

(19)



(11) Publication number:

**SG 171929 A1**

(43) Publication date:

**28.07.2011**

(51) Int. Cl:

;

(12)

## Patent Application

(21) Application number: **2011040359**

(22) Date of filing: **04.12.2009**

(30) Priority: **US 61/200,814 04.12.2008**

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(54) **Title:**  
**METHODS AND APPARATUS FOR MOVING ALIQUOT  
SAMPLES OF FLUID**

(57) **Abstract:**  
Methods and apparatus for moving aliquot samples of fluid using  
a shuttle valve are disclosed.



(51) International Patent Classification:  
**B01L 3/02** (2006.01)

(21) International Application Number:  
PCT/US2009/006397

(22) International Filing Date:  
4 December 2009 (04.12.2009)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
61/200,814 4 December 2008 (04.12.2008) US

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

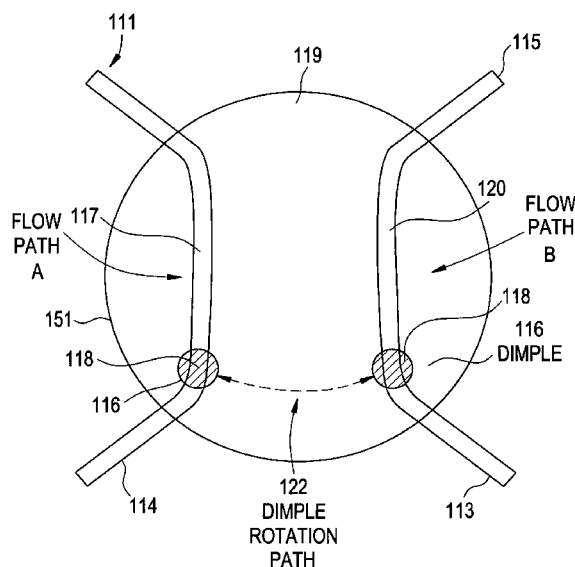
(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV,

[Continued on next page]

(54) Title: METHODS AND APPARATUS FOR MOVING ALIQUOT SAMPLES OF FLUID

(57) Abstract: Methods and apparatus for moving aliquot samples of fluid using a shuttle valve are disclosed.

FIG. 1





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MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, **Published:**  
TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, — *with international search report (Art. 21(3))*  
ML, MR, NE, SN, TD, TG).

## **METHODS AND APPARATUS FOR MOVING ALIQUOT SAMPLES OF FLUID**

### **FIELD OF THE INVENTION**

**[0001]** The present invention is directed to methods and apparatus for moving aliquot samples of fluid.

### **BACKGROUND OF THE INVENTION**

**[0002]** There is a need in the art for methods of efficiently and effectively moving aliquot samples of fluid. There is also a need in the art for an apparatus capable of effectively moving aliquot samples of fluid.

### **SUMMARY OF THE INVENTION**

**[0003]** The present invention relates to the discovery of methods for moving aliquot samples of fluid. The disclosed methods provide a number of advantages over known methods of moving aliquot samples of fluid. For example, the disclosed methods of the present invention may be utilized to remove a very small sample volume, or aliquot, of fluid from a much larger volume of fluid, such as the flow of a stream through a channel. The disclosed methods of the present invention may also be utilized to remove a very small sample volume, or aliquot, of fluid from a much larger volume of fluid, such as the flow of a stream through a channel, and transfer the sample to another volume of fluid or container.

**[0004]** The present invention is directed to methods of moving aliquot samples of fluid. In one exemplary embodiment, the method of moving an aliquot sample of fluid comprises the steps of providing a first fluid, providing a second fluid, using a shuttle valve to remove an aliquot from the first fluid to the second fluid while maintaining a continuous flow path through the shuttle valve of the second fluid. In one embodiment, the first fluid comprises a continuous flow path through the shuttle valve which remains open when the aliquot is removed from the first fluid. In another embodiment, both the first fluid and the second fluid comprise continuous paths through the shuttle valve which remain open as the aliquot sample is removed from the first fluid.

**[0005]** In another exemplary embodiment according to the present invention, a method of moving an aliquot sample of fluid includes the steps of providing a first fluid; using a shuttle valve to remove an aliquot sample from the first fluid without substantially affecting flow properties of the first fluid through the shuttle valve. At least a portion of flow of the first fluid through the shuttle valve may be substantially

laminar, due to at least a portion of the first fluid flow path being substantially straight through the valve. In a further exemplary embodiment, the pressure of the first fluid through the shuttle valve remains substantially constant and/or it does not substantially increase. In an alternative embodiment, the aliquot sample is transferred from a first fluid to a second fluid. The second fluid may comprise a continuous flow path through the shuttle valve.

**[0006]** In a further exemplary embodiment according to the present invention, the method of moving an aliquot sample of fluid comprises the steps of providing a static body having at least two channels therethrough such that at least a portion of each channel is parallel to and intersects with a first surface of the static body, providing a dynamic body having an aliquot dimple that intersects with a first surface of the dynamic body, the first surface of the static body and dynamic body being contiguous with each other and the channels and the aliquot dimple located such that the aliquot dimple may be in fluid communication with one channel in a first position and in fluid communication with another channel in a second position, flowing a first fluid through one of said channels, flowing a second fluid through another of said channels, aligning the aliquot dimple in the first position, allowing a sample portion of the first fluid to flow into the aliquot dimple, and moving the aliquot dimple to the second position, whereby the sample portion is transferred to the second fluid.

