United States Patent [19]
Takano et al.

[11] **3,929,411**
[45] **Dec. 30, 1975**

[54] SAMPLE TRANSFER DEVICE AND METHOD FOR ANALYTICAL SYSTEM

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[73] Assignee: **Hitachi, Ltd.**, Japan

[22] Filed: **Aug. 28, 1973**

[21] Appl. No.: **392,294**

[30] **Foreign Application Priority Data**

Sept. 14, 1972 Japan 47-91731

[52] **U.S. Cl.** .... **23/259**; 23/253 R; 23/230 R; 73/425.4 R; 137/572; 141/54

[51] **Int. Cl.²** **G01N 1/14**

[58] **Field of Search** ...... 23/259, 253 R, 230 R, 260; 137/572, 14, 205, 206, 154, 209; 417/121, 122; 141/4, 5, 50, 54, 56; 134/22-R, 37; 73/425.4 R

[56] **References Cited**

UNITED STATES PATENTS

1,456,102	5/1923	Fogler	23/259
2,880,070	3/1959	Gilbert et al.	23/253 R X
2,974,130	3/1961	Moberly	23/253 R X
3,098,819	7/1963	Sager	23/259 X
3,256,068	6/1966	Burke, Jr. et al.	23/285
3,334,025	8/1967	Reid	23/259 X
3,409,409	11/1968	Sackett, Sr.	23/253 R X
3,551,111	12/1970	Carlson	23/253 R
3,557,077	1/1971	Brunfeldt et al.	23/259 X
3,631,012	12/1971	Zapf et al.	23/285 X
3,647,390	3/1972	Kubodera et al.	23/259 X
3,684,452	8/1972	Bessman	23/259 X
3,713,778	1/1973	Karamian	23/259
3,717,435	2/1973	Ertl et al.	23/253 R X
3,740,320	6/1973	Arthur	23/253 R X
3,773,469	11/1973	Hiser et al.	23/253 R
3,791,221	2/1974	Kirschner et al.	23/253 R X
3,836,329	9/1974	Jordan	23/230 R

Primary Examiner—R. E. Serwin
Attorney, Agent, or Firm—Craig & Antonelli

[57] ABSTRACT

An apparatus for chemical treatments has an enclosed vessel provided with lines for conveying samples and selectively openable valves in communication with sources of gases at atmospheric, increased, and reduced pressures. A plurality of such vessels may be combined, instead, in which case the pressure of the atmosphere in each vessel is made higher than that in the following vessel, so that the sample can be transferred to the following vessels. The vessel or vessels may be equipped with means for agitation, fixed-quantity sampling, liquid level detection, washing, filtration, extraction, thermostatic control, aeration, thermal concentration and distillation. An additional vessel equipped with pH-adjusting means and capable of maintaining an atmospheric pressure inside may be installed.

