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(71) Applicant *(for all designated States except US)*: **HORIZON TECHNOLOGY, INC.** [US/US]; 8 Commerce Drive, Atkinson, NH 03811 (US).

(72) Inventor; and
(75) Inventor/Applicant *(for US only)*: **JOHNSON, Robert, S.** [US/US]; 25 Blue Heron, Hampstead, NH 03841 (US).

(74) Agents: **GROSSMAN, Steven, J.**; Hayes, Soloway, Hennessey, Grossman & Hage, P.C., 175 Canal Street, Manchester, NH 03101 et al. (US).

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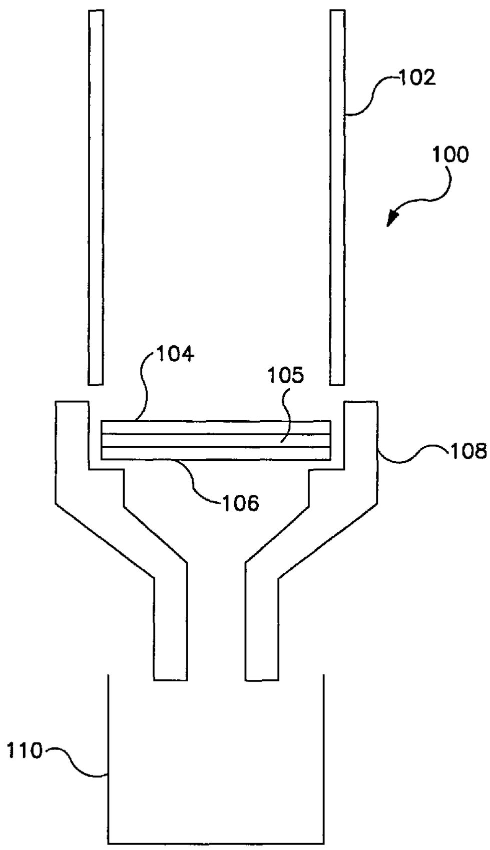
(54) Title: WATER SEPARATION FROM SOLVENT



(57) Abstract: An apparatus (100) and method for separating residual water from a solvent. The device comprises a reservoir (102) containing a solution comprising solvent containing residual water, the reservoir having an opening to allow the solution to drain from the reservoir. A membrane layer is provided comprising a first layer (104) of fluoropolymer and a second layer of fluoropolymer (105). The membrane is positioned in series with the reservoir opening. Vacuum is generated on one side of the membrane layer wherein the solvent containing water passes through the membrane therein removing water from the solvent to provide a solvent with a water level of less than or equal to 1.0 ppm.

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WATER SEPARATION FROM SOLVENT

CROSS REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of copending U.S. provisional patent application serial No. 60/215,055 filed June 29, 2000, the teachings of which are incorporated herein by reference.

FIELD OF THE INVENTION

This invention generally relates to the field of chemical laboratory equipment for sample preparation and particularly to the use of a hydrophobic membrane to separate water from an organic solvent, and more particularly to an apparatus and method for increasing the flow rate of the solvent through the membrane without adversely affecting the performance of the membrane.

BACKGROUND OF THE INVENTION

When samples are to be analyzed for organic and/or inorganic trace compounds, the samples are typically extracted with an organic solvent. The solvent extracts the compounds from the sample, due to selective chemistry.

Before the extract can be analyzed, all residual water should preferably be removed from the extracting solvent. This is due to the adverse effect residual water can have on subsequent sample preparation steps which are required to prepare and analyze the samples.

Current practice embodies the use of a drying agent called sodium sulfate and has been the standard technique to remove the residual water from solvent extracts. Sodium sulfate is a granular material that has a high binding capacity for residual water. The sodium sulfate is first heated to drive off any water that has been adsorbed into the material. This typically requires heating overnight at 400C. The sodium sulfate is then placed into a glass funnel containing filter paper, or a chromatography column. The funnel or column is then washed with extracting solvent to wash off any impurities. The extracting solvent is then discarded. Once the sodium sulfate is clean, the solvent extract is poured on top of the sodium sulfate. As the solvent drains slowly through, the residual water becomes bound to the surface of the sodium sulfate. The collected solvent passing through is now dry and ready for analysis.