**[0007]** The present invention is also directed to an apparatus capable of moving an aliquot sample of fluid. In one exemplary embodiment, the apparatus for moving an aliquot sample of fluid comprises hardware operatively adapted to remove a very small sample volume, or aliquot, of fluid from a much larger volume of fluid, for example, such as the flow of a stream through a channel. The disclosed apparatus of the present invention may also be utilized to remove a very small sample volume, or aliquot, of fluid from a much larger volume of fluid, for example, such as the flow of a stream through a channel, and transfer the sample to another volume of fluid or container.

**[0008]** In one exemplary embodiment, an apparatus capable of moving an aliquot sample of fluid comprises a first fluid, a second fluid, and a shuttle valve capable of removing an aliquot from the first fluid to the second fluid while maintaining a continuous flow path through the shuttle valve of the second fluid. In one embodiment, the apparatus is capable of removing the aliquot from the first fluid while maintaining a continuous flow path through the shuttle valve of the first fluid. In another embodiment, the apparatus is capable of removing the aliquot from the first fluid while maintaining continuous flow paths of both the first fluid and the second fluid.

**[0009]** In another embodiment according to the present invention, an apparatus capable of moving an aliquot sample of fluid comprises a first fluid channel, a second fluid channel, and a shuttle valve capable of removing an aliquot of fluid from the first channel to the second channel without substantially affecting the flow properties of fluid in the first channel through the valve. At least a portion of the first channel through the valve may be substantially straight. In this embodiment, the pressure of fluid in the first channel through the shuttle valve does not substantially increase. In another exemplary embodiment, at least a portion of the first channel may be substantially parallel to the aliquot dimple, which provides laminar flow of fluid in the first channel through the valve. In a further embodiment, at least a portion of the second channel through the valve may be substantially straight. In this embodiment, the pressure of fluid in the second channel through the shuttle valve does not substantially increase. In another exemplary embodiment, the second channel may be substantially parallel to the aliquot dimple, which provides laminar flow of fluid in the second channel through the valve.

**[0010]** In a further exemplary embodiment according to the present invention, an apparatus capable of moving an aliquot sample of fluid comprises a static body having at least two channels therethrough such that a portion of each channel intersects with a first surface of the static body, a dynamic body having an aliquot dimple that intersects with a first surface of the dynamic body, the first surface of the static body and the first surface of the dynamic body being contiguous with each other, and the channels and the aliquot dimple located such that the aliquot dimple may be in fluid communication with one channel in a first position and in fluid communication with another channel in a second position, wherein at least a portion of the first channel is substantially parallel to the first surface of the static body. In an alternative exemplary embodiment, at least a portion of the first channel through the valve may be substantially straight. In an exemplary embodiment, the pressure of fluid in the first channel through the shuttle valve does not substantially increase. In another exemplary embodiment, at least a portion of the first channel may be substantially parallel to the aliquot dimple. In an exemplary embodiment, the flow of fluid in the first channel through the valve is laminar. In a further embodiment, at least a portion of the second channel through the valve may be substantially straight. In a further embodiment, the pressure of fluid in the second channel through the shuttle valve does not substantially increase. In another exemplary embodiment, the second channel may be substantially parallel to the aliquot dimple. In an embodiment, the flow of fluid in the second channel through the valve may be laminar.

**[0011]** In a further exemplary embodiment according to the present invention, an apparatus capable of moving an aliquot sample of fluid comprises a static body having at least two channels therethrough such that a portion of each channel intersects with a first surface of the static body, a dynamic body having an aliquot dimple that intersects with a first surface of the dynamic body, the first surface of the static body and the first surface of the dynamic body being contiguous with each other, and the channels and the aliquot dimple located such that the aliquot dimple may be in fluid communication with one channel in a first position and in fluid communication with another channel in a second position, wherein at least a portion of the second channel is substantially parallel to the first surface of the static body.

**[0012]** In a further exemplary embodiment, the apparatus of the present invention may be configured such that the static body includes an aliquot dimple and the dynamic body includes at least two channels therethrough. Moreover, the apparatus of the present invention may include at least one body that is dynamic, such as for example, two or more dynamic bodies with no static body.

**[0013]** These and other features and advantages of the present invention will become apparent after a review of the following detailed description of the disclosed embodiments and the appended claims.

#### **BRIEF DESCRIPTION OF THE FIGURES**

**[0014]** FIG. 1 depicts the operation of an exemplary shuttle valve suitable for use in the present invention;

**[0015]** FIG. 2 depicts a cross-sectional view of an exemplary shuttle valve suitable for use in the present invention;

**[0016]** FIGS. 3A-3C depict exemplary static bodies of the shuttle valve suitable for use in the present invention;

**[0017]** FIG. 4 depicts an exemplary dynamic body of the shuttle valve suitable for use in the present invention;

**[0018]** FIG. 5 depicts an exemplary dynamic body of the shuttle valve suitable for use in the present invention;

**[0019]** FIG. 6A-6B depicts a cross-sectional view of the operation of an exemplary shuttle valve suitable for use in the present invention;

**[0020]** FIG. 7 depicts an exemplary shuttle valve as part of a sample analyzer suitable for use in a chromatography system; and

**[0021]** FIG. 8 depicts an exemplary shuttle valve as a sample injection valve suitable for use in a chromatography system.

