampler vessel is 304 stainless steel.

10

In accordance with another embodiment, there is provided a cryogenic liquid sampler comprising:

- a sampler vessel comprising an inner volume, an inner wall, and an internal length,
- a cryogenic liquid inlet conduit in fluid connection with an inlet valve,
- a weir tube in fluid connection with the inlet valve, wherein the weir tube comprises at least one weir hole, wherein the weir tube extends into the inner volume such that the at least one weir hole is a distance (d) from the inner wall,
- a cryogenic liquid outlet conduit in fluid connection with inner volume and in fluid connection with an outlet valve, and
- a purge tube in fluid connection with the outlet valve,

15

20

25

wherein the size of the weir hole is configured to prevent the exiting fluid from being a two-phase flow, such that the weir tube has an outside diameter of  $D_{wt}$ , wherein the at least one weir hole has a generally circular shape and a diameter of  $D_{wh}$ , and wherein  $D_{wh} / D_{wt}$  is between about 1/4 and about 1/2, or

30

wherein the weir tube has an outside diameter of  $D_{wt}$ , wherein the at least one weir hole has a generally rectangular shape, a height of  $H_{wh}$ , a width of  $W_{wh}$  and wherein  $H_{wh} / D_{wt}$  is between about 1/3 and about 3/4, and wherein  $W_{wh} / D_{wt}$  is between about 1/3 and about 3/4.

In accordance with another embodiment, the sampler vessel further comprises a useful internal length (L), which is the overall length of the inner volume which may be filled with a cryogenic liquid, wherein the distance (d) is between about 1/4 and 1/2 of the useful internal length (L).

5

### **Brief Description of the Figures**

For a further understanding of the nature and aspects of the present invention, reference should be made to the following detailed description, taken in conjunction with the accompanying drawings, in which like elements are given the same or analogous reference numbers and wherein:

10

Figure 1a is a schematic representation of one embodiment of the present invention.

Figure 1b is a schematic representation of one embodiment of the present invention.

15

Figure 2a is a schematic representation of the weir tube with a circular weir hole, in accordance with one embodiment of the present invention.

Figure 2b is a schematic representation of the weir tube with a circular weir hole, in accordance with one embodiment of the present invention.

20

Figure 2c is a schematic representation of the weir tube with a rectangular weir hole, in accordance with one embodiment of the present invention.

Figure 2d is a schematic representation of the weir tube with a rectangular weir hole, in accordance with one embodiment of the present invention.

Figure 3a is a schematic representation of the attachment phase, in accordance with one embodiment of the present invention.

25

Figure 3b is a schematic representation of the filling phase, in accordance with one embodiment of the present invention.

30

Figure 3c is a schematic representation of the filling phase, in accordance with one embodiment of the present invention.

Figure 3d is a schematic representation of the filling phase, in accordance with one embodiment of the present invention.

5 Figure 3e is a schematic representation of the fluid level adjustment phase, in accordance with one embodiment of the present invention.

Figure 3f is a schematic representation of the fluid level adjustment phase, in accordance with one embodiment of the present invention.

10 Figure 3g is a schematic representation of the fluid level adjustment phase, in accordance with one embodiment of the present invention.

Figure 3h is a schematic representation of the thermal equilibrium phase, in accordance with one embodiment of the present invention.

15 Figure 4a is a schematic representation illustrating the fluid velocity entering weir holes of various sizes during the fluid level adjustment phase, in accordance with one embodiment of the present invention.

Figure 4b is a schematic representation illustrating the fluid velocity entering weir holes of various sizes during the fluid level adjustment phase, in accordance with one embodiment of the present invention.

20 Figure 4c is a schematic representation illustrating the fluid velocity entering weir holes of various sizes during the fluid level adjustment phase, in accordance with one embodiment of the present invention.

Figure 5 is a schematic representation illustrating the useful internal length of the sampler vessel.

25 **Element Numbers**

100 = cryogenic liquid sampler

101 = cryogenic liquid inlet conduit

102 = inlet valve

103 = weir tube

30 104 = weir tube top plug

105 = weir hole (in weir tube)

- 106 = minimum fill point (of weir hole)  
 107 = sampler vessel  
 108 = inner volume (of sampler vessel)  
 5 109 = inner wall (of sampler vessel)  
 110 = cryogenic liquid outlet conduit  
 111 = outlet valve  
 112 = purge tube  
 113 = cryogenic liquid  
 10 114 = cryogenic vapor  
 115 = free surface of cryogenic liquid  
 116 = cryogenic liquid level (at free surface of cryogenic liquid)  
 117 = cryogenic liquid source  
 118 = pressure indicator

15

### Description of Preferred Embodiments

Illustrative embodiments of the invention are described below. While the invention is susceptible to various modifications and alternative forms, specific embodiments thereof have been shown by way of example in the drawings and are herein described in detail. It should be understood, however, that the description herein of specific embodiments is not intended to limit the invention to the particular forms disclosed, but on the contrary, the intention is to cover all modifications, equivalents, and alternatives as understood by persons skilled in the art having regard to and the benefit of the specification as a whole.

25 It will of course be appreciated that in the development of any such actual embodiment, numerous implementation-specific decisions must be made to achieve the developer's specific goals, such as compliance with system-related and business-related constraints, which will vary from one implementation to another. Moreover, it will be appreciated that such a development effort might be complex and time-  
 30 consuming, but would nevertheless be a routine undertaking for those of ordinary skill in the art having the benefit of this disclosure.

As used herein, the term “cryogenic” is defined in its normal meaning as concerning any liquid at a temperature below  $-73^{\circ}$  C. This definition of course includes, but is not limited to, other liquefied gases including, but not necessarily limited to, oxygen, nitrogen, hydrogen, hydrocarbon gases (e.g. methane and the like) at temperatures of approximately  $-162$  C.