14 Claims, 25 Drawing Figures

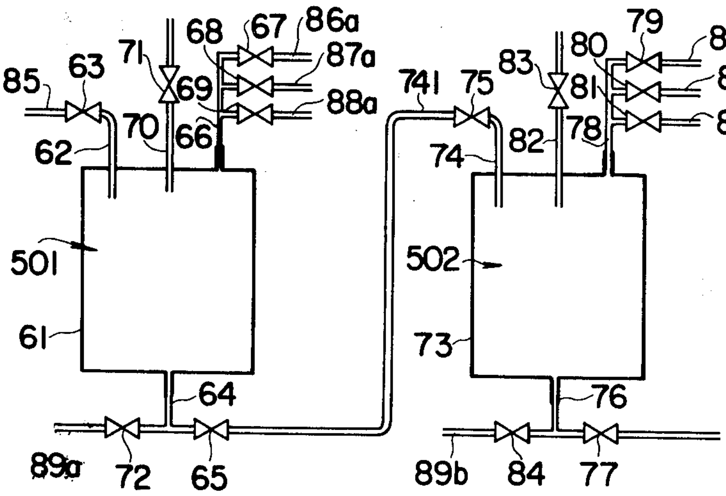


FIG. 1 PRIOR ART

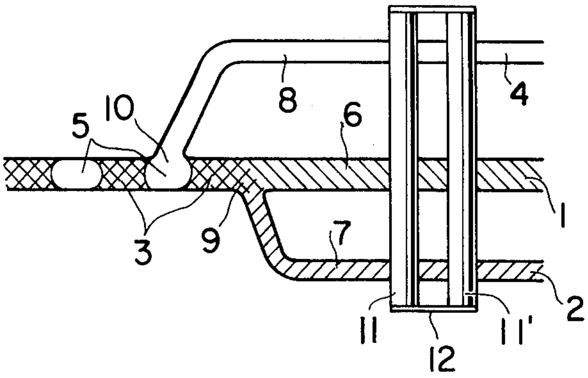


FIG. 2 PRIOR ART

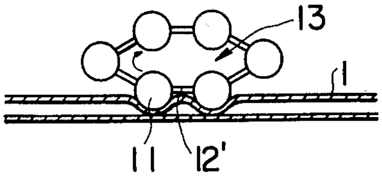


FIG. 3 PRIOR ART

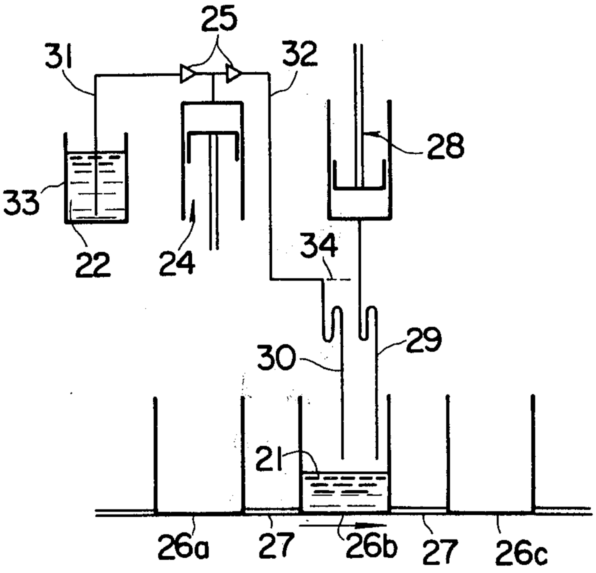


FIG. 4 PRIOR ART

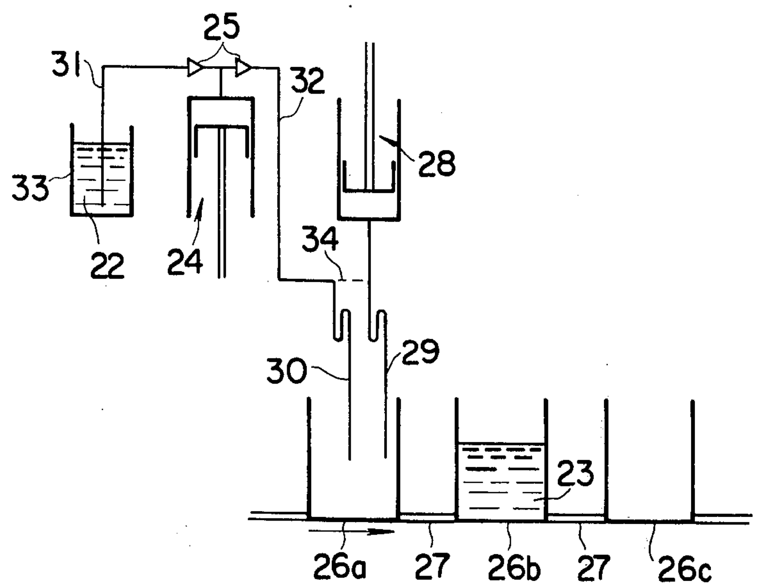


FIG. 6

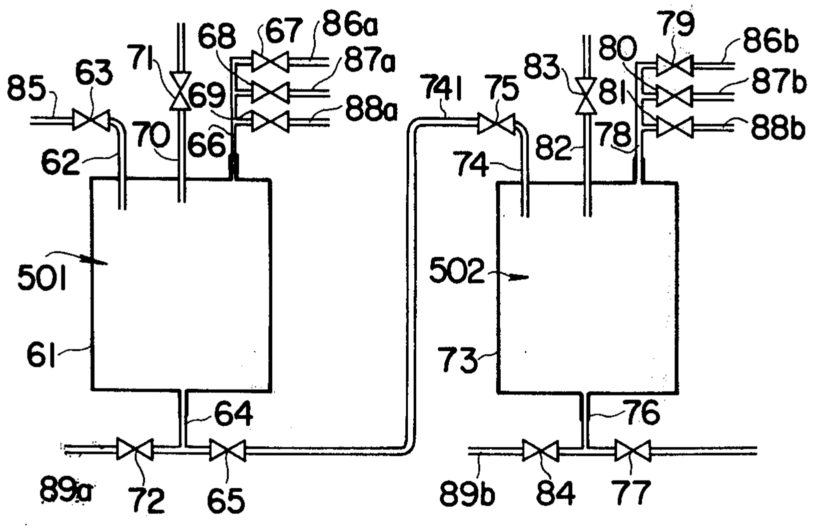
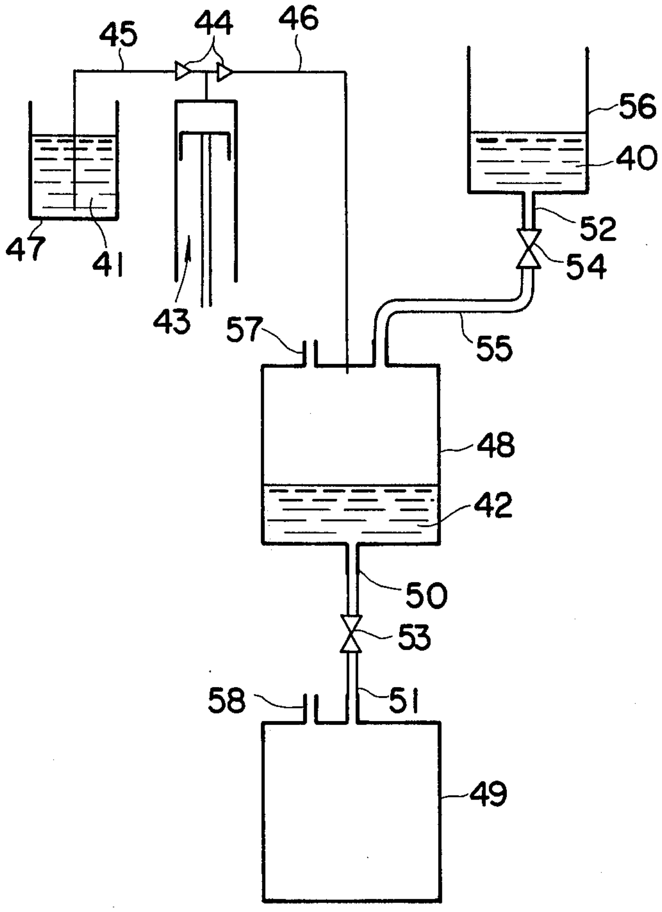


FIG. 5 PRIOR ART



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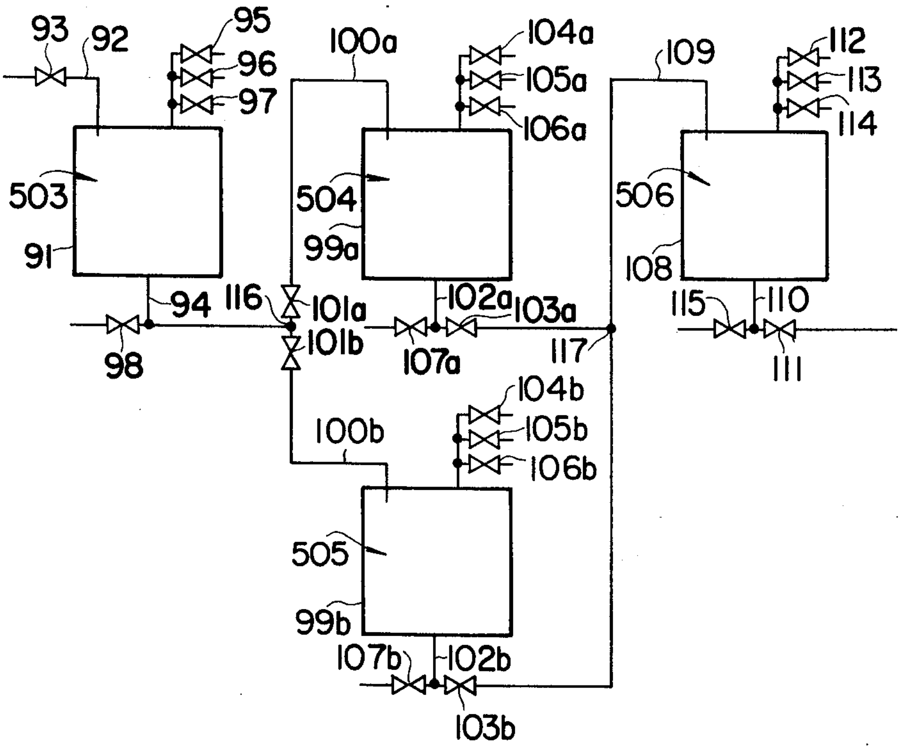
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FIG. 8

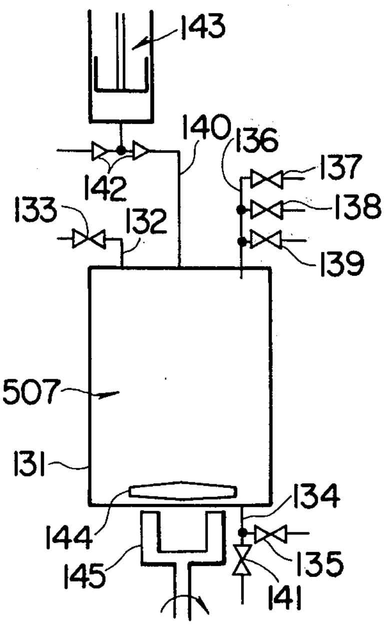
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FIG. 9

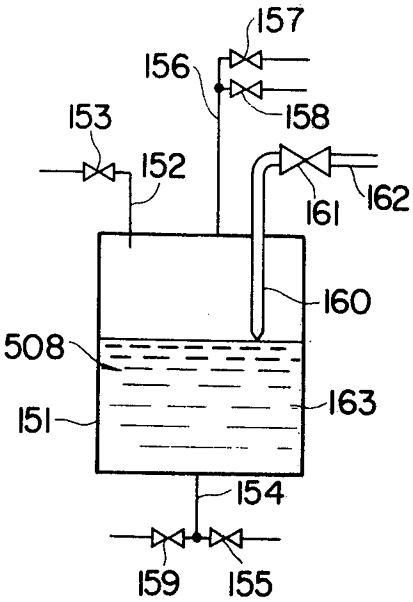
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FIG. 10

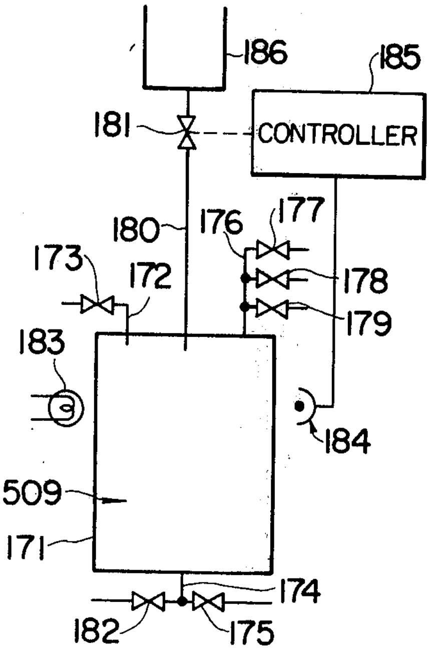
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FIG. 11

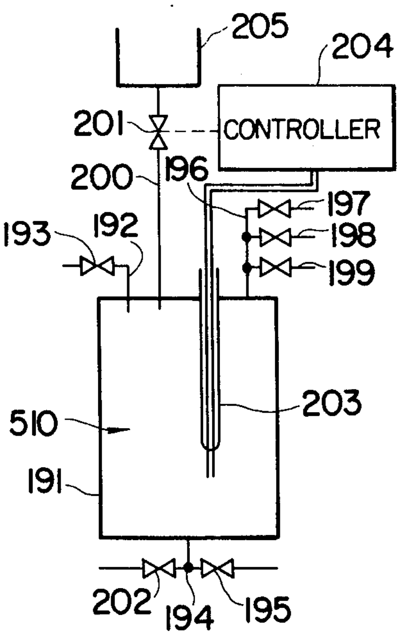
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FIG. 12