#### **DETAILED DESCRIPTION OF THE INVENTION**

**[0022]** To promote an understanding of the principles of the present invention, descriptions of specific embodiments of the invention follow and specific language is used to describe the specific embodiments. It will nevertheless be understood that no limitation of the scope of the invention is intended by the use of specific language. Alterations, further modifications, and such further applications of the principles of the present invention discussed are contemplated as would normally occur to one ordinarily skilled in the art to which the invention pertains.

**[0023]** It must be noted that as used herein and in the appended claims, the singular forms "a", "and", and "the" include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to "a solvent" includes a plurality of such solvents and reference to "solvent" includes reference to one or more solvents and equivalents thereof known to those skilled in the art, and so forth.

**[0024]** "About" modifying, for example, the quantity of an ingredient in a composition, concentrations, volumes, process temperatures, process times, recoveries or yields, flow rates, and like values, and ranges thereof, employed in describing the embodiments of the disclosure, refers to variation in the numerical quantity that may occur, for example, through typical measuring and handling procedures; through inadvertent error in these procedures; through differences in the ingredients used to carry out the methods; and like proximate considerations. The term "about" also encompasses amounts that differ due to aging of a formulation with a particular initial concentration or mixture, and amounts that differ due to mixing or processing a formulation with a particular initial concentration or mixture. Whether modified by the term "about" the claims appended hereto include equivalents to these quantities.

**[0025]** As used herein, the term "shuttle valve" means a control valve that regulates the supply of fluid from one or more source(s) to another location. The shuttle valve may utilize rotary or linear motion to move a sample from one fluid to another and may be configured such that at least one body or part is dynamic.

**[0026]** As used herein, the term "fluid" means a gas, liquid, and supercritical fluid.

**[0027]** As used herein, the term "laminar flow" means smooth, orderly movement of a fluid, in which there is no turbulence, and any given subcurrent moves more or less in parallel with any other nearby subcurrent.

**[0028]** As used herein, the term "substantially" means within a reasonable amount, but includes amounts which vary from about 0% to about 50% of the absolute value, from about 0% to about 40%, from about 0% to about 30%, from about 0% to about 20% or from about 0% to about 10%.



**[0029]** The present invention is directed to methods of moving aliquot samples of fluid. The present invention is further directed to apparatus capable of moving aliquot samples of fluid. The present invention is even further directed to computer software suitable for use in an apparatus or apparatus component that is capable of moving aliquot samples of fluid, wherein the computer software enables the apparatus to perform one or more method steps as described herein.

**[0030]** A description of exemplary methods of moving aliquot samples of fluid and apparatus capable of moving aliquot samples of fluid is provided below.

*I. Methods of Moving Aliquot Samples of Fluid*

**[0031]** The present invention is directed to methods of moving aliquot samples of fluid. The methods of moving aliquot samples of fluid may contain a number of process steps, some of which are described below.

**[0032]** In this exemplary embodiment, the shuttle valve according to the present invention actively controls the transfer of aliquot sample of fluid from one vessel or stream to another. As used herein, the phrase “actively controls” refers to the ability of a given shuttle valve to control fluid transfer from one vessel or stream to another even though there may be changes in fluid flow rate of the streams through the shuttle valve. Unlike “passive” flow splitters that merely split fluid flow, the shuttle valves used in the present invention control removal of aliquot samples of fluid from one stream to the other regardless of possible fluctuations in fluid flow within the sample stream such as, for example, flow restrictions, total flow rate, temperature, and/or solvent composition.

**[0033]** The step of actively controlling transfer of aliquot samples of fluid from one stream or vessel to another may comprise, for example, sending an activation signal to a shuttle valve of the present invention to (i) activate the shuttle valve, (ii) deactivate the shuttle valve, (iii) change one or more flow and/or pressure settings of the shuttle valve, or (iv) any combination of (i) to (iii). Suitable flow and pressure settings include, but are not limited to, (i) a valve position, (ii) shuttle valve pressure, (iii) air pressure to a valve, or (iv) any combinations of (i) to (iii). Typically, the activation signal is in the form of, for example, an electrical signal, a pneumatic signal, a digital signal, or a wireless signal.

In one exemplary embodiment, the method of moving an aliquot sample of fluid comprises the steps of providing a first fluid, providing a second fluid, using a shuttle valve to remove an aliquot from the first fluid to the second fluid while maintaining a continuous flow path through the shuttle valve of the second fluid. In one embodiment, the first fluid comprises a continuous flow path through the shuttle valve which remains open when the aliquot is removed from the first fluid. In

another embodiment, both the first fluid and the second fluid comprise continuous paths through the shuttle valve which remain open as the aliquot sample is removed from the first fluid.