As used herein, the term “free surface” is defined as meaning the surface of a fluid that is subject to zero parallel shear stress, such as the boundary between two homogeneous fluids, in this case, the boundary between a cryogenic liquid and a cryogenic vapor. As used herein, the “free surface” demarks the upper boundary of the cryogenic liquid, in a direction that is perpendicular to the effects of gravity.

The cryogenic liquid source **117**, may be any device, method, or operation that produces, stores, or processes any liquid at cryogenic temperatures. In one embodiment, cryogenic liquid source **117** may be a product stream generated by a cryogenic air separation unit (not shown). Often, the purity of the cryogenic liquid will need to be checked or verified. Cryogenic liquid source **117**, which is presumed to be homogeneous, has a constituent composition, which is defined as the in-situ ratios of the various components and contaminants. It is critical, when taking a sample of this cryogenic liquid, to maintain the constituent composition.

Turning to Figures 1a, 1b, 2a, 2b, and 5, cryogenic liquid sampler **100** is provided. Cryogenic liquid sampler **100** includes cryogenic liquid inlet conduit **101**, cryogenic liquid outlet conduit **110**, inner wall **109**, and an inner volume **108**. Cryogenic liquid sampler **100** may be made of any material that is compatible with the cryogenic liquid to be sampled, the cryogenic temperatures to be encountered, and the elevated pressures that will be present during transport. Cryogenic liquid sampler **100** may be made of stainless steel, preferably **304** stainless steel. Cryogenic liquid sampler **100** may also include pressure indicator **118**.

Cryogenic liquid inlet conduit **101** includes inlet valve **102** and weir tube **103**. Weir tube **103** includes weir tube top plug **104** and at least one weir hole **105**. As illustrated in Figures 2a and 2b, weir hole **105** may be circular, with a diameter of  $D_{wh}$ . As illustrated in Figures 2c and 2d, weir hole **105** may be rectangular, with a width of  $W_{wh}$  and a height of  $H_{wh}$ . Weir tube **103** extends into inner volume **108** of

sampler vessel **107**. The bottom of weir hole **105** is the minimum fill point **106** and is the point along the perimeter of weir hole **105** that is closest to inner wall **109**, being situated a predetermined distance **116** from inner wall **109**. Cryogenic liquid outlet conduit **110** includes outlet valve **111** and purge tube **112**. As will be discussed below, the predetermined distance **116** will ultimately determine the liquid sample volume.

Now turning to Figures 3a – 3h, a method of taking a sample of a cryogenic liquid is provided. What may be referred to as “the attachment phase, is indicated in Figure 3a. In the attachment phase, cryogenic liquid source **117** is attached to cryogenic liquid inlet conduit **101**. At this time, the inner volume **108** of sampler vessel **107** has a pressure of  $P_0$ .  $P_0$  may be approximately atmospheric pressure. Cryogenic liquid source **117** has a delivery pressure  $P_1$ .  $P_1$  may be greater than  $P_0$ .

What may be referred to as the “filling phase” is indicated in Figures 3b – 3d. When it is desired to actually take the cryogenic liquid sample, as indicated in Figure 3b, inlet valve **102** and outlet valve **111** are opened, allowing cryogenic liquid **113** to flow through weir tube **103** and begin filling inner volume **108** of sampler vessel **107**.

As indicated in Figure 3c, once cryogenic liquid **113** completely occupies inner volume **108**, it then flows out cryogenic liquid outlet conduit **110**, outlet valve **111**, and through purge tube **112**, where it is vented or otherwise properly disposed of (not shown). At this time, it may be desirable to partially close outlet valve **111** in order to reduce the flowrate of cryogenic liquid **113** out of purge tube **112**. Once a steady stream of cryogenic liquid **113** is flowing out of purge tube **112**, and no more residual air is present in inner volume **108**, inlet valve **102** and outlet valve **111** are simultaneously closed, as indicated in Figure 3d. Cryogenic liquid source **117** is then detached from cryogenic liquid inlet conduit **101**. At this time, the cryogenic liquid that fills inner volume **108** is at a pressure of approximately  $P_1$ .

What may be referred to as the “fluid level adjustment phase” is indicated in Figures 3e – 3g. As indicated in Figure 3e, inlet valve **102** is now opened, preferably partially, to allow cryogenic liquid **113** to enter weir hole(s) **105**, flow through weir tube **103** and inlet valve **102** and out cryogenic liquid inlet conduit to be vented or otherwise properly disposed of (not shown). As outlet valve **111** remains closed, the

removal of cryogenic liquid **113** results in a lower pressure of P2 within inner volume **108**, and the creation of a region of cryogenic vapor **114**. P2 may be less than P1.

As indicated in Figure 3f, cryogenic liquid **113** will cease to exit sampler vessel **107** once the free surface **115** of the cryogenic liquid is level **116** with the minimum fill point **106**. If inlet valve **102** remains open beyond this time, only cryogenic vapor **114** will exit as the internal pressure of sampler vessel **107** continues to drop. At this time, a lower pressure P3 is present with inner volume **108**, and the region of cryogenic vapor **114** is larger. P3 may be less than P2. As indicated in Figure 3g, at this time inlet valve **102** is closed and the sampler vessel **107** is sealed. At this time, sample vessel is still at a very low temperature. Without some external refrigeration source, heat from the surrounding environment will enter sample vessel **107** and gradually the temperatures will reach equilibrium.

What may be referred to as the “thermal equilibrium phase” is indicated in Figure 3h. As sampler vessel **107** reaches thermal equilibrium with the external environment, the temperature will rise to approximately ambient temperature, and the internal pressure P4 will simultaneously rise as all of the cryogenic liquid **113** becomes cryogenic vapor **114**. P4 may be greater than P3. P4 may be greater than P1. Once this thermal equilibrium is approximately achieved, internal pressure P4 may be between 1000 psig and 1800 psig. Internal pressure P4 may be between 1100 psig and 1500 psig. Once sampler vessel **107** has reached the above equilibrium, it may be placed in a carrying case if desired (not shown) and then may be transported to facility for testing.