The use of sodium sulfate, even though easy to use, requires many physical manipulations. Sodium sulfate requires the use of glassware that must be subsequently washed so as not to introduce contaminants into the samples and requires the purchase of, and the disposal of, the used sodium sulfate. The labor time and the materials costs, add significantly to the total cost of performing sample extractions.

U.S. Patent 5,268,150 assigned to Corning Incorporated, discloses the use of a hydrophobic membrane in an extraction device which allows a solvent to pass therethrough, yet will not allow a significant amount of water from the sample liquid to pass therethrough. The patent discloses that hydrophobic membranes incorporating polytetrafluoroethylene (PTFE) have been found to be very effective in achieving the desired results of letting solvent pass, while retaining the sample usually consisting of a relatively large portion of water or an aqueous solution. The patent goes on to state that the typical dimensions of the membrane range from 10 to 50 millimeters in diameter with a thickness ranging from 0.1 to 5.0 microns with a pore size ranging from 0.2 to 5.0 microns, depending upon the sample being processed.

Accordingly, it is an object of the invention to improve on the above referenced designs and provide a more efficient technique for separation water from a given solvent. More specifically, it is an object of the present invention to provide a method and apparatus and improved membrane design to improve the purification flow rate of a solvent/water mixture or emulsion through said membrane, to remove water, without adversely effecting membrane performance.

SUMMARY OF THE INVENTION

A method/apparatus for separating residual water from a solvent, comprising the steps of providing a reservoir containing a solution comprising solvent containing residual water, the reservoir having an opening to allow the solution to drain from the reservoir, and passing the solution in the reservoir through a fluoropolymer membrane supported on a fluoropolymer screen. The supported membrane is positioned in series with the reservoir opening, the membrane having a first side in contact with the solution and an opposing second side. Pressure is decreased on the second side of the supported membrane relative to the first side of said supported membrane to thereby increase the flow rate of the solvent through the membrane, wherein the fluoropolymer membrane operates to remove water from the solvent.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a sectional view of a first separator apparatus in accordance with the present invention, and

Figure 2 is a sectional view of a second separator apparatus in accordance with the present invention.

Figure 3 is an exploded view of a preferred separator apparatus in accordance with the present invention.

The above and other objects, feature, and advantages of the present invention will be apparent in the following detailed description thereof when read in conjunction with the appended drawings wherein the same reference numerals denote the same or similar parts throughout the several views.

DETAILED DESRIPTION OF THE DRAWINGS

Referring to the drawings, there is illustrated generally a first concentrator/extractor apparatus 100. The concentrator/extractor apparatus 100 comprises a column 102 and fluoropolymer material layers 104 and 105. Preferably, fluoropolymer layer 104 is laminated to fluoropolymer layer 105 to provide a membrane type construction. A preferred fluoropolymer for layer 104 is PTFE and a preferred fluoropolymer for layer 105 is ethylene-chlorotrifluroethylene (ECTFE).

A screen support layer is shown at 106, in addition to a base assembly 108, and a collection vessel 110. The column 102 forms a reservoir to hold a solvent. The column 102, which may be pressed down on top of the membrane (fluoropolymer layer 104 laminated to fluoropolymer layer 105) may be used to hold the membrane in place. The column 102 may seal the membrane and prevent any solvent from passing around the edge of the membrane. The column 102 and the collection vessel 110 are preferably made of glass. The screen support member 106 is preferably an ECTFE or ETFE fluoropolymer fabric screen with 0.5-1.0 mm openings, 0.5 –1.0 mm thick, and a 0.25-0.50 mm thread.