**[0034]** In another exemplary embodiment according to the present invention, a method of moving an aliquot sample of fluid includes the steps of providing a first fluid; using a shuttle valve to remove an aliquot sample from the first fluid without substantially affecting flow properties of the first fluid through the shuttle valve. At least a portion of flow of the first fluid through the shuttle valve may be substantially laminar, due to at least a portion of the first fluid flow path being substantially straight through the valve. In a further exemplary embodiment, the pressure of the first fluid through the shuttle valve remains substantially constant and/or it does not substantially increase. In an alternative embodiment, the aliquot sample is transferred from a first fluid to a second fluid. The second fluid may comprise a continuous flow path through the shuttle valve.

**[0035]** In a further exemplary embodiment according to the present invention, the method of moving an aliquot sample of fluid comprises the steps of providing a static body having at least two channels therethrough such that at least a portion of each channel is parallel to and intersects with a first surface of the static body, providing a dynamic body having an aliquot dimple that intersects with a first surface of the dynamic body, the first surface of the static body and dynamic body being contiguous with each other and the channels and the aliquot dimple located such that the aliquot dimple may be in fluid communication with one channel in a first position and in fluid communication with another channel in a second position, flowing a first fluid through one of said channels, flowing a second fluid through another of said channels, aligning the aliquot dimple in the first position, allowing a sample portion of the first fluid to flow into the aliquot dimple, and moving the aliquot dimple to the second position, whereby the sample portion is transferred to the second fluid.

**[0036]** FIGS. 1-2 depict an exemplary shuttle valve of the present invention and how it operates by removal of an aliquot sample of fluid from one fluid stream to another. As shown in FIG. 1, shuttle valve 100 comprises an inlet 111 of a first stream, which provides fluid flow from a sample stream or vessel to shuttle valve 100; channel 117 connecting inlet 111 to an outlet 114 of the first stream; an incoming sample aliquot volume 118 in dimple 116 of dynamic body 119; outlet 114 provides fluid flow from shuttle valve 100 to the sample stream or vessel, or a different stream or vessel; inlet 115, which provides fluid flow of a second stream through shuttle valve 100; outgoing sample aliquot volume 118 in dimple 116;

channel **120** connecting inlet **115** to outlet **113**, which provides fluid flow through the shuttle valve **100** to a another stream or vessel.

[0037] As fluid flows through shuttle valve **100** from to inlet **111** to outlet **114** via channel **117**, incoming sample aliquot volume **118** in dimple **116** is filled with a specific volume of fluid referred to herein as sample aliquot **118** (shown as the shaded area in FIG. 1). At a desired time, shuttle valve **100** transfers sample aliquot **118** within dimple **116** taken from channel **117** to channel **120** by rotating the dimple **116** in dynamic body **119** via dimple rotation path **121**. Once sample aliquot **118** is transferred into channel **120**, gas or liquid flowing from inlet **115** through channel **120** transports sample aliquot **118** to outlet **113**. Another advantage of the shuttle valve of the present invention relates to the fluidics design of the channels through the valve. In order to minimize backpressure through the valve, the flow through channels **117** and **120** is continuous. This is accomplished by locating channels **117** and **120** in static body **122** such that no matter what position the dynamic body **119** is in, the flow through shuttle valve **100** is continuous (as shown in FIG. 2). As shown in FIG. 1, at least a portion of the channel **117** and channel **120** may be substantially planar and/or linear, which reduces turbulence and further minimizes pressure increase through the valve. In addition, at least a portion of the channel **117** and channel **120** may be substantially parallel to dimple **116**, which further limits turbulent flow and any increase in pressure in the valve. For example, the term "substantially increase the pressure" through the shuttle valve would include those configurations that do not increase pressure within the valve of more than 50 psi, preferably not more than 30 psi, more preferably not more than 20 psi, and even more preferably not more than 10, 9, 8, 7, 6, 5, 4, 3, 2, or 1 psi. Dimple **116** is located in the dynamic body **119** and is in fluid communication with the face of the dynamic body that is contiguous with the static body **122**, whereby when the dynamic body **119** is in a first position, the dimple **116** will be in fluid communication with channel **117**, and when moved to a second position, the dimple **116** will be in fluid communication with channel **120**. The dimple **116** may be of any shape but is depicted as a concave semi sphere, and it may be of any size. In an exemplary embodiment, the dimple may be extremely small in size (e.g., less than 2000 nL, preferably less than about 500 nL, more preferably less than about 100 nL, and even more preferably less than about 1 nL, but may include any size from 1 nL to 2000 nL, which allows for rapid sampling. In addition, small dimple **116** size allows for a very short dimple rotation path **121**, which significantly reduces wear on the surfaces of the dynamic body **119** and the static body **122** and results in a shuttle valve **100** having extended service life before maintenance is required (e.g., more than 10 million cycles are possible before service).

**[0038]** Shuttle valve **100** may be programmed to remove a sample aliquot (e.g., sample aliquot **118**) from a sample for transport to at least one detector at a desired sampling frequency. In one exemplary embodiment, the sampling frequency is at least 1 sample aliquot every 10 seconds (or at least 1 sample aliquot every 5 seconds, or at least 1 sample aliquot every 3 seconds, or at least 1 sample aliquot every 2 seconds, or 1 sample aliquot every 0.5 seconds, or at least 1 sample aliquot every 0.1 seconds). This shuttle valve is further described in conjunction with a chromatography system in copending U.S. provisional patent application No. 61/005,590, the entire subject matter of which is incorporated herein by reference.