The addition of at least one weir hole **105** in weir tube **103** reduces the velocity of the fluid entering weir tube **103**. During the initial stages of the fluid level adjustment phase, as indicated in Figure 4a, there will be a region within sampler vessel **107** that experiences a transition of cryogenic liquid **113** into a vapor phase **114**. During the initial stages, the weir hole will largely be immersed in liquid cryogen, but any turbulence that is experienced within sampler vessel **107** may cause a region of two phase (i.e. cryogenic liquid and cryogenic vapor) to form.

As indicated in Figures 3f and 3g, as the free surface **116** of the cryogenic liquid is at minimum fill point **106**, weir hole **105**, no additional liquid should exit

sampler vessel **107**, but the operator should only note cryogenic vapor **114** exiting. This should be the indication to close outlet valve **111**. However, if weir hole **105** is improperly sized, entrained liquid may still exit sampler vessel **107**, and an unknown amount of cryogenic liquid **113** may remain.

5           Such configurations are illustrated in Figures 4a – 4c. In Figures 4a – 4c the weir hole **105** is represented as being circular. However, this is merely representative and, as illustrated in Figures 2c and 2d, weir hole **105** may be rectangular. In Figure 4a, weir hole **105** is too large and the velocity  $V_1$  of the fluid entering from inner volume **105** is too high. This configuration allows for rapid filling and fluid level adjustment but also allows for a velocity that is sufficiently high as to  
10 allow two-phase fluid **115** to exit weir tube **103**. In Figure 4b, weir hole **105** is too small and the velocity  $V_2$  of the fluid entering from inner volume **105** is too low. This configuration allows accurate fluid level adjustment and allows only cryogenic vapor **114** to enter weir tube **103** at the end of the fluid level adjustment period. However,  
15 this configuration requires a prohibitively long filling phase.

Figure 4c illustrates a weir hole **105** that is appropriately sized. The velocity  $V_3$  of the fluid entering from inner volume **105** is sufficiently high to allow for a reasonable filling and fluid level adjustment time. But this configuration does not have sufficiently high velocity to allow excess entrained liquid to enter weir tube **105**  
20 at the end of the fluid level adjustment period, only allowing cryogenic vapor **114**.

The distance **116** of minimum fill point **106** from the inner wall **109** of sampler vessel **107** depends on the specific requirements of the particular cryogenic liquid sampler **100**. As indicated in Figure 5, a useful internal length  $L$  of sampler vessel **107**, may be defined as the distance between the inner wall **109a** at one end, and the  
25 inner wall **109b** at the opposite end of sampler vessel **107**. This useful internal length  $L$  will depend on the actual shape of the particular sampler vessel, but will generally be the length of the internal volume **108**, which will be filled with cryogenic liquid **113** during the filling phase of the method. In some embodiments distance **116** may be between about  $1/4$  and about  $1/2$  of  $L$ .

30           The diameter  $D_{wh}$  of a circular weir hole **105** depends on the specific requirements of the particular cryogenic liquid sampler **100**. If  $D_{wt}$  is the nominal

outside diameter of weir tube **103**, then in some embodiments  $D_{wh}$  may be between about 1/4 and about 1/2 of  $D_{wt}$ .

5 The height  $H_{wh}$  and/or  $W_{wh}$  width of a rectangular weir hole **105** depends on the specific requirements of the particular cryogenic liquid sampler **100**. If  $D_{wt}$  is the nominal outside diameter of weir tube **103**, then in some embodiments  $W_{wh}$  may be between about 1/4 and about 1/2 of  $D_{wt}$ . In some embodiments  $W_{wh}$  may be between about 1/3 and about 3/4 of  $D_{wt}$ . In some embodiments  $H_{wh}$  may be between about 1/3 and about 3/4 of  $H_{wt}$ .

10 It will be understood that many additional changes in the details, materials, steps and arrangement of parts, which have been herein described in order to explain the nature of the invention, may be made by those skilled in the art having regard to and the benefit of the specification as a whole. Thus, the present invention is not intended to be limited to the specific embodiments in the examples given above.

15

What is claimed is:

1. A cryogenic liquid sampler comprising:

- a sampler vessel comprising an inner volume, an inner wall, and an internal length,
- a cryogenic liquid inlet conduit in fluid connection with an inlet valve,
- a weir tube in fluid connection with the inlet valve, wherein the weir tube comprises at least one weir hole, wherein the weir tube extends into the inner volume such that the at least one weir hole is a distance from the inner wall,
- a cryogenic liquid outlet conduit in fluid connection with inner volume and in fluid connection with an outlet valve, and
- a purge tube in fluid connection with the outlet valve,

wherein the size of the weir hole is configured to prevent the exiting fluid from being a two-phase flow, such that the weir tube has an outside diameter of  $D_{wt}$ , wherein the at least one weir hole has a generally circular shape and a diameter of  $D_{wh}$ , and wherein  $D_{wh} / D_{wt}$  is between about  $1/4$  and about  $1/2$ , or

wherein the weir tube has an outside diameter of  $D_{wt}$ , wherein the at least one weir hole has a generally rectangular shape, a height of  $H_{wh}$ , a width of  $W_{wh}$  and wherein  $H_{wh} / D_{wt}$  is between about  $1/3$  and about  $3/4$ , and wherein  $W_{wh} / D_{wt}$  is between about  $1/3$  and about  $3/4$ .

2. The cryogenic liquid sampler of claim 1, further comprising a pressure indicator in fluid connection with the inner volume.

3. The cryogenic liquid sampler of claim 1 or claim 2, wherein the sampler vessel further comprises an internal length ( $L$ ), which is the overall length of the inner volume which may be filled with a cryogenic liquid, wherein the distance is between about  $1/4$  and  $1/2$  of the internal length ( $L$ ).