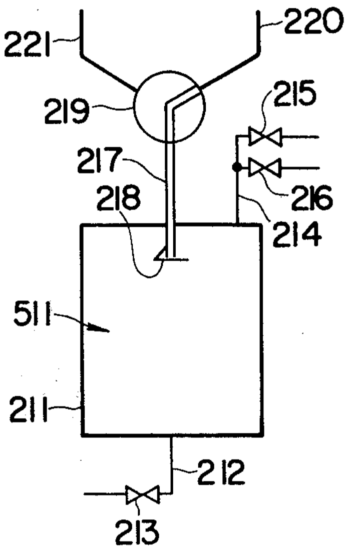
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FIG. 13

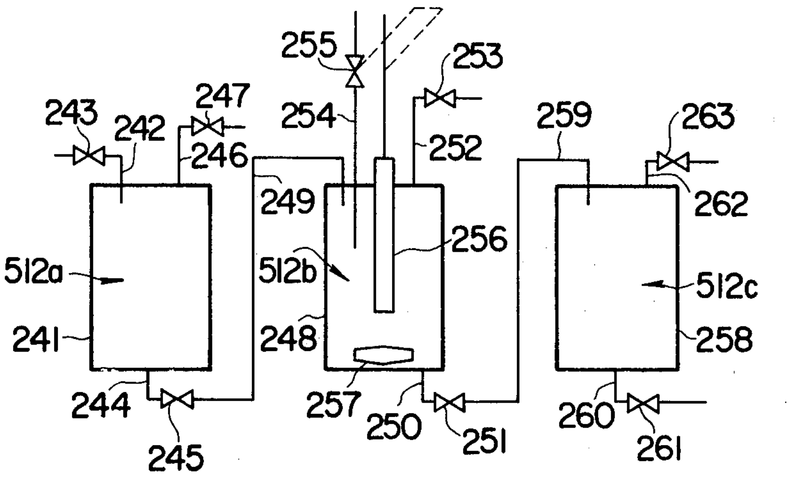
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FIG. 14

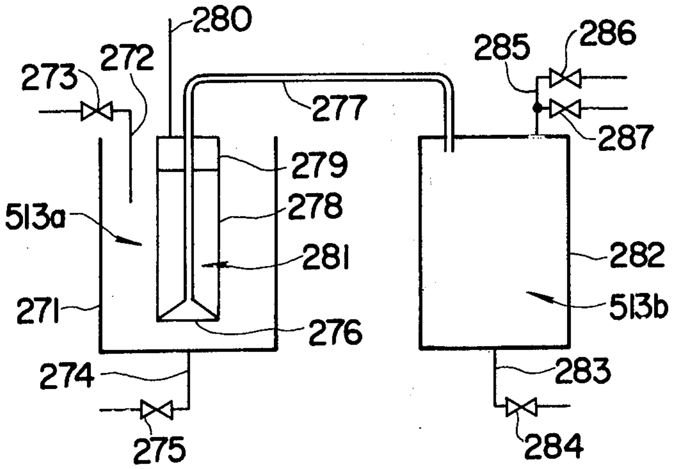
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FIG. 15

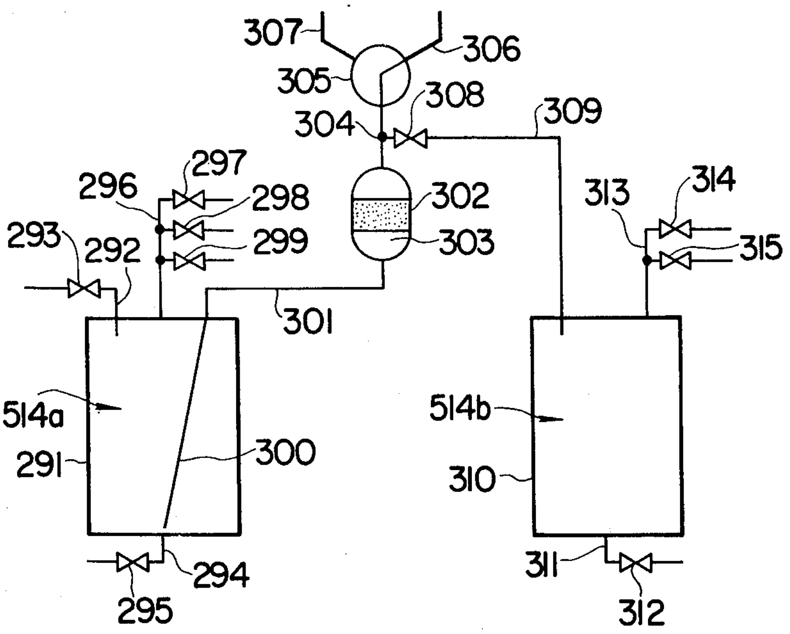
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FIG. 16

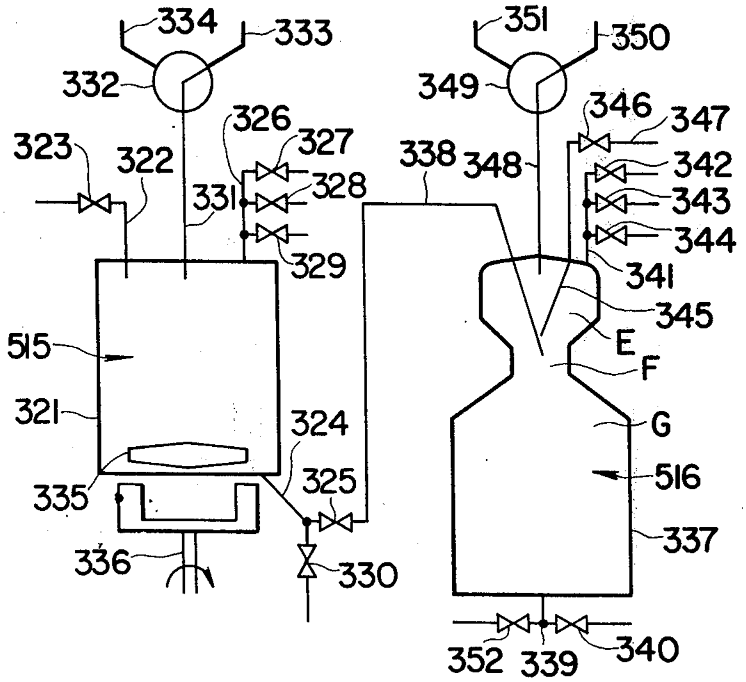
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FIG. 17

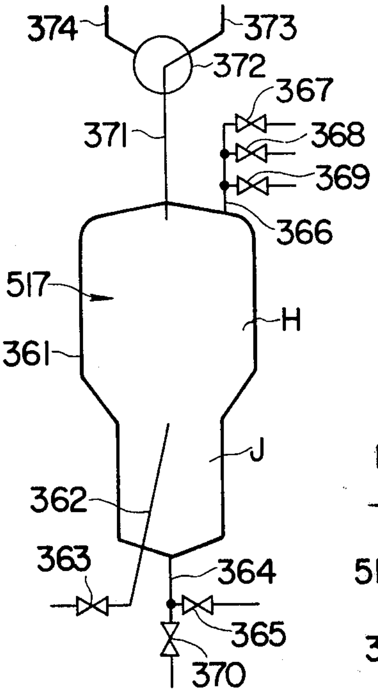


FIG. 18

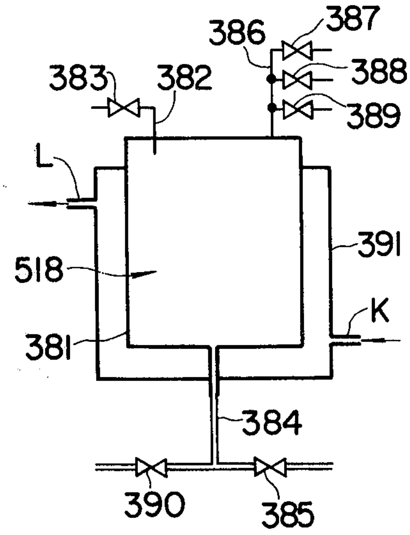
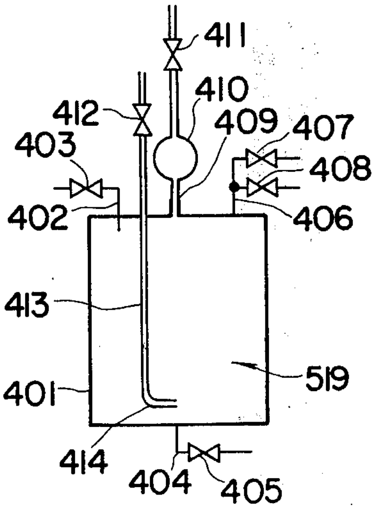