*II. Apparatus for Moving Aliquot Samples of Fluid*

**[0039]** The present invention is also directed to an apparatus capable of moving an aliquot sample of fluid. In one exemplary embodiment, the apparatus for moving an aliquot sample of fluid comprises hardware operatively adapted to remove a very small sample volume, or aliquot, of fluid from a much larger volume of fluid, such as the flow of a stream through a channel. The disclosed apparatus of the present invention may also be utilized to remove a very small sample volume, or aliquot, of fluid from a much larger volume of fluid, such as the flow of a stream through a channel, and transfer the sample to another volume of fluid or container.

**[0040]** In one exemplary embodiment, an apparatus capable of moving an aliquot sample of fluid comprises a first fluid, a second fluid, and a shuttle valve capable of removing an aliquot from the first fluid to the second fluid while maintaining a continuous flow path through the shuttle valve of the second fluid. In one embodiment, the apparatus is capable of removing the aliquot from the first fluid while maintaining a continuous flow path through the shuttle valve of the first fluid. In another embodiment, the apparatus is capable of removing the aliquot from the first fluid while maintaining continuous flow paths of both the first fluid and the second fluid.

**[0041]** In another embodiment according to the present invention, an apparatus capable of moving an aliquot sample of fluid comprises a first fluid channel, a second fluid channel, and a shuttle valve capable of removing an aliquot of fluid from the first channel to the second channel without substantially affecting the flow properties of fluid in the first channel through the valve. At least a portion of the first channel through the valve may be substantially straight. In this embodiment, the pressure of fluid in the first channel through the shuttle valve does not substantially increase. In another exemplary embodiment, at least a portion of the first channel may be substantially parallel to the aliquot dimple, which provides laminar flow of fluid in the first channel through the valve. In a further embodiment,

at least a portion of the second channel through the valve may be substantially straight. In this embodiment, the pressure of fluid in the second channel through the shuttle valve does not substantially increase. In another exemplary embodiment, the second channel may be substantially parallel to the aliquot dimple, which provides laminar flow of fluid in the second channel through the valve.

**[0042]** In a further exemplary embodiment according to the present invention, an apparatus capable of moving an aliquot sample of fluid comprises a static body having at least two channels therethrough such that a portion of each channel intersects with a first surface of the static body, a dynamic body having an aliquot dimple that intersects with a first surface of the dynamic body, the first surface of the static body and the first surface of the dynamic body being contiguous with each other, and the channels and the aliquot dimple located such that the aliquot dimple may be in fluid communication with one channel in a first position and in fluid communication with another channel in a second position, wherein at least a portion of the first channel is substantially parallel to the first surface of the static body. In an alternative exemplary embodiment, at least a portion of the first channel through the valve may be substantially straight. In an exemplary embodiment, the pressure of fluid in the first channel through the shuttle valve does not substantially increase. In another exemplary embodiment, at least a portion of the first channel may be substantially parallel to the aliquot dimple. In an exemplary embodiment, the flow of fluid in the first channel through the valve is laminar. In a further embodiment, at least a portion of the second channel through the valve may be substantially straight. In a further embodiment, the pressure of fluid in the second channel through the shuttle valve does not substantially increase. In another exemplary embodiment, the second channel may be substantially parallel to the aliquot dimple. In an embodiment, the flow of fluid in the second channel through the valve may be laminar.

**[0043]** In a further exemplary embodiment according to the present invention, an apparatus capable of moving an aliquot sample of fluid comprises a static body having at least two channels therethrough such that a portion of each channel intersects with a first surface of the static body, a dynamic body having an aliquot dimple that intersects with a first surface of the dynamic body, the first surface of the static body and the first surface of the dynamic body being contiguous with each other, and the channels and the aliquot dimple located such that the aliquot dimple may be in fluid communication with one channel in a first position and in fluid communication with another channel in a second position, wherein at least a portion of the second channel is substantially parallel to the first surface of the static body.

**[0044]** In a further exemplary embodiment according to the present invention, an apparatus capable of moving an aliquot sample of fluid comprises a static body having at least two channels therethrough such that a portion of each channel intersects with a first surface of the static body, a dynamic body having an aliquot dimple that intersects with a first surface of the dynamic body, the first surface of the static body and the first surface of the dynamic body being contiguous with each other, and the channels and the aliquot dimple located such that the aliquot dimple may be in fluid communication with one channel in a first position and in fluid communication with another channel in a second position, wherein the shuttle valve longevity is at least about 1 million cycles, 2 million, 3 million, 4 million, 5 million, 6 million, 7 million, 8 million, 9 million, 10 million or more cycles before servicing is required.

**[0045]** The above-described FIGS. 1-2 depict elements of an exemplary embodiment of the apparatus according to the present invention. The configuration of the channels in the shuttle valve provides continuous flow through the valve, reduces substantial pressure increase in the streams flowing through the valve, and/or provides laminar flow through the valve.