The membrane comprises layers 104 and 105 are preferably characterized as follows:

Pore Size: 0.05 to 0.2 micron;

Bubble Point: Individual between 24.0 psi and 34.0 psi (47 mm membrane; isopropanol at 21°C)

WEP: 50.0 psi minimum individual

Gurley Number: Mean $\leq$ 30.0 seconds (100 cc air through 1 in^2 orifice, 4.88" water pressure drop)

Thickness: Preferably 1.0 mils to 20 mils.

The following definitions apply to the above:

Gurley number: A measure of the air permeability of the fluoropolymer. The Gurley number is the time in second required for 100cc of air to pass through a one square inch area of membrane, when a constant pressure of 4.88 inches of water is applied.

Bubble point: The minimum pressure in KG/CM^2 required to force air through the fluoropolymer that has been prewetted with water, isopropanol, or methanol.

Water entry pressure: The pressure at which water permeates through the membrane. This is a visual test.

In a preferred embodiment, the PTFE layer 104 has usable diameters in the range of 40-100 mm. The fluoropolymer layer 104 and fabric support member 105 are positioned in series between the column 102 and the collection vessel 110. In a most preferred embodiment, a 3 mil thick PTFE layer 104 with a 0.1 micron pore size is supported on a 10 mil thick non-woven layer 105, comprised of ECTFE polymer, which ECTFE polymer is preferably obtained from Ausimont and sold under the tradename "HALAR".

It is worth noting that in a preferred embodiment, a 3.0 mil PTFE layer is laminated to a 10 mil ECTFE layer, and a resulting thickness of 3-7 mils is produced for the laminate as a result of the heat setting laminating process.

In accordance with the present invention, the screen layer 106 is preferably ethylene-trifluroethylene copolymer (ETFE). The screen layer serves to gap or space laminated layers 104 and 105 on the funnel surface such that it is possible to distribute the pressure differential across the entire cross-sectional area of the funnel surface to achieve more efficient performance. However, while it can be appreciated that screen layer 106 is a separate components, it can be appreciated that screen layer 106 may actually be incorporated directly into the surface of the funnel upon which the laminated layers 104 and 106 rest. This would provide the equivalent effect of spacing laminated layers 104 and 106 to evenly distribute the pressure differential created by vacuum.

Furthermore, in the context of the present invention it should be appreciated that the removal of water from a given solvent containing, e.g., some analyte to be evaluated by techniques such as gas-chromatography/mass spectrometry (GC/MS), is such that the removal of water is highly efficient and allows for the generation of a GC/MS analysis that is not compromised by the presence of water. In that regard, it has been found that the present invention allows for removal of water down to a level at or below 1.0 ppm.

Expanding upon the above, it will be appreciated that with respect to the removal of water herein, it has been found that by reference to the generation of a GC/MS analysis that is not compromised by the presence of water, it should also be understood that this is reference to the fact that the water removal herein is sufficient to reduce the water levels to that level wherein the possibility of contamination of the GC column by a water soluble inorganic acid is removed or attenuated. In addition, the possibility of any degradation of the GC column due to the presence of water soluble inorganic salts is also equally attenuated or removed, and GC/MS can proceed without such problems.

Additionally, it is worth noting that the invention herein is preferably applied to a water/solvent mixture wherein the solvent is denser than water. However, in broad context the invention herein is not so limited.