FIG. 19



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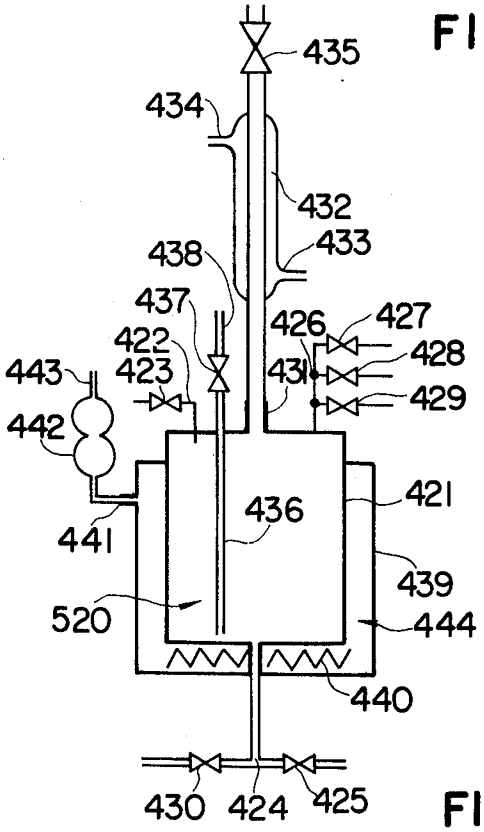
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FIG. 21

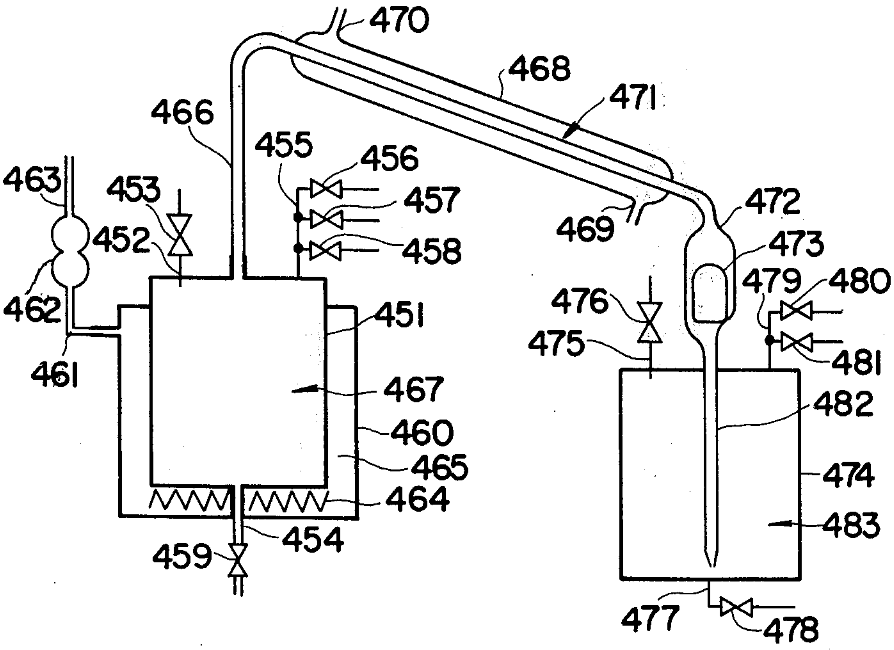
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FIG. 22

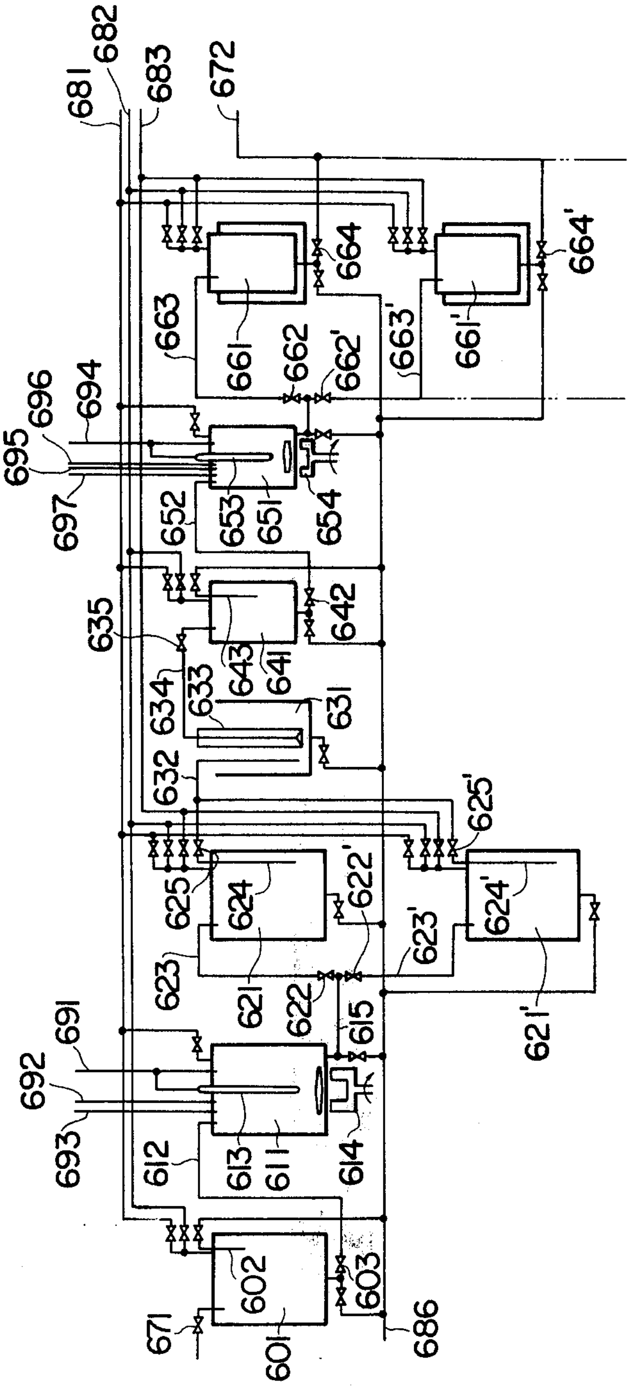
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FIG. 23

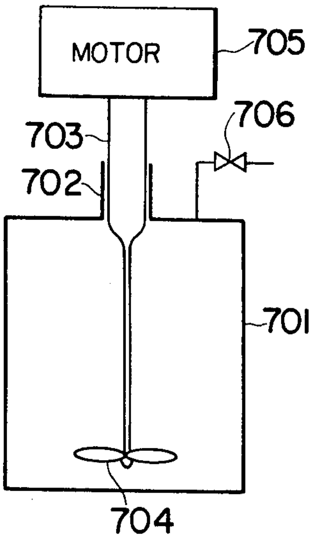


FIG. 24a

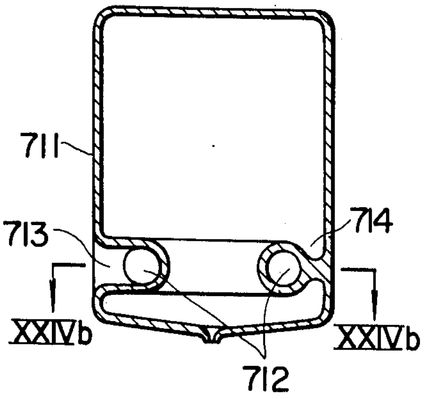
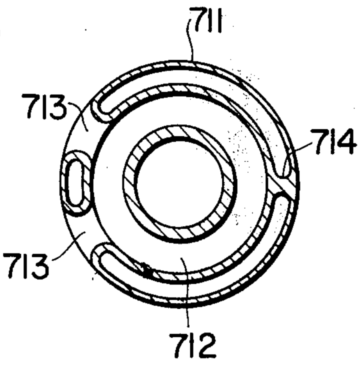


FIG. 24b



SAMPLE TRANSFER DEVICE AND METHOD FOR ANALYTICAL SYSTEM

This invention relates to an apparatus for chemical treatments, and more specifically to a chemical equipment for pretreating a sample of water by a chemical treating procedure, such as filtration, distillation, extraction, or color development, and then automatically performing a quantitive analysis of the sample's metallic and non-metallic contents by using an analyzer (or detector), for example, for the atomic absorption method or absorption spectrometry.