**[0046]** FIGS. 3A-3C depict exemplary channel configurations of the valve according to the present invention. At least a portion of the channels in the valve are substantially parallel to a first surface of the static body. For example, FIG. 3A illustrates a cross-sectional view of a shuttle valve 100 according to one exemplary embodiment of the present invention. The static body 122 includes at least two channels 117 and 120 that are parallel to a first surface 102, which are contiguous with the entire width of static body first surface 102. In an alternative exemplary embodiment, the channels 117 and 120 are parallel and contiguous with at least a portion of the first surface 102 of the static body 122 (see FIG. 3B). In a further exemplary embodiment, the channels 117 and 120 are parallel to the surface and extend in a circumferential direction (see FIG. 3C). The portion of the channels 117 and 120 that are contiguous with the first surface 102 of the static body 122 may vary in size and shape, but is typically larger than the size of the dimple 116 in the dynamic body 119. For example, the portions of the channels 117 and 120 that are contiguous with the first surface 102 of the static body 122 may be rectangular, circular, elliptical, and may be in a variety of locations on the face of the static body, but typically are located such that they will intersect with the dimple 116 when rotated from one channel 117 to the other 120.

**[0047]** In another exemplary embodiment, the dimple 116 of the dynamic body 119 may be configured such that may be easily rotated from channel 117 to channel 120. The dimple 116 may be of any shape, e.g., rectangular, circular,

elliptical, square, etc., that allows for rapid fluid or mass transfer but is depicted as a concave semi sphere, and it may be any size (see FIG. 4). In an exemplary embodiment, the dimple **116** may be extremely small in size (e.g., less than 2000 nL, preferably less than about 500 nL, more preferably less than about 100 nL, and even more preferably less than about 1 nL, but may include any size from 1 nL to 2000 nL, which allows for rapid sampling. In addition, small dimple **116** size allows for a very short dimple rotation path **121**, which significantly reduces wear on the surfaces of the dynamic body **119** and the static body **122** and results in a shuttle valve **100** having extended service life before maintenance is required (e.g., more than 10 million cycles are possible before service). The dimple **116** is located on a first surface **104** of the dynamic body **119** such that it readily intersects with the channels **117** and **120**.

**[0048]** In alternative embodiments, the shuttle valve of the present invention may comprise more than two channels and/or more than one dimple, which may enable multiple transfers of aliquot samples at the same time or in rapid succession and/or multiple samples being transferred to and from multiple channels at the same time or sequentially. For example, the dynamic body **119** may include multiple dimples **116** along the same circumference such that the dynamic body only **119** rotates in one direction (FIG. 5).

**[0049]** In other embodiments, the shuttle valve of the present invention may be in configurations other than those that rotate around an axis. For example, the shuttle valve may be designed such that linear motion is utilized to move the aliquot sample of fluid. FIG. **6A-B** depicts a cross-sectional view of a linear motion shuttle valve **151** where the dynamic body **119** moves in a linear motion over static body **122** such that in one position (shown in FIG. **6A**), dimple **118** is aligned with channel **117** and in another position (shown in **6B**), dimple **118** is aligned with channel **120**. In this manner, sample aliquot is transferred from channel **117** to channel **120**.

**[0050]** In even further exemplary embodiments, the shuttle valve **100** is constructed such that the dynamic body **119** and static body **122** produce the least amount of wear on these parts. For example, because the dimple **116** and channels **117** and **120** are designed to minimize the number of ports, grooves or channels, and the surface area with which these openings occupy, this allows increased longevity of the shuttle valve **100** (e.g., at least about 1 million cycles, preferably at least about 2 million cycles, more preferably at least about 5 million cycles, and even more preferably at least about 10 million cycles). Additionally, this design allows for the use of increased operational pressures, such as pressures at least about 10 psi, preferably at least about 100 psi, more preferably at least about 1000 psi, and even more preferably at least about 10,000 psi (e.g., above 20,000 psi).

**[0051]** In an additional exemplary embodiment, the shuttle valve **100** is constructed of materials that increase the longevity of the valve. The static body **122** and dynamic body **119** are constructed of materials that are easily machined but provide suitable sealing, low torque, and resistance to wear between the static body **122** and dynamic body **119**. For example, such materials include organic materials including polymeric materials such as polyethylene (e.g., high molecular weight polyethylenes), polyethers (e.g., polyetheretherketones), fluoropolymers (e.g., polytetrafluoroethylene), polypropylenes, polyamides, polyimides, etc., and blends thereof; and inorganic materials such as ceramics, metals, etc. The materials may include mixtures or composites of these materials, or may be coated with such materials. In one exemplary embodiment, the dynamic body **119** is constructed of ultra-high molecular weight polyethylene and the static body **122** is constructed of natural polyetheretherketone.

#### *IV. Applications/Uses*

**[0052]** The above-described methods and apparatus may be used to move an aliquot sample of fluid from one fluid to another. The above-described methods and apparatus find applicability in any industry that utilizes fluidics including, but not limited to, the petroleum industry, the pharmaceutical industry, analytical labs, etc.

**[0053]** FIG. 7 demonstrates how a shuttle valve operates within a given liquid chromatography system. As shown in FIG. 7, shuttle valve **100** comprises chromatography column inlet **111**, which provides fluid flow from a chromatography column (e.g., column **11**) to shuttle valve **100**; an incoming sample aliquot volume **118** in dimple **116**; fraction collector outlet **114**, which provides fluid flow from shuttle valve **100** to a fraction collection (e.g., fraction collection **14**); gas or liquid inlet **115**, which provides gas (e.g., air, nitrogen, etc.) or liquid (e.g., an alcohol) flow using pump **140** through a portion of shuttle valve **100**; outgoing sample aliquot volume **118**; and detector outlet **113**, which provides fluid flow from shuttle valve **100** to a detector (e.g., detector **131**, such as a ELSD).