As shown in Figure 2, there is illustrated generally a second concentrator/extractor apparatus 200. The concentrator/extractor apparatus 200 comprises a column 202, a fluoropolymer layer 204 (PTFE) and a fluoropolymer layer 205 (ECTFE) that, as noted above, are preferably laminated to one another. In addition, a support screen member 206 is shown, a base assembly 208, and a collection vessel 210. The apparatus 200 can be coupled to an external low-level vacuum 216. A low level vacuum is one that preferably creates a pressure drop of less than 6" Hg. Alternatively, the assembly 200 could include a vacuum generator device that uses a compressed gas source to create a pressure differential. This assembly 200 could be manufactured as a unit and could sit in a hood, directly underneath a separatory funnel. Once the gas source is set, the operator may select one of a plurality of vacuum levels on a vacuum level selector panel 214. The vacuum selector panel 214 controls the pressure drop across the membrane. These levels may include: off, low, medium, and high. Alternatively, the vacuum level may be continuously variable. Being able to select from a variety of different vacuum levels has shown to be useful, as samples which create a significant emulsion can be quite easily broken if no vacuum is used. Once the emulsion has broken, then the vacuum setting can be increased to significantly reduce the sample process time. For example, 10ml of methylene chloride may take about 4 minutes to flow through with a 5"Hg vacuum, but the same sample through the same membrane may only take 15-20 second at 6"Hg. This is a significant time savings.

A controller 212 coupled to the vacuum 216 can be added that will vary the pressure drop across the membrane as a function of time. For example, the controller 212 can be programmed to have an initial predetermined period of time during which no vacuum or a very low first predetermined vacuum level is applied and a second predetermined period of time during which an increased second predetermined vacuum level is applied. The controller 212 can also be programmed to turn off the vacuum after a third predetermined period of time to prevent the apparatus from pulling residual water through the membrane. Given sufficient time, approximately 6 - 12 hours, any residual water on the surface of the membrane may "wet" the membrane and flow through with the organic solvent. Therefore, there is a limited time window for allowing water to reside on the membrane, but this time is not a problem for the application that this device will be used for.

In addition, testing has shown that draining the emulsion directly into the membrane reservoir aids with the breaking of emulsions. Once the emulsion has broken, if the analyst desires, after each drying step, the retained water and emulsion can be poured back into the separatory funnel for additional extractions. This could possibly significantly increase recovery values.

As noted, Figure 3 is an exploded view of a preferred separator apparatus in accordance with the present invention. More specifically, as shown therein there can be seen locking ring 310, wave spring 312, thrust ring 314, reservoir 316, base 318 for membrane and screen (not shown), stopcock 322, shut-off connectors 324 and 326 (through which vacuum may be applied), bracket 328 and support rod 330.

It should be understood that, while the present invention has been described in detail herein, the invention can be embodied otherwise without departing from the principles thereof, and such other embodiments are meant to come within the scope of the present invention as defined in the following claims.

CLAIMS

What is claimed is:

1. A method for separating residual water from a solvent, comprising the steps of:

providing a reservoir containing a solution comprising solvent containing residual water, the reservoir having an opening to allow the solution to drain from the reservoir,

resisting the flow of the solution from the reservoir with a membrane layer comprising a first layer of fluoropolymer and a second layer of fluoropolymer, said membrane positioned in the series with the reservoir opening,

decreasing the pressure on the second side of said supported membrane relative to the first side of said supported membrane to thereby increase the flow rate of the solvent through the membrane;

therein removing said water from said solvent to provide a solvent with a water level of less than or equal to 1.0 ppm.

2. The method of claim 1 wherein said first layer of fluoropolymer comprises PTFE.

3. The method of claim 1 wherein said second layer of fluoropolymer comprises ECTFE.

4. The method of claim 2 wherein said first layer comprising PTFE has a thickness of about 1-5 mils.

5. The method of claim 3 wherein said second layer of ECTFE has a thickness of about 5-15 mils.

6. The method of claim 1 wherein said membrane is characterized with a Gurley Number of $\leq$ 30.0 seconds and a pore size of 0.05 – 2.0 microns.