With the environmental destruction attracting more and more serious attraction, close monitoring of air and water pollution has been urgently called for. For the detection of water pollution and quantitative analysis of water quality, a number of methods are known. Most popular among them, in Japan, are the Testing Methods for Waste Water from Industrial Plants set forth in Japanese Industrial Standards K0102-1971, modified to conform to the Environmental Standards Concerning Water Pollution established by the Government on the basis of the Basic Law against Public Nuisances. [Other known methods include the Testing Methods for Industrial Waste Water, JIS-K0101, the methods defined in the Water-works Law (the Ministerial Ordinance Concerning Water Standards), and the Federal Water Quality Administration methods of the U.S.]

The JIS methods, all designed for manual control, are characterized in that each sample to be handled ranges in volume from 10 ml to 200 ml (or even 500 ml in some cases). From the viewpoint of the conveyance of samples in such volumes, the conventional methods have not proved satisfactory for the reasons to be explained later. Establishment of a new conveyance system has, therefore, been urgently needed for the perfection of automatic chemical analyses.

Characteristics features of existing features of existing automatic analyzers will now be briefly discussed with a primary emphasis laid on the conveyance of samples in ordinary pretreatment equipment.

One of the method uses a continuous flow divided by air bubbles into small-quantity portions. Wherein a reagent line merges with a main sample line and an air line is open into the sample line downstream of said merging point of the reagent line. All these lines are made of elastic material and the sample line and associated lines are squeezed by a squeeze pump having rollers to convey the contents forward, thereby air bubbles equidistantly join the flow of sample-reagent mixture to divide the same into equal portions. Thenceforth the sample-reagent mixture and air bubbles alternately form a stream and move altogether through the main sample line. This method has the following limitations. The sample pipe to be used must have an inner diameter small enough to avoid the disappearance of air bubbles therein, and this places an important limitation upon the quantity of the sample that can be handled. The arrangement is not adapted for such chemical treatment as extraction and dissolution of solids. The inside diameters of the lines which may be chosen are actually limited and only a few sizes are available. This confines the mixing ratio of the reagent and sample within a certain range. The pipes to be used must be elastic enough to endure squeezing and must be chemically stable to the sample and reagent to be encountered. Because of these limitations, some special method must be developed and adopted.

Another known method consists of retaining a sample in a container chemically treating the sample, and then transferring the sample to another place where it is to be subjected to another chemical treatment, either by moving the vessel or drawing up the sample by suction into the pipetter and discharging the same into another vessel. This method also has some limitations. It is impossible in this method to perform such chemical operations as extractive filtration, and distillation. The volume that the pipetter can handle is limited. The fact that the reaction vessels have to be moved together makes it necessary to handle only a small quantity of sample or even to adopt a special analytical procedure. The moving part of the equipment tend to be complicated in structure and increased in size. The sample is exposed to the atmosphere.

A third method known in the art is to convey a sample gravitationally by natural dropping. This method is characterized by the retention of the sample in a vessel during its chemical treatment and by the dependence upon natural downflow by gravity for the transport of the sample and the like. In this arrangement, the transfer lines must be held as vertically as possible and therefore the components parts that may be used are limited. Also a variety of samples cannot be smoothly handled. Each border of each reaction tank or the like requires a valve. To reduce the resistance of the pipes and valves is of value in facilitating the transport of the sample but brings a penalty of increased dead space, which in turn may cause undesirable intermingling of different samples when they are to be analyzed in succession.

From the standpoint of transport of samples, the existing automatic analyzers, classified by features into three types, have so far been briefly described.

The present invention has been perfected with the view to eliminating the foregoing disadvantages of the prior art equipment, and has for an object to provide a large-capacity apparatus for chemical treatments adapted for practicing a novel method of transporting fluids and capable of chemically analyzing many different samples.

Another object of the invention is to provide an apparatus for chemical treatments capable of automatizing all of the chemical analytical procedures that can be manually performed.

Still another object of the invention is to provide an apparatus for chemical treatments which can be increased in capacity and easily adapted for modifications in analytical procedures.

A further object of the invention is to provide an apparatus for chemical treatments capable of handling solid samples as well as fluid ones, with the system hermetically sealed.

Thus, according to the present invention, an apparatus for chemical treatments is provided which comprises closed vessels, groups of lines and selectively openable valves provided on the upper and bottom parts of the vessels for the conveyance of sample, an atmospheric-pressure gas source, an increased-pressure gas source, and a reduced-pressure gas source, said sources being communicated with said valve groups, one for each, said valve groups being selectively operated to control the pressure of the atmosphere in said vessels so that the sample can be transferred from the outside into the vessels or vice versa.

The foregoing and other objects and features of the invention will appear more fully from a reading of the following description taken in connection with the accompanying drawings, in which:

FIGS. **1** and **2** are diagrammatic views illustrating the conveyance of sample by a prior art technique;

FIGS. **3** and **4** are schematic sectional views of an automatic analyzer of a known type;

FIG. **5** is a schematic sectional view of an automatic analyzer of another known type;

FIg. **6** is a schematic view explanatory of the principle of fluid conveyance for the chemical apparatus according to this invention;

FIG. **7** is a schematic view illustrating connections for the apparatus of the invention;

FIG. **8** is a schematic view of a unit equipment of the apparatus according to the invention;

FIGS. **9** through **21** are schematic views of other unit equipments according to the invention;

FIG. **22** is a schematic view of an arrangement for chemical treatments embodying the invention; and

FIGS. **23** and **24***a* are diagrammatic sectional view of other forms of unit equipments embodying the invention and FIG. **24***b* is a sectional view along the line XXIVb—XXIVb of FIG. **24***a*.

Before explaining the present invention with reference to embodiments thereof shown in the drawings, the three methods employed in the existing automatic analyzers will now be described more definitely by referring to FIGS. **1** to **5**.

FIGS. **1** and **2** schematically show the concept of the first prior method using a continuous flow divided by air bubbles into small-quantity portions. A reagent line **7** merges with a main sample line **6** at a junction **9**, whereas an air line **4** is open into the sample line at a junction **10**. A plurality of rollers **11, 11'**, are connected with chains **12** to constitute a squeeze pump, generally indicated at **13**, which is driven in the direction indicated by an arrow in FIG. **2**, so that the sample line **1** and the associated lines can be squeezed to convey the contents forward.

Since the pump **13** squeezes the pipes at a constant speed, the quantities of the sample and other fluids that flow through them depend primarily upon the inner cross sectional areas of the respective lines. Now it is assumed that a sample **1** runs in the sample line **6**, a reagent **2** in the reagent line **7**, and clean air **4** in the air line **8**. The reagent **2** first merges into the sample **1** at the junction **9** to form a sample-reagent mixture **3**, and then air bubbles **5** enter the mixture at the junction **10**. The mixing ratio of the sample **1** to the reagent **2** is governed by the ratio of the inner cross sectional area of the sample line **6** to that of the reagent line **7**. The air bubbles **5** equidistantly join the flow of the sample-reagent mixture **3** at the intervals dictated by the ratio of the inner cross sectional area of the air line **8** to the sum of the inner cross sectional areas of the sample line **6** and reagent line **7**, thereby dividing the sample-reagent mixture **3** into equal portions. Each of the air bubbles **5** serves as a barrier wall to avoid intermixing of the adjacent sample-reagent mixture portions. Thenceforth the sample-reagent mixture **3** and air bubbles **5** alternately form a stream and move altogether through the main sample line **6**.