4. The cryogenic liquid sampler of any one of claims 1 to 3, wherein the sampler vessel is stainless steel.

5. The cryogenic liquid sampler of any one of claims 1 to 4, wherein the sampler vessel is 304 stainless steel.

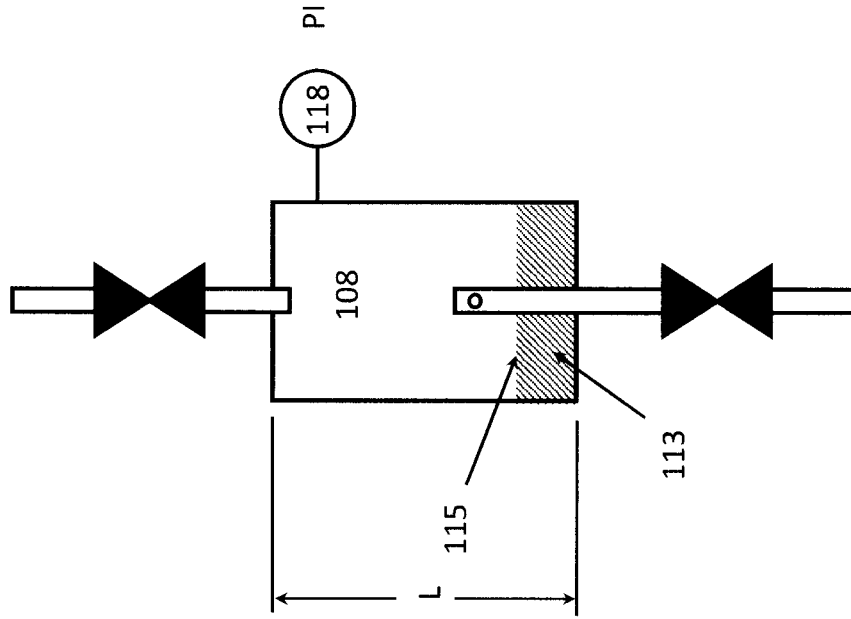


Figure 1b

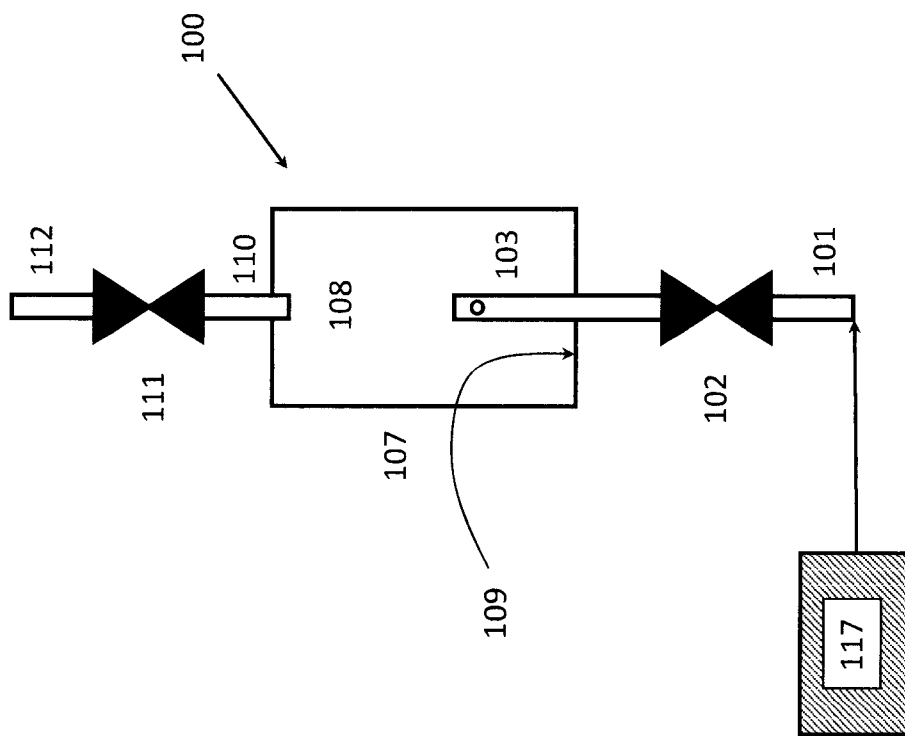


Figure 1a



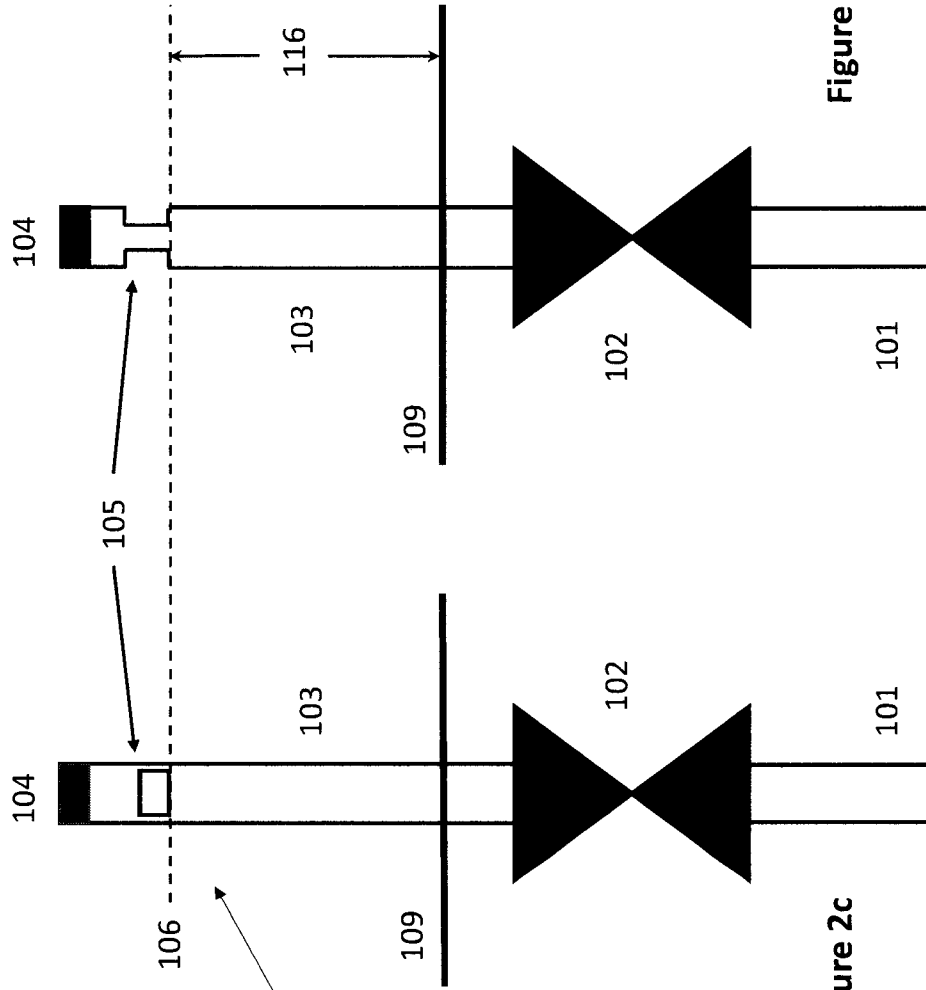
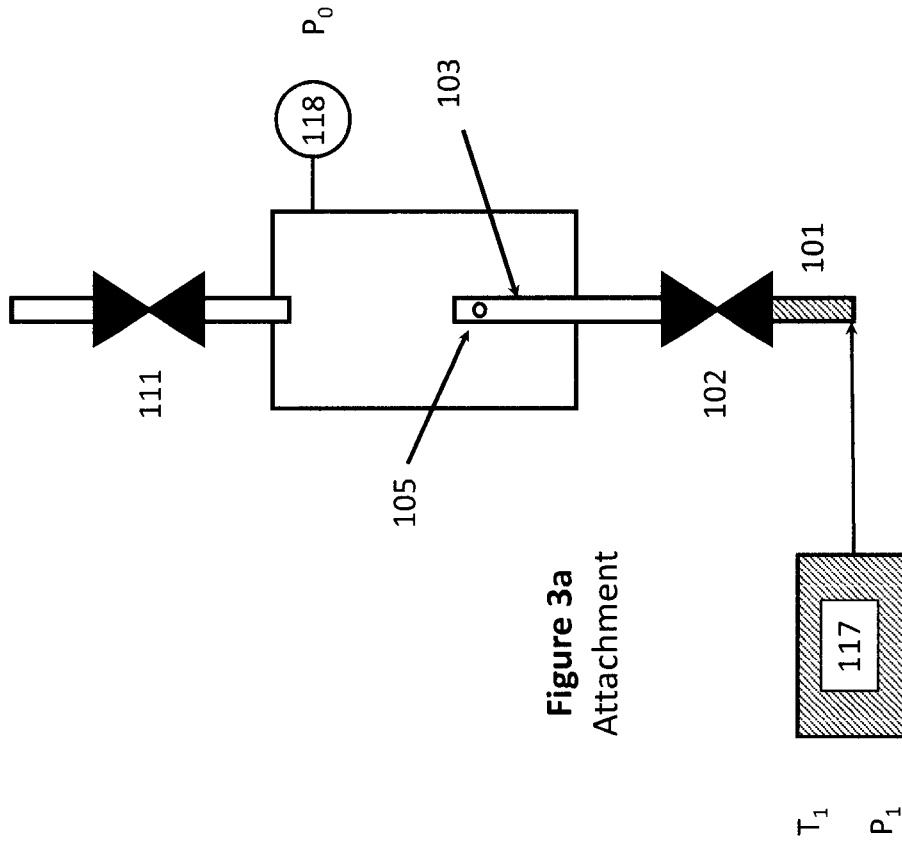
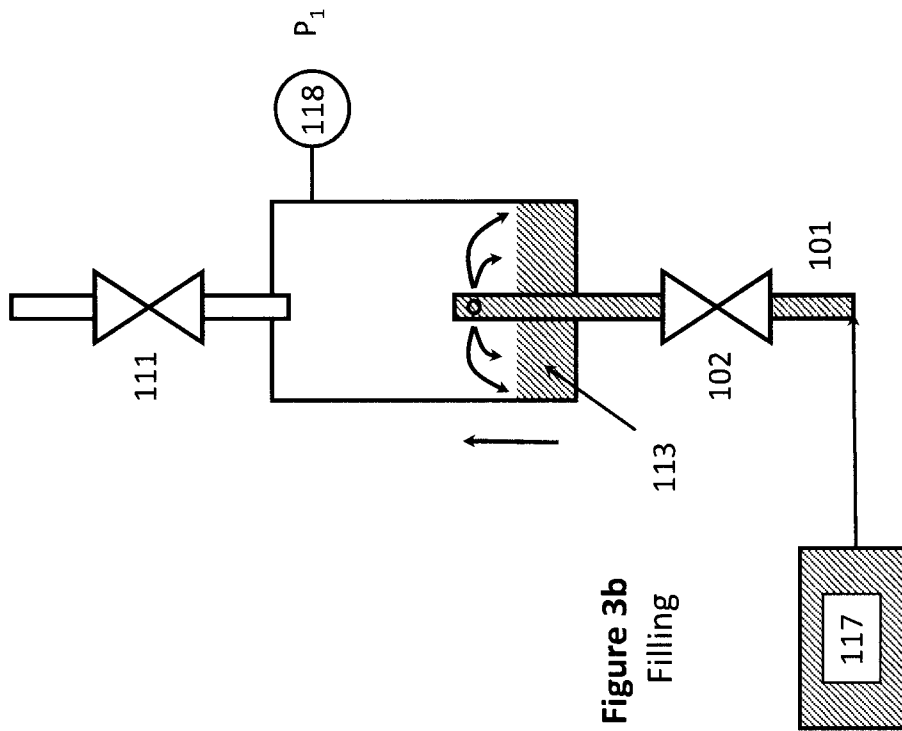