7. The method of claim 1 wherein said membrane has a pore size is about 0.05 – 2.0 micron.

8. The method of claim 1 wherein the step of decreasing the pressure on the second side of the membrane relative to the first side of the membrane is done by applying a vacuum

9. The method of claim 8 wherein the vacuum is varied.

10. The method of claim 8 wherein the vacuum ranges from about 1-15" Hg.

11. The method of claim 8 wherein the vacuum ranges from about 1-5" Hg.

12. The method of claim 1 wherein the decreasing of the pressure is delayed a selected period of time.

13. A method for separating residual water from a solvent, comprising the steps of:

providing a reservoir containing a solution comprising solvent containing residual water, the reservoir having an opening to allow the solution to drain from the reservoir,

resisting the flow of the solution from the reservoir with a membrane layer comprising a first layer of polytetrafluroethylene (PTFE) and a second layer of ethylene-chlorotrifluroethylene (ECTFE) layer, said membrane positioned in the series with the reservoir opening, the membrane having said first layer in contact with the solution, and

decreasing the pressure on the second side of said supported membrane relative to the first side of said supported membrane to thereby increase the flow rate of the solvent through the membrane.

14. The method of claim 13 wherein said membrane itself is further characterized with a Gurley Number of ≤ 25.0 seconds and a pore size of 0.05 – 2.0 microns.

15. The method of claim 14 wherein said pore size is about 0.1 micron.

16. The method of claim 13 wherein said PTFE layer has a thickness of about 1-5 mils and said ECTFE layer has a thickness of about 5-15 mils.

17. The method of claim 13 wherein the step of decreasing the pressure on the second side of the membrane relative to the first side of the membrane is done by applying a vacuum

18. The method of claim 17 wherein the vacuum is varied.

19. The method of claim 17 wherein the vacuum ranges from about 1-15" Hg.

20. The method of claim 19 wherein the vacuum ranges from about 1-5" Hg.

21. The method of claim 1 wherein the decreasing of the pressure is delayed a selected period of time.

22. A method for separating residual water from a solvent, comprising the steps of:

providing a reservoir containing a solution comprising solvent containing residual water, the reservoir having an opening to allow the solution to drain from the reservoir,

resisting the flow of the solution from the reservoir with a membrane layer comprising a first layer of fluoropolymer and a second layer of fluoropolymer, said membrane positioned in the series with the reservoir opening, said membrane supported on a screen layer,

decreasing the pressure on the second side of said supported membrane relative to the first side of said supported membrane to thereby increase the flow rate of the solvent through the membrane;

therein removing said water from said solvent to provide a solvent with a water level of less than or equal to 1.0 ppm.

23. The method of claim 22 wherein said screen layer comprises a fluoropolymer polymer.

24. The method of claim 23 wherein said fluoropolymer comprises ETFE.

25. An apparatus for separating residual water from a solvent, comprising:

a reservoir containing a solution comprising solvent containing residual water, the reservoir having an opening to allow the solution to drain from the reservoir,

a membrane layer comprising a first layer of fluoropolymer and a second layer of fluoropolymer, said membrane positioned in the series with the reservoir opening,

a device for generating vacuum on said second layer of fluoropolymer, wherein said solvent containing water passes through said membrane layer therein removing water from said solvent to provide a solvent with a water level of less than or equal to 1.0 ppm.