**[0054]** As fluid flows through shuttle valve **100** from chromatography cartridge to inlet **111** to fraction collector outlet **114** via channel **117**, dimple **116** is filled with a specific volume of incoming sample aliquot volume **118** (shown as the shaded area in FIG. 7). At a desired time, shuttle valve **100** transfers incoming sample aliquot volume **118** in dimple **116** via dimple rotation path **121** to channel **120** as shown in FIG. 7. Once sample aliquot **118** is transferred to channel **120**, gas or liquid flowing from inlet **115** through channel **120** transports sample aliquot **118** to detector **131** (e.g., an ELSD) via detector outlet **113**.



**[0055]** In another exemplary embodiment, the shuttle valve may be utilized to transfer a single aliquot from a first fluid to a second fluid. For example, the first fluid may be introduced into the sample diple and one single motion to place the sample aliquot into the second fluid could then be completed. In this configuration, the shuttle valve of the present invention may be utilized to inject samples for separation into chromatography systems or columns. This sample introduction is allowed to proceed through the column or system completely before another is injected. This injection mode embodiment would typically be used in more traditional HPLC applications where a single sample aliquot (one diple volume) is fully analyzed before another sample volume is injected into the system. Since the design of the shuttle valve of the present invention allows for very small aliquot samples of fluid, this valve may also be utilized in micro and nano chromatography systems. FIG. 8 illustrates an exemplary embodiment of such a design where shuttle valve 151 is utilized to inject an aliquot from sample fluid 111 to fluid 113 and then to chromatography column 11.

**[0056]** In an alternative exemplary embodiment, the shuttle valve of the present invention may be utilized as a dosing device. For example, such a valve may be used in many manufacturing processes including industries such as pharmaceuticals, food flavoring, chemical dosing, recreational water (pool and spa) chemical introduction, and agricultural distribution of fertilizers. In one exemplary embodiment, dosing apparatus may include two flow paths, each flowing at their own flow rates. Chemical A is introduced into the main flow path at a particular rate. With another valve of the present invention, a second chemical B could be introduced into the second flow path at a discrete rate. With multiple valves, complex chemical additions could be added to flowing streams and the streams dispensed into multiple containers of product. Mixing would be accomplished simultaneously as the chemical is introduced into the stream(s) since the flow of the stream naturally mixes the added chemical. On a large dosing volume scale, many consumer products are produced with a main carrier component such as water. As opposed to dispensing with pumps requiring cleaning and maintenance, the valve of the present invention provides a simple alternative for certain applications. On a smaller scale, a dosing apparatus may include a shuttle valve of the present invention to produce routine mixtures of chemicals at any component concentration. Alternatively, if gravity is used to introduce chemical doses, the shuttle valve of the present invention may be utilized whereby disposable containers of the dosing chemical may be temporarily attached to the valve and replaced at specified intervals. In this embodiment, pumping equipment may not be required, thereby saving on the cost of additional hardware. This may be advantageous in various

markets such as the agricultural business and also for home use as chemicals could be distributed in certain applications using low power consumption (e.g., solar power).

## **EXAMPLES**

**[0057]** The present invention is further illustrated by the following examples, which are not to be construed in any way as imposing limitations upon the scope thereof. On the contrary, it is to be clearly understood that resort may be had to various other embodiments, modifications, and equivalents thereof which, after reading the description herein, may suggest themselves to those skilled in the art without departing from the spirit of the present invention and/or the scope of the appended claims.

### **Example 1**

**[0058]** In this example, the flash REVELERIS™ system (available from Grace Davison Discovery Sciences) was utilized. 4 mL of a mixture containing dioctyl phthalate and butyl paraben was injected into a 4 g GRACERESOLVE™ C18 flash cartridge (available from Grace Davison Discovery Sciences), which was mounted in the flash system. A 80/20 methanol/water mobile phase was pumped through the system using an ALLTECH™ model 300 LC pump. The column effluent was directed to a shuttle valve as described herein that diverted 300uL/min of the column effluent to an ALLTECH™ 3300 ELSD. The balance of the effluent flowed through an Ocean Optics UV detector to a Gilson fraction collector.

**[0059]** While the invention has been described with a limited number of embodiments, these specific embodiments are not intended to limit the scope of the invention as otherwise described and claimed herein. It may be evident to those of ordinary skill in the art upon review of the exemplary embodiments herein that further modifications, equivalents, and variations are possible. All parts and percentages in the examples, as well as in the remainder of the specification, are by weight unless otherwise specified. Further, any range of numbers recited in the specification or claims, such as that representing a particular set of properties, units of measure, conditions, physical states or percentages, is intended to literally incorporate expressly herein by reference or otherwise, any number falling within such range, including any subset of numbers within any range so recited. For example, whenever a numerical range with a lower limit,  $R_L$ , and an upper limit  $R_U$ , is disclosed, any number  $R$  falling within the range is specifically disclosed. In particular, the following numbers  $R$  within the range are specifically disclosed:  $R = R_L + k(R_U - R_L)$ , where  $k$  is a variable ranging from 1% to 100% with a 1% increment,

e.g., k is 1%, 2%, 3%, 4%, 5%. ... 50%, 51%, 52%. ... 95%, 96%, 97%, 98%, 99%, or 100%. Moreover, any numerical range represented by any two values of R, as calculated above is also specifically disclosed. Any modifications of the invention, in addition to those shown and described herein, will become apparent to those skilled in the art from the foregoing description and accompanying drawings. Such modifications are intended to fall within the scope of the appended claims. All publications cited herein are incorporated by reference in their entirety.