In the manner described a reagent can be added at a suitably controlled rate to a continuous flow of sample, and a desirable period of time for a chemical reaction can be obtained through a judicious choice of line

length. These lend themselves fundamentally to the automatization of chemical treatments. Because it permits chemical treatments of a sample in the course of transport through a sample line, the method renders it possible to extremely simplify the construction and reduce the size of the equipment for pretreatments of the sample. The reagent and sample which run through fluidtightly sealed lines, cannot be contaminated by any outside source. On the other hand, the method has certain limitations. If any bubble keeping apart two sample-reagent mixture portions of different compositions should break, the two liqud portions would be intermingled, thus interrupting the testing procedure. For this reason the sample pipe to be used must have an inner diameter small enough to avoid the disappearance of air bubbles therein. Practically the upper limit of the diameter is about 5 mm, and this places an important limitation upon the capacity of the sample line, or the flow rate of the sample that can be handled. In addition, the arrangement is not adapted for such chemical treatments as extraction and dissolution of solids. The inside diameters of the lines which may be chosen are actually limited and only a few sizes are available. Consequently the mixing ratio of the reagent and sample is confined within a certain range. The pipes to be employed must be elastic enough to endure squeezing and must be chemically inert to the sample and reagent to be encountered. Because of these requirements, some special method must be developed and adopted. Thus, as compared to other approaches, the method has major limitations in limitations chemical analyses involved and in the accuracy or reliability of the results.

FIGS. **3** and **4** schematically represent the concept of the second known method consisting the steps of retaining a sample in a container, chemically treating the sample, and then transferring the sample to another place where it is to be subjected to another chemical treatment, either by moving the vessel or drawing up the sample by suction and discharging the same into another vessel. As shown, reaction vessels **26***a*, **26***b*, **26***c* are connected with chains **27** in an orderly manner and are moved stepwise by drives (not shown) in the direction indicated by an arrow. A pipetter, designated **28**, is capable of drawing up by suction the contents of a reaction vessel or discharging the contents into an empty vessel through a nozzle **29** equipped with drives (not shown) for its vertical and horizontal movements. A dispenser **24** is operatively connected to two valves **25**, so that a reagent **22** from a reagent bottle **33** can be admitted into a reaction vessel via lines **31, 32** and through a nozzle **30** equipped with drives (not shown) for its vertical movement. The nozzle **30** may be independent of the nozzle **29** or may be connected thereto with a bridging tube **34**.

On an automatic analyzer of the type described, the sample can be transferred from one place to another where another chemical operation is to be performed, in either of two ways. One way is to cause the pipetter **28** to draw up by suction the contents of a reaction vessel (e.g., the vessel **26***b*) by way of the nozzle **29**, and then move the nozzle **29** to a point above another reaction vessel (e.g., **26***c*) and allow it to discharge the liquid into the latter vessel. The other is to take up the nozzles **29, 30** of the pipetter **29** and dispenser **24** from the reaction vessel and move the group of reaction stepwise by drives in the direction indicated by an arrow (that is, from the positions shown in FIG. **3** to those in FIG. 4). In either case, the reagent **22** can be added to the sample **21** by means of the dispenser **24** and the chemical reaction time can be controlled by adjusting the time intervals for the horizontal movement of the pipetter nozzle **29** or for the movement of all the reaction vessels. These possibilities provide bases for the automatization of operations for chemical analyses.

According to the method, a chemical treatment is carried out with the sample retained in a reaction vessel and the transfer of the sample is accomplished by moving the vessel containing the same. This presents an advantage of simplicity in the analytical operation and hence in the fundamental construction of the apparatus, and provides an additional advantage of the containment of different samples in independent vessels which precludes intermingling of the samples. On the other hand, it is impossible with this arrangement to perform such chemical operations as extractive filtration, and distillation. The volume that the pipetter can handle is limited. The fact that the reaction vessels have to be moved together makes it necessary to handle only a small quantity of sample, or even to adopt a special analytical procedure. The moving parts of the equipment tend to be complicated in structure and increased in size. Among the other disadvantages is the exposure of the sample to the atmosphere.

FIg. **5** schematically represents the concept of the third method known in the art in which a sample is conveyed gravitationally by natural dropping. Reaction tanks **48, 49** are communicated to each other by pipes **50, 51** open in the respective tanks, with a valve **53** for shutoff purpose installed between the two pipes. The tanks **48, 49** are formed with vents **57, 58,** which are open in the atmosphere. A sample storage tank **56** is communicated to the upper part of the reaction tank **48** with pipes **52, 55,** which are open in the respective tanks and are separated by a valve **54** installed midway. A dispenser **43** is operatively connected to valves **44** to enable the reagent **41** from a reagent bottle **47** to flow into the reaction tank **48** via pipes **45, 46.**

Opening the valve **54** allows the sample **40** to run down gravitationally, at a controlled rate, into the reaction tank **48** through the pipes **52, 55.** Meanwhile a given quantity of the reagent **41** is added to the sample in the reaction tank **48** by means of the dispenser **43,** the addition being followed by a certain waiting period. These functions constitute some requisites for chemical analyzing operations. If necessary, the sample-reagent mixture **42** is conveyed by gravity through the pipe **50,** valve **53,** and pipe **51** into the lower reaction tank **49.**

This third method is characterized by the retention of the sample in a vessel during its chemical treatment and by the dependence upon natural downflow by gravity for the transport of the sample and the like, which eliminates power requirement. This means, however, that the transfer lines must be held as vertically as possible and therefore the component parts that may be used are limited. A variety of samples cannot be smoothly handled. Each border of each reaction tank or the like requires a valve. To reduce the resistances of the pipes and valves is of value in facilitating the transport of the sample but brings a penalty of increased dead space, which in turn may cause undesirable intermingling of different samples when they are to be analyzed in succession.

With reference specifically to FIG. **6,** the fundamental principle of the present invention will be described hereunder. The method of transporting a sample in the apparatus for chemical treatments in accordance with this invention is to convey the sample by controlling the atmosphere surrounding the same, that is, by changing it pressure to atmospheric, positive or negative one. Here, numerals **61, 73** indicate reaction tanks wherein sample mixtures are retained and subjected to chemical treatments. They are equipped with auxiliary means so that they can perform practically analogous functions. In the upper parts of the reaction tanks **61, 73** are open sample lines **62, 74,** the other ends of which are connected to sampleline valves **63, 75** for opening and closing the lines. Sample-drain pipes **64, 76** are open in the lower parts of the reaction tanks **61, 73** and, on the other ends of these pipes, sample-line valves **65, 77** and waste-liquid line valves **72, 84** are installed as shown. The sample-line valves **65, 75** are connected via sample pipe **741.** One end of each of manifolds **66, 78** is open in the upper parts of the reaction tanks **61, 73.** Three ports in the other parts of the manifolds are provided with atmospheric-pressure line valves **67, 79,** increased-pressure line valves **68, 80,** and reduced-pressure line valves **69, 81.** Reagent inlet pipes **70, 82** are open in the upper parts of the reaction tanks **61, 73,** and reagent inlet valves **71, 83** are installed at the other ends of pipes **70, 82.**

The reaction tanks **61, 73** equipped with the groups of pipes and valves above described constitute closed reaction tank units **501, 502,** respectively.

For their operations these reaction tank units are connected to necessary pipe groups and necessary external sources. A sample pipe **85** is connected to the sample-line valve **63** and is in communication with a sample reservoir (not shown) at the atmospheric pressure or an increased pressure. Atmospheric-pressure pipes **86*a*, 86*b*** are preferably open in the atmosphere through filters or are communicated with an inert-gas reservoir (not shown) at the atmospheric pressure, because the reaction tank units form closed systems. Increased-pressure pipes **87*a*, 87*b*** are likewise in communication through filters to a clean-air or inert-gas source (not shown) under pressure (positive pressure) of 0.01–1 kg/cm^{2}G. Reduced-pressure pipes **88*a*, 88*b*** are connected to a reduced-pressure (negative pressure) source (not shown), desirably at a pressure between −0.01 and 0.5 kg/cm^{2}G. Waste-liquid pipes **89*a*, 89*b*** communicate with a suction source (not shown) at a pressure between −0.01 and 0.5 kg/cm^{2}G, which constantly draws up by suction the liquid or gas that flows through the pipes.