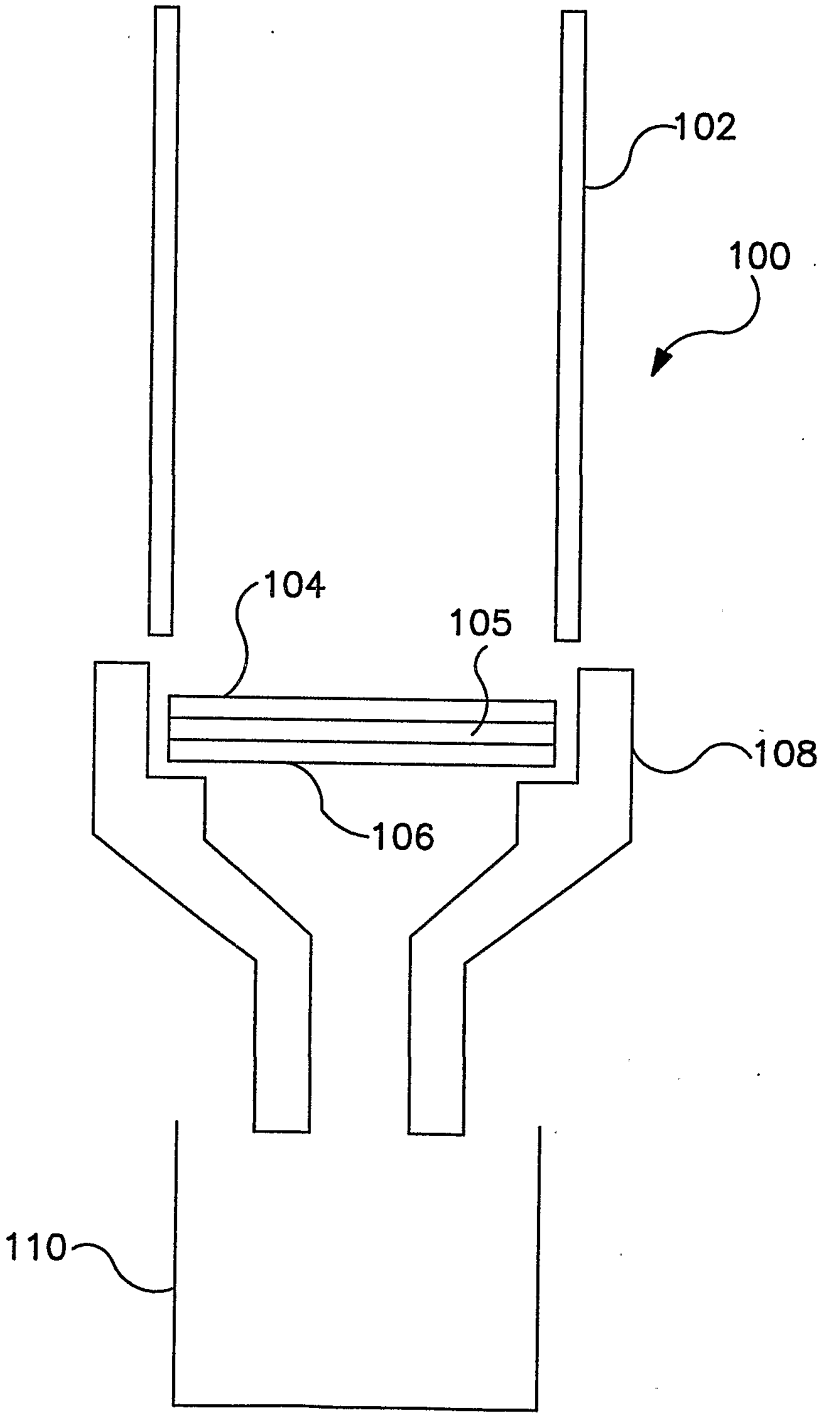

FIG. 1

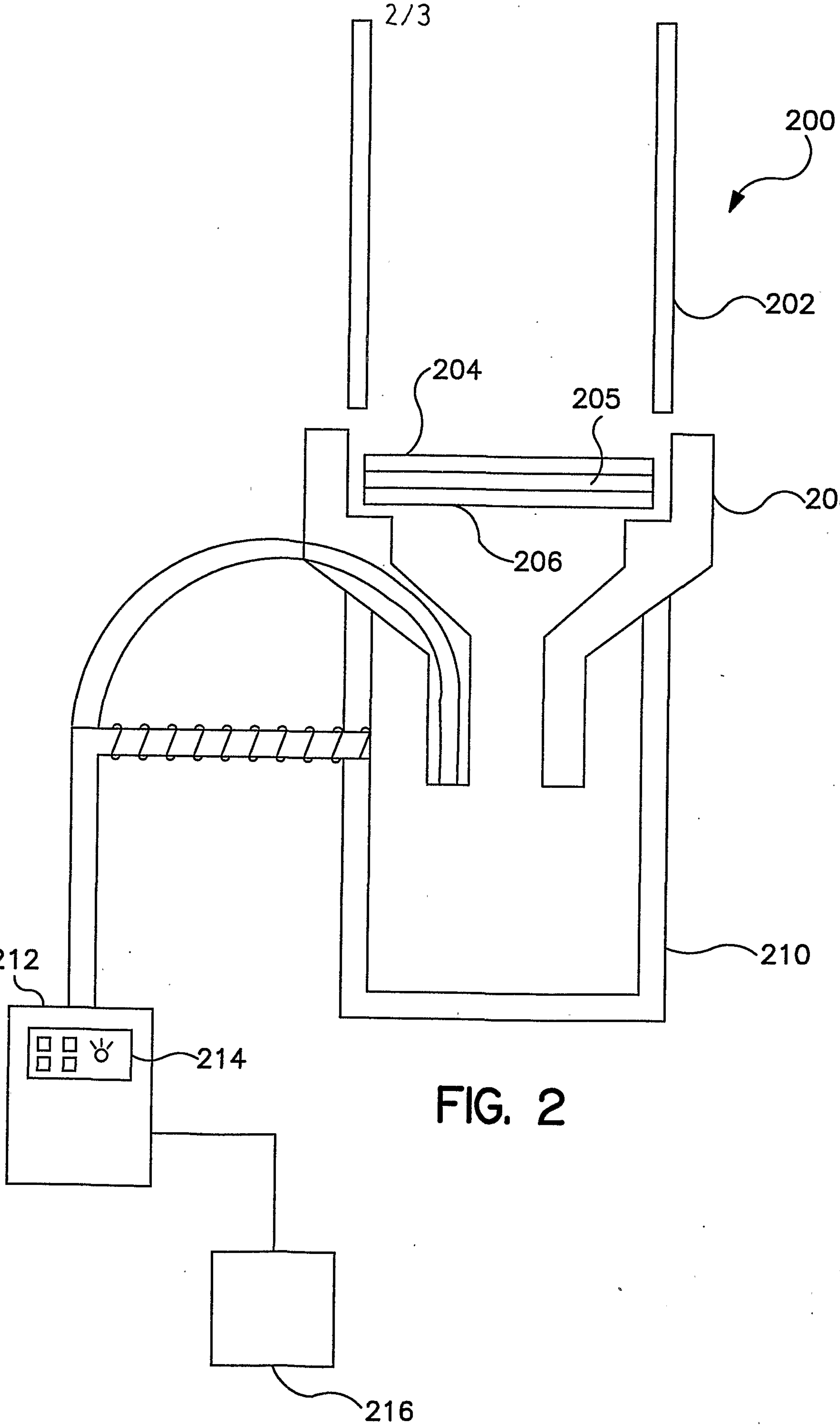

FIG. 2

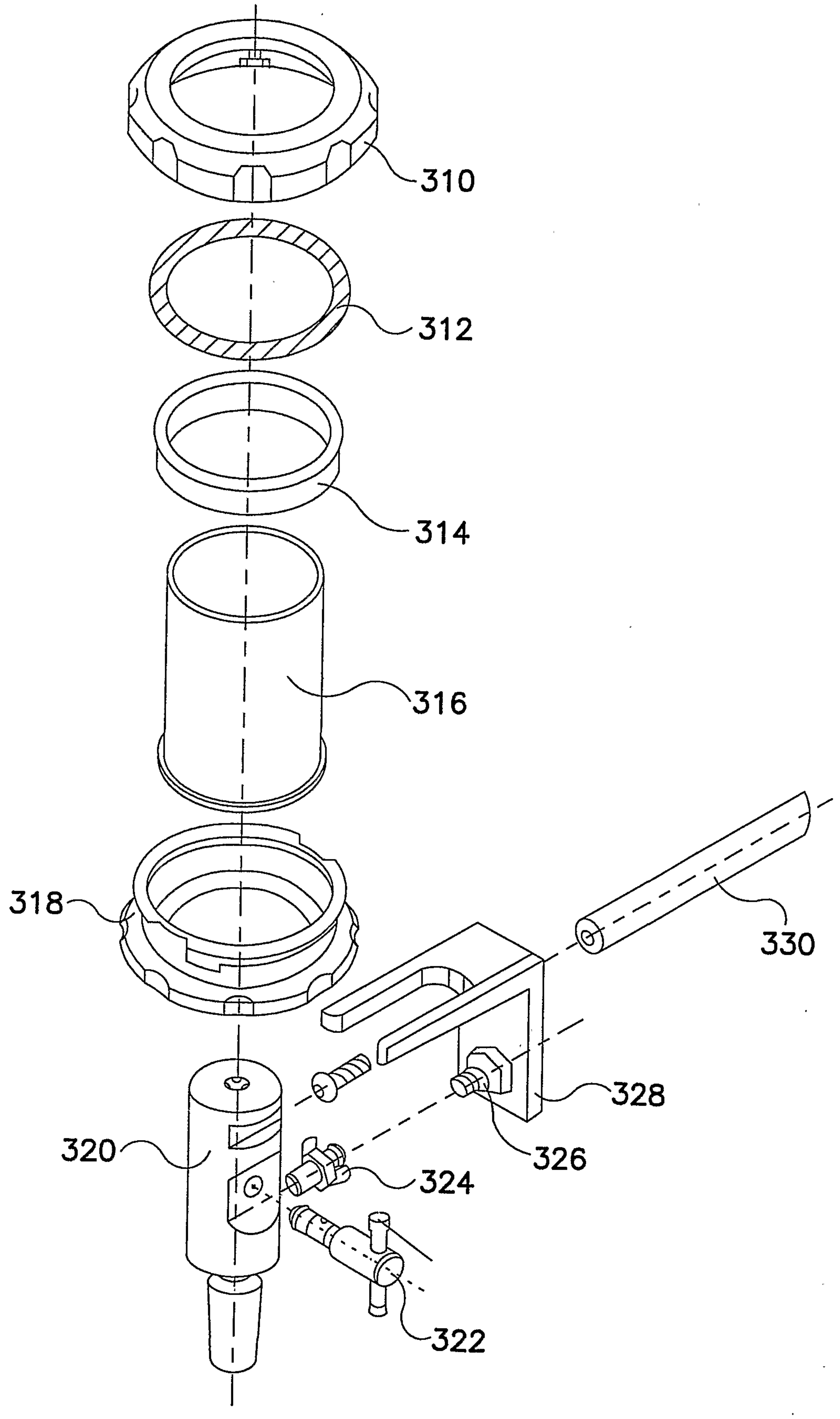

FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US01/20555

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :B01D 61/00
US CL :210/767, 651, 640, 321.6, 321.75; 422/101; 95/52
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)

U.S. : 210/767, 651, 640, 321.6, 321.75; 422/101; 95/52

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

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

WEST 2.0, search terms membrane , layers, ptfe, ectpe, vacuum, water, solvent separation, containeror resevoir

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,792,425 A (CLARK et al) 11 August 1998. Entire disclosure.	25
Y		1-24
Y	US 5,454,951 A (HOOPMAN) 03 October 1995, abstract, Fig. 3, column 4, lines 7-27, 59-68, column 5, lines 39-52).	3, 5, 13
Y	US 5,976,380 A (MOYA) 02 November 1999, entire disclosure.	1-24
Y	US 4,909,810 A (NAKAO et al) 20 march 1990, entire disclosure.	1-24

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

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Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231
Facsimile No. (703) 305-3230

Authorized officer
ANA FORTUNA
Jean Proctor
Paralegal Specialist
Telephone No. (703) 308-

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