**WHAT IS CLAIMED IS:**

1. A method of moving an aliquot sample of fluid from one fluid to another comprising the steps of;
  - (a) providing a first fluid,
  - (b) providing a second fluid, and
  - (c) using a shuttle valve to remove the aliquot sample of fluid from the first fluid to the second fluid while maintaining a continuous flow path of the second fluid through the shuttle valve.
2. The method according to claim 1, wherein a continuous flow path of the first fluid through the shuttle valve is maintained when the aliquot sample of fluid is removed from the first fluid.
3. The method according to claim 1, wherein a continuous flow path of the first fluid and second fluid is maintained through the shuttle valve as the aliquot sample of fluid is removed from the first fluid.
4. A method of moving an aliquot sample of fluid comprising the steps of;
  - (a) providing a first fluid,
  - (b) using a shuttle valve to remove the aliquot sample of fluid from the first fluid while maintaining a continuous flow path through the shuttle valve of the first fluid.
5. The method according to claim 4, wherein the flow of the first fluid through the shuttle valve is substantially laminar.
6. The method according to claim 4, wherein the pressure of the first fluid through the shuttle valve remains substantially constant.
7. A method of moving an aliquot sample of fluid comprising the steps of;
  - (a) providing a static body having at least two channels therethrough such that a portion of each channel intersects with a first surface of the static body,
  - (b) providing a dynamic body having an aliquot dimple that intersects with a first surface of the dynamic body, the first surface of the static body and dynamic body being contiguous with each other and the channels and the aliquot dimple located such that the aliquot dimple is in fluid communication with one channel in a first position and in fluid communication with another channel in a second position,

(c) flowing a first fluid through one of said channels, flowing a second fluid through another of said channels, aligning the aliquot dimple in the first position, allowing a sample portion of the first fluid to flow into the aliquot dimple, and moving the aliquot dimple to the second position, whereby the sample portion is transferred to the second fluid,

(d) wherein at least a portion of at least one channel is substantially parallel to the first surface.

**8.** An apparatus capable of moving an aliquot sample of fluid comprising;

- (a) a first fluid path,
- (b) a second fluid path, and
- (c) a shuttle valve capable of removing an aliquot sample of fluid from the first fluid path to the second fluid path while maintaining a continuous second fluid path through the shuttle valve.

**9.** The apparatus according to claim 8, wherein the shuttle valve is capable of removing the aliquot sample of fluid from the first fluid path while maintaining a continuous first fluid path through the shuttle valve.

**10.** The apparatus according to claim 8, wherein the shuttle valve is capable of removing the aliquot sample of fluid from the first fluid path while maintaining continuous first and second fluid paths through the shuttle valve.

**11.** An apparatus capable of moving an aliquot sample of fluid comprising;

- (a) a first fluid path,
- (b) a second fluid path, and
- (c) a shuttle valve capable of removing the aliquot sample of fluid from the first fluid path to the second fluid path while maintaining a substantially constant flow in the first fluid path through the shuttle valve.

**12.** The apparatus according to claim 11, wherein the flow in the first fluid path through the shuttle valve is substantially laminar.

**13.** The apparatus according to claim 11, wherein the pressure in the first fluid path through the shuttle valve remains substantially constant.

**14.** An apparatus capable of moving an aliquot sample of fluid comprising,

(a) a static body having at least two paths therethrough such that a portion of each path intersects with a first surface of the static body,

(b) a dynamic body having an aliquot dimple that intersects with a first surface of the dynamic body, the first surface of the static body and dynamic body being contiguous with each other and the paths and the aliquot dimple located such that the aliquot dimple is in fluid communication with one path in a first position and in fluid communication with another path in a second position,

(c) wherein at least a portion of the first path is substantially parallel to the aliquot dimple.

**15.** The apparatus according to claim 14, wherein at least a portion of the first path is parallel to the first surface of the static body.

**16.** The apparatus according to claim 14, wherein at least a portion of the second path is parallel to the first surface of the static body.

**17.** The apparatus according to claim 14, wherein the apparatus comprises a dosing device.

**18.** The apparatus according to claim 14, wherein the apparatus comprises a sample removal device for sample analysis.

**19.** The apparatus according to claim 14, wherein the apparatus comprises a sample injection device for chromatography systems.

**20.** The apparatus according to claim 14, wherein the apparatus possesses a longevity of at least about 5 million cycles.

**21.** The apparatus according to claim 14, wherein the dynamic body is constructed of ultra-high molecular weight polyethylene and the static body is constructed of natural polyetheretherketone.