Figure 2d

Figure 2c



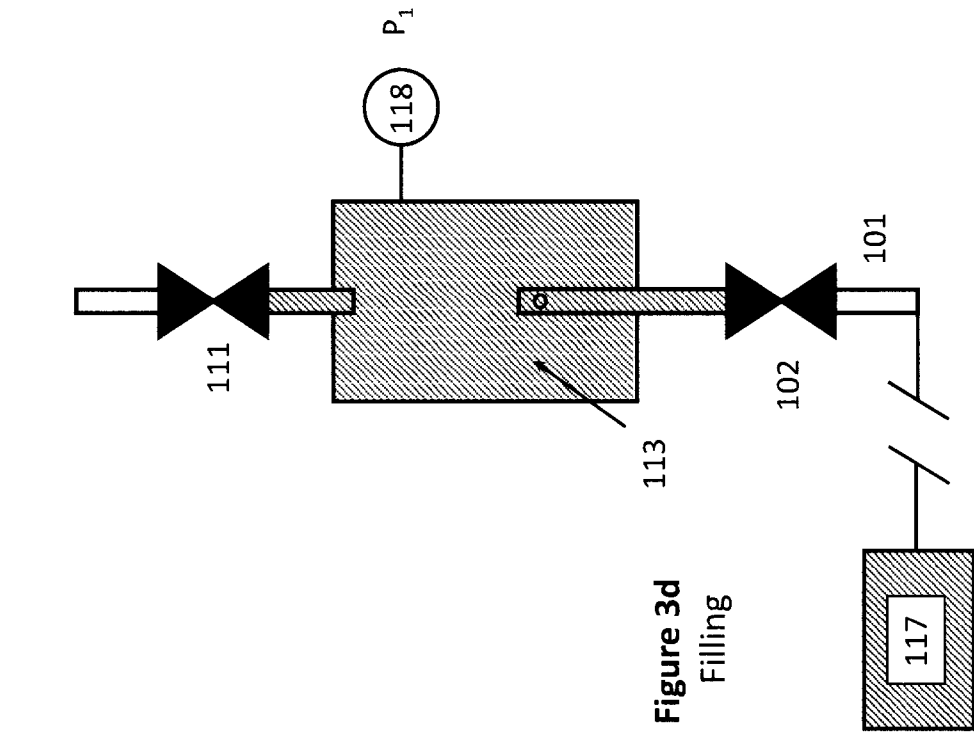


Figure 3c  
Filling