The procedure for feeding samples to these reaction tank units will now be explained. Unless otherwise specified, it should be understood that all valves in the vavle groups are closed. In order to introduce a sample into the reaction tank **61,** it is only necessary to open the sample-line valve **63** and atmospheric-pressure line valve **67** if the sample reservoir is kept under pressure or, if the pressure in the reservoir is atmospheric, the sample-line valve **63** and reduced-pressure line valve **69** have only to be opened, so that the pressure in the reaction tank **61** is reduced to attract the sample into the vessel. In either case, all valves are closed after a predetermined amount of sample has been fed to the reaction tank **61** and, immediately thereafter, the atmospheric-pressure line valve **67** is temporarily opened to maintain the atmospheric pressure in the tank. Transference of the sample from the reaction tank **61** to the tank **73** may be accomplished in either of twc ways. One is to enable the reaction tank **73** to have a passive function (after which the procedure is hereinafter called the "passive transference"). In this procedure the increased-pressure line valve **68**, sample-line valves **65, 75,** and atmospheric-pressure line valve **79** are opened. Now that the sample-line valves between the two reaction tanks are open, the sample-line is open, too, and the sample in the reaction tank **61** is forced down into the reaction tank **73** by the increased pressure (positive pressure) being exerted from the above liquid level in the tank **61.** The sample admitted into the reaction tank **73** is, of course, kept at the atmospheric pressure. If it is assumed that the flow passage between the two reaction tanks is equivalent to a pipe 2.4 mm in inside diameter and 20 cm in length, then 100 ml of water will be transferred from the former to the latter in about 20 seconds by simple exertion of a positive pressure of about 0.1 kg/cm^2 on the increased-pressure pipe **87***a*.

The other procedure is to permit the reaction tank **73** to have an active function (hereinafter called the "active transference"). This time the atmospheric-pressure line valve **67**, sample-line valves **65, 75,** and reduced-pressure line valve **81** are opened. Communication is thus established between the two reaction tanks and, because the pressure in the tank **73** is reduced (negative) whereas the sample in the tank **61** is at the atmospheric pressure, the sample is conveyed from the tank **61** to **73.** If the passage and conditions for the conveyance of the sample are the same as in the passive transference, then a negative pressure of about 0.1 kg/cm^2 applied to the reduced-pressure pipe **88***b* will be sufficient to effect the conveyance. Here it is appreciated that the passive transference to the reaction tank **73** means the active transference from the tank **61** and vice versa. Therefore, the afore-described method of supplying the sample to the reaction tank **61** with the reduced-pressure line valve **69** opened corresponds to the active transference to the tank **61.** Whichever procedure is followed, the pressure in the vessel after the supply of the sample is kept positive or negative for an excess period of time, so that any sample that may have adhered to the surrounding wall of the passage is blown off clearly by the stream of air or inert gas. Consequently there is no possibility of undesirable intermingling of different samples along any relatively long passage. This is another major advantage of the transference by this procedure. When the sample in the reaction tank **73** is to be transferred to some other place, the increased-pressure line valve **80** and sample-line valve **77** have only to be opened in order that the reaction tank **73** may accomplish the active transference. If any waste material is to be delivered out for abandonment from either the reaction tank **61** or **73,** it is merely necessary to open the waste-liquid line valve **72** or **84** and atmospheric-pressure line valve **67** or **79** as the case may be, and then drain the waste material into the waste-liquid line **89***a* or **89***b* which is ready to draw in the waste by suction. As an alternative to this passive transference for the either tank, the active procedure may be resorted to by opening the waste-liquid line valve and increased-pressure line valve of the particular tank.

The reaction tank units **501, 502** are provided with reagent lines (not shown) through which and the reagent inlet valves **71, 83** a reagent or reagents can be supplied from reagent bottles. The reagent or reagents can be added to the samples in the tanks by the passive

or active transference and with the use of the reagent inlet valves **71, 83.** This, when combined with the contollability of the length of time for which the sample is retained in either reaction tank or the both, will provide the basis for automatization of treatments for chemical analyses.

It is to be noted that the sample pipe **741,** if cut off midway, will provide two identical reaction tank units **501, 502.** Each of these units comprises a reaction tank, a sample pipe (for sample feeding) and a valve installed on the upper part of the tank, a sample pipe (for sample discharging) and a valve on the lower part, and a group of valves and lines provided above the vessel to make the pressure therein positive, atmospheric, or negative for the purpose of sample conveyance. Considering these reaction tank units as unit equipments each combining active and passive functions, it follows that the units can be connected both in series and parallel. Any unit equipment may be disconnected from, or may be added to, any of complex combinations of unit equipments, without affecting the function of the original combination and that of the automatic controls including the valves.

Aside from the reaction tank units taken as examples of unit equipments in the foregoing description, such other chemical apparatus as filters, aerators, thermal distillers, thermal concentrators, agitators, pH-adjusters, extractors, separators, and dissolvers may fall into the domain of units of which the present invention is equally applicable. If the sample container of any such units enumerated above is combined with groups of pipes and valves for sample conveyance and groups of valves and pipes for making the pressure in the vessel positive, atmospheric, or negative so as to convey the sample just in the same way as with a reaction tank unit, then such a chemical apparatus will be interchangeable with any of the reaction tank units.

Briefly stated, combination of the automatic control of such unit equipments with that of sample conveyance provides automatic control of every operation for chemical treatment.

Serial connection of reaction tank units has already been described in connection with the fundamental principle of the present invention. Next, parallel connection of the reaction tank units in an embodiment of the invention and the procedure for sample transference involved will be explained with reference to FIG. 7. For the sake of simplicity, reagent inlet pipes and valves are omitted from all of the reaction tank units illustrated. A first reaction tank unit **503,** like the tank units already described, comprises a reaction tank **91,** sample pipe **92,** sample-line valve **93,** sample-drain pipe **94,** atmospheric-pressure line valve **95,** increased-pressure line valve **96,** reduced-pressure line valve **97,** and waste-liquid line valve **98.** It differs from the reaction tank units **501, 502** in that the sample-drain pipe **94** is not terminated with a sample-line valve but is connected to a tee **116.** Second and third reaction tank units **504, 505** are quite similar to the units **501, 502** shown in FIG. **6.** Smaple-line valves **103***a*, **103***b* of these reaction tank units are communicated with a tee **117,** so that the tank units **504, 505** are on equal terms with the first unit **503.** A fourth reaction tank unit **506** comprises a reaction tank **108,** sample pipe **109,** sample-line valve **111,** atmospheric-pressure line valve **112,** increased-pressure line valve **113,** reduced-pressure line valve **114,** and waste-liquid line valve **115.** The sample pipe **109** communicates to the tee **117** instead of a sample-line valve. The tee **117** is in communication with the sample-line valves **103***a*, **103***b*. Stated differently, the second reaction tank unit **504** and the third unit **505** are disposed between and in parallel to the first and fourth units **503**, **506**. Description of the pipe groups and external supply sources will be omitted hereinafter because, unless otherwise stated, they are in essence the same as those already described in connection with the fundamental principle of this invention.

It is now assumed that in operations involving three-step chemical treatment the treating time required for the first or third step is a half of the period for the second step. In this case the reaction tank units are desirably connected as illustrated in FIG. **7**. Unless otherwise stated, all valves are construed to remain closed. First, the sample is introduced into the reaction tank unit **503** by the active transference, that is, by opening the sample-line valve **93** and reduced-pressure line valve **97** and thereby reducing the pressure in the tank **91**. After the introduction, the atmospheric-pressure line valve **95** is once opened to increase the pressure of the sample to the atmospheric level, and then the first-step chemical treatment is carried out. Next, the sample is transferred to the second reaction tank unit **504**. As noted already, the transference may be accomplished in either of two ways. One method is, in this case, the passive transference to the reaction tank unit **504**, whereby the increased-pressure line valve **96**, sample-line valve **101***a*, and atmospheric-pressure line valve **104***a* are opened to place the sample inside the reaction tank **91** under an increased pressure. The other is the active transference to the same unit **504** whereby the atmospheric-pressure line valve **95**, sampleline valve **101***a*, and reduced-pressure line valve **106***a* are opened. In the subsequent increased-pressure or reduced-pressure operations with the other reaction tanks or sample containers to be mentioned later, it is to be noted that, unless otherwise specified, the atmospheric-pressure line valve is once opened to maintain the pressure in the vessels at the atmospheric level. Here the second-step chemical treatment is effected. Since the time required for the second step treatment is twice as much as for the first step, the first reaction tank unit **503** is allowed to repeat the first-step treatment with another sample while, at the same time, the second step is in progress. The first sample is then transferred to the third reaction tank unit **505** in the same manner as when it was conveyed from the first unit **503** to the second **504**, except that the sample-line valve **101***b* is employed this time. During this, the second-step treatment is repeated. As will be explained later, the method of sample transference is limited to one, passive or active, depending upon the type of unit equipment to be employed for a particular chemical treatment or upon the type of sample or reagent to be handled. The sample is then transferred from the second reaction tank unit **504** to the fourth unit **506**. Again, two alternatives are open. One is the passive transference to the unit **506**, whereby the increased-pressure line valve **105***a*, sample-line valve **103***a*, and atmospheric-pressure line valve **112** are opened to convey the sample. The other is the active transference whereby the atmospheric-pressure line valve **104***a*, sample-line valve **103***a*, and reduced-pressure line valve **114** are opened for the conveyance purpose. In this stage the third-step chemical treatment is performed. The increased-pressure line valve **113** and sample-line valve **111** are opened and, by this active transference from the unit **506**, the sample is transferred elsewhere. In order to transfer the sample from the reaction tank **99***b* to the tank **108**, it is simply necessary to use the sample-line valve **103***b* and resort to the passive or active transference from the reaction tank unit **506** in the manner above described. If any undesired residue (such as the washings to be described later) is found in any reaction tank unit, it may be discharged into the waste-liquid line by opening the waste-liquid line valve and following the procedure for passive or active transference from the particular tank unit.