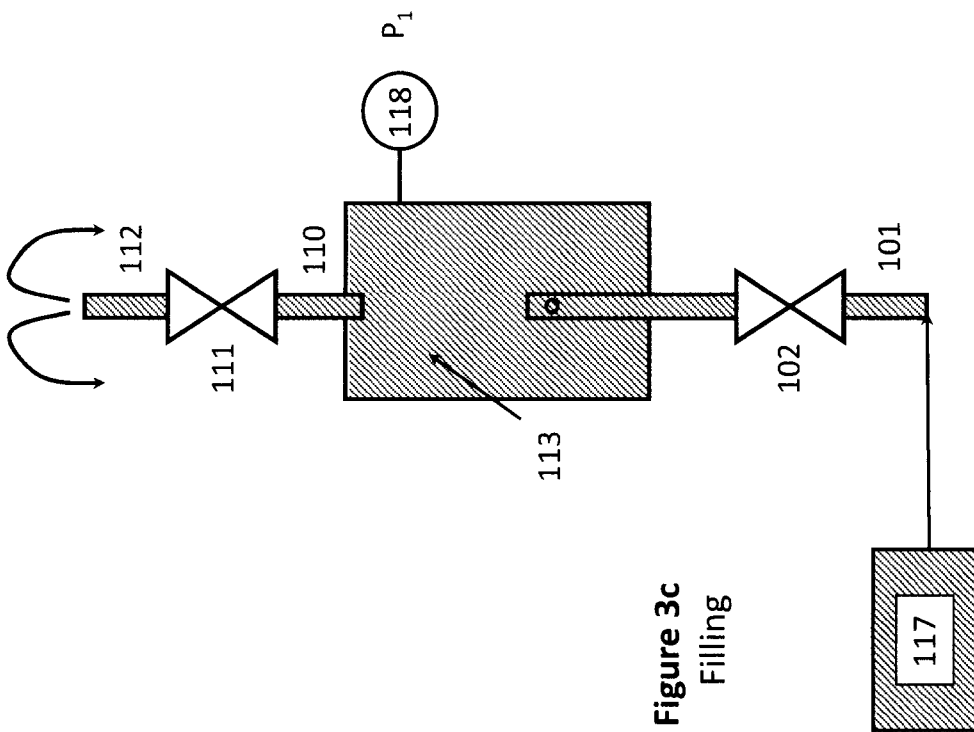
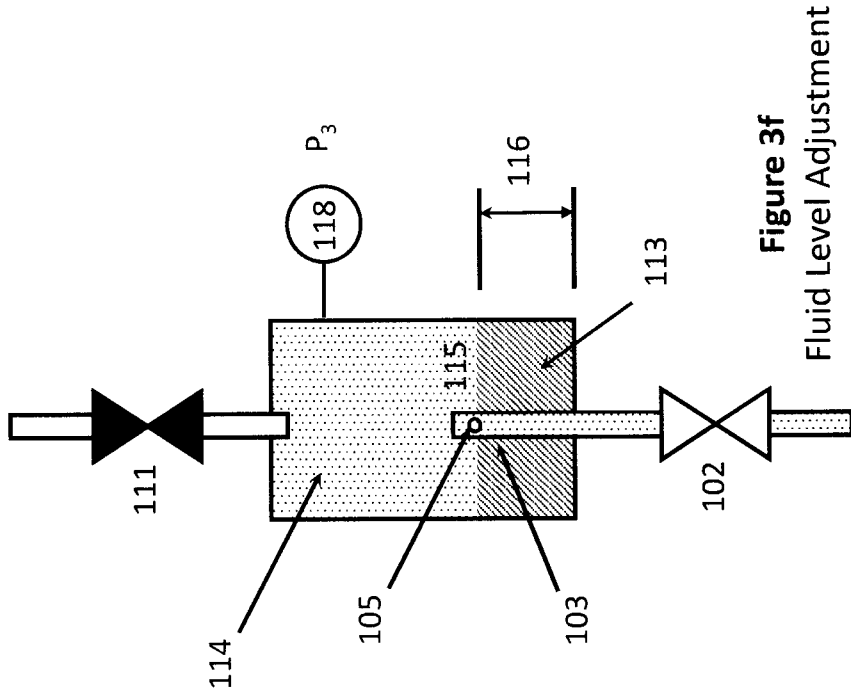
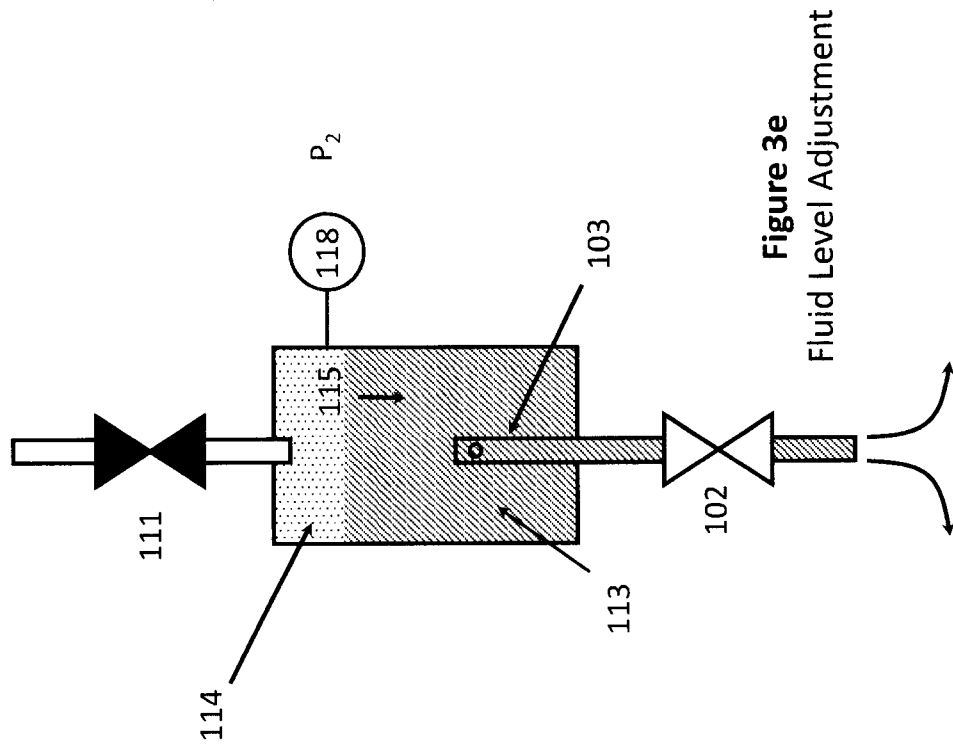


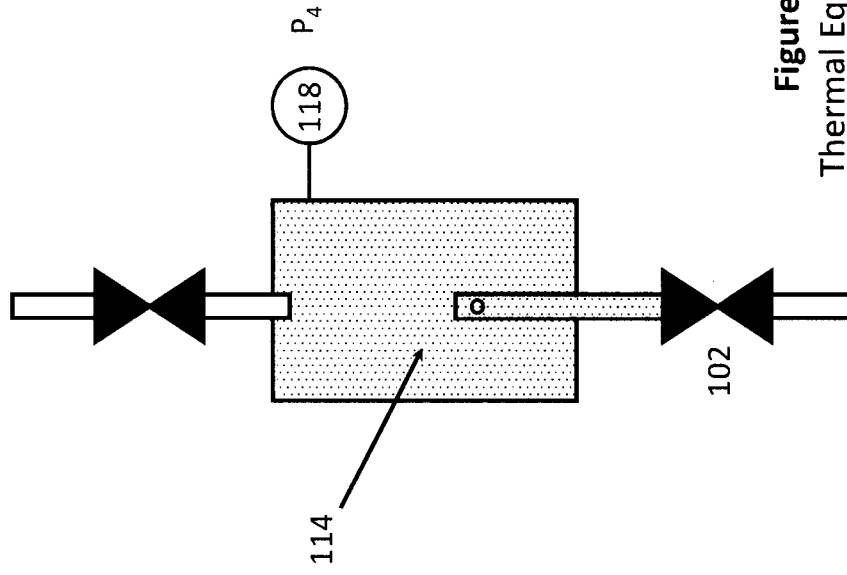
Figure 3d  
Filling



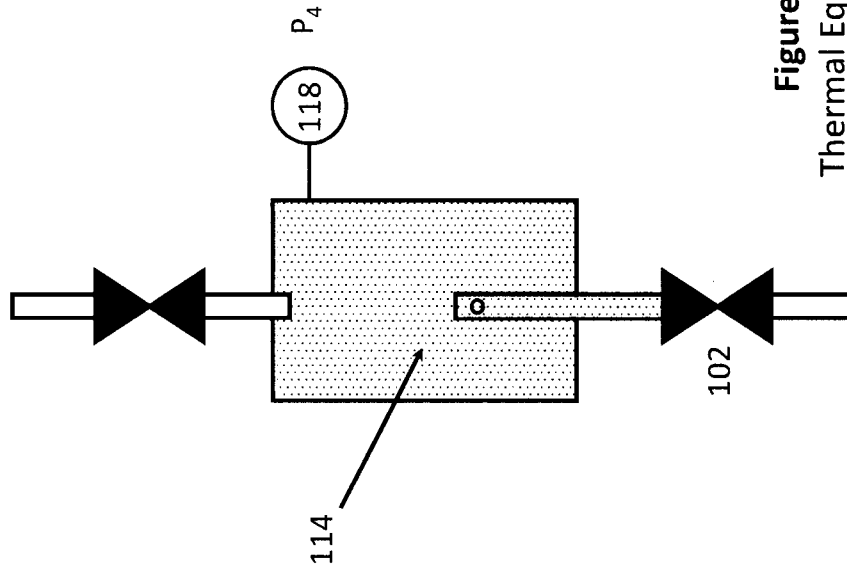
**Figure 3f**  
Fluid Level Adjustment



**Figure 3e**  
Fluid Level Adjustment



**Figure 3g**  
Fluid Level Adjustment



**Figure 3h**  
Thermal Equilibrium

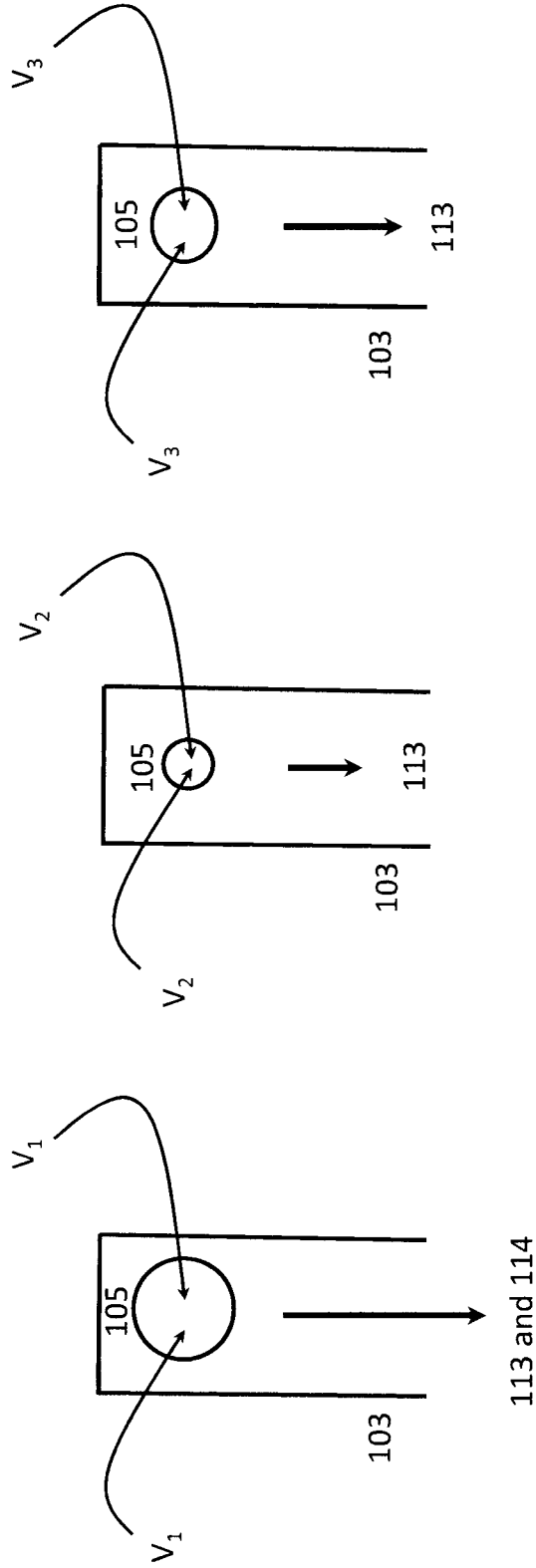
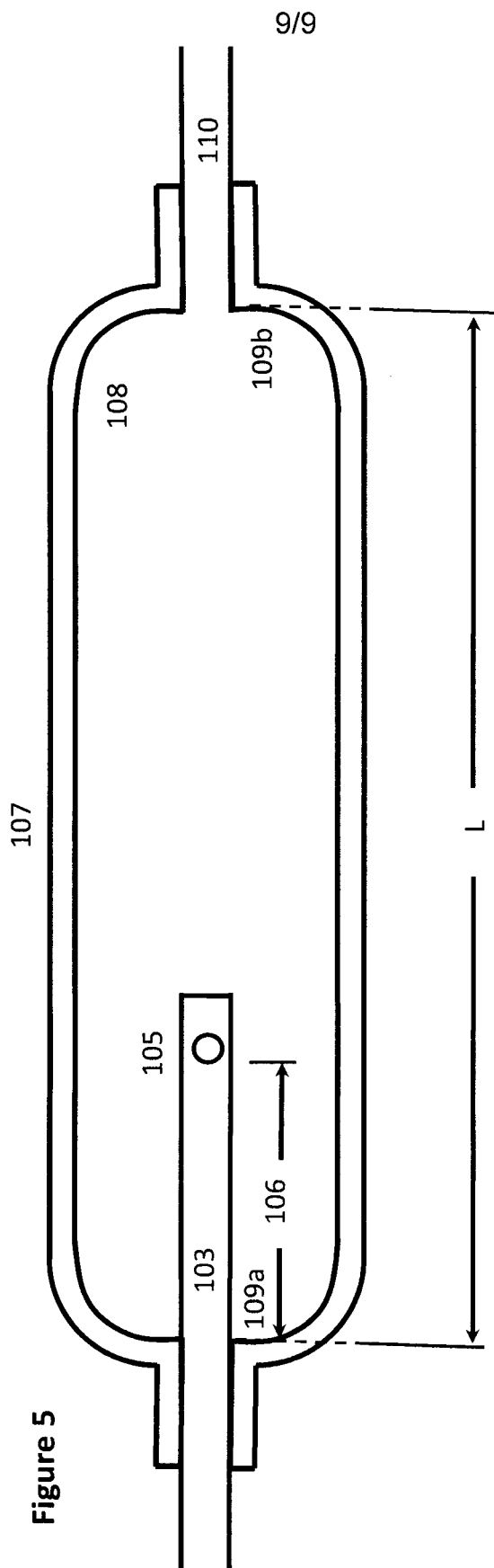


Figure 4c

Figure 4b

Figure 4a



9/9

Figure 5