Although the example given above uses a pair of reaction tank units for parallel connection, it should be obvious from the description of the principle of this invention that more reaction tank units may be connected in parallel or, as a further alternative, groups of serially connected units may be connected altogether in parallel.

In the foregoing description the reaction tank units have been regarded as components of a unit equipment. Now that equipments having separate functions of chemical treatments will be considered.

One of such unit equipments is a unit for the addition of a reagent, as schematically illustrated in FIG. **8**. A sample pipe **132** is open in the upper part of a reaction tank **131** and is connected at the other end to a sample-line valve **133**. A sample-drain pipe **134** which is open in the lower part of the reaction tank **131** is communicated with a sample-line valve **135** and a waste-liquid line valve **141**. A manifold **136** which is open in the upper part of the tank communicates to an atmospheric-pressure line valve **137**, an increased-pressure line valve **138**, and a reduced-pressure line valve **139**. A reagent line that extends from a reagent bottle (not shown) through valves **142**, which are operatively connected to a dispenser **143**, terminates in the form of a reagent pipe **140**, which in turn is open in the upper part of the reaction tank **131**. If agitation is required, an agitator consisting, for example, of an agitation blade **144** inside the tank and an external magnetic stirrer **145**, may be installed. In this way a reagent-addition unit **507** is constructed.

The operation, function, and performance of this unit **507** will be described later hereunder. Here again the description of the lines and external supply sources required for the operation will be omitted because they are essentially the same as those which have already been described. Also, unless otherwise stated, it should be appreciated that all valves are normally closed and the reaction tank or other vessel to be described later is hermetically sealed. The same applies to all of the equipments to be described later and, therefore, these provisos will be omitted for brevity from the the following description.

First, the sample-line valve **133** and atmospheric-pressure line valve **137** or reduced-pressure line valve **139** are opened to admit the sample into the reaction tank **131** by the passive or active transference to the reaction tank unit **507**. After the transference, the atmospheric-pressure line valve **137** is opened for some time to maintain the sample at the prevailing atmospheric pressure. Next, while the valve **137** is kept open, the valves **142** operatively connected to the dispenser **143** are manipulated, so that a given amount of the reagent can be added to the sample by way of the reagent pipe **140**. This may be effected, if necessary, while the magnetic stirrer **145** is being driven and the sample-reagent mixture is being agitated by the blade **144.**

For the addition of the reagent, a valve such as indicated at **71** in FIG. **6** may be employed provided that the given amount of the reagent can be measured into the tank by some suitable means. Importantly, the valve to be used must be capable of hermetically closing the reagent-addition unit, even on a temporary basis. Also it should be clear that, while one type of reagent is handled in the unit being described, many different reagents may be added, instead, in a similar way.

After the reagent and sample have thoroughly reacted with each other (usually with the atmospheric-pressure line valve **137** closed, although the valve must be kept open for certain reaction systems), the atmospheric-pressure line valve is closed and agitation is discontinued. In order to transfer the reaction product to some other place, either the passive or active transference from the reaction tank unit **507** is effected by opening the sample-line valve **135** and atmospheric-pressure line valve **137** or increased-pressure line valve **138.** If useless sample is to be discarded, the waste-liquid line valve **141** is used in lieu of the sample-line valve **135.**

Another example of unit equipment is a fixed-quantity sampling unit **508,** as schematically shown in FIG. **9.** A sample-line valve **153** is installed in communication with a sample pipe **152,** which in turn is open in the upper part of a container **151.** A sample-drain pipe **154** open at one end in the lower part of the container **151** is communicated at the other end with a sample-line valve **155** and a waste-liquid line valve **159.** In communication with a manifold **156** which is open in the upper part of the container **151,** there are installed an atmospheric-pressure line valve **157** and an increased-pressure line valve **158.** A nozzle **160** is open in a suitable position inside the container via a gastight seal (not shown) capable of moving up and down in the upper part of the vessel. The other end of the nozzle communicates to a line **162** through a valve **161.** Such is the construction of a fixed-quantity sampling unit **508.** The line **162,** inside of which is kept at a reduced pressure by some suitable means, attracts fluid, either liquid or gas.

The operation of this fixed-quantity sampling unit **508** will now be explained. The sample-line valve **153** and valve **161** are opened first. This results in a reduced pressure inside the container **151,** and the sample begins to be conveyed through the pipe **152** into the vessel. Once the sample level has reached the opening of the nozzle **160,** any excess of the sample is drawn up by suction into the line **162** through the nozzle **160** and valve **161,** with the consequence that the liquid level of the sample **163** is kept constant. Even if the sample level has temporarily exceeded the opening of the nozzle **160,** the excess sample will be taken up by the nozzle **160** when the sample-line valve **153** is closed while, at the same time, the atmospheric-pressure line valve **157** is opened. As a result, the liquid level of the sample **163** will be maintained constant. The opening position of the nozzle **160** may be preset so that a predetermined amount of the sample **163** can be held within the container. When considering this sampling method with the valve **161** replaced by a reduced-pressure line valve, it is appreciated that the method is tantamount to the active transference to the sampling unit **508.** The measured amount of the sample **163** is either transferred to some other place or abandoned by the active transference from the unit by opening the increased-pressure line valve **158** and sample-line valve **155** or waste-liquid line valve **159.**

This fixed-quantity sampling unit may be utilized to collect the supernatant fluid from a solution containing sediments, in which case the opening position of the nozzle **160** has only to be chosen so that the portion of the liquid which tends to be relatively easily clarified can be collected.

The third example of unit equipment is a dilution unit, either of a photoelectric type or an electric conductivity type, as schematically represented in FIG. **10** or **11,** respectively. The unit shown in FIG. **10** will be described first. In the upper part of a reaction tank **171** is open a sample pipe **172** which is equipped with a sample-line valve **173.** In the lower part of the tank **171** is open a sample-drain pipe **174,** which in turn communicates to a sample-line valve **175** and a waste-liquid line valve **182.** A manifold **176** open at one end in the upper part of the tank **171** is also in communication with an atmospheric-pressure line valve **177,** an increased-pressure line valve **178,** and a reduced-pressure line valve **179.** From the bottom of a reagent bottle **186,** a reagent pipe **180** extends downward through a valve **181** and opens in the reaction tank **171.** Further, along both sides of the tank there are located a light source **183** and a light-beam detector **184,** in positions opposite to each other and in such a way that they can be moved up and down by some suitable means (not shown) with respect to the tank **171.** Signals from the light-beam detector **184** are sent to a controller **185,** so that the sample-line valve **181** can be opened or closed depending upon the presence or absence of the detection signals. Such is the construction of a dilution unit **509.**

The unit is operated in the following manner. It is assumed that the reaction tank **171** is filled with a given quantity of sample by the procedure already described in connection with the reagent-addition unit, and that the sample is to be diluted, for example, with water. The light source **183** and light-beam detector **184** are located on a level equal to that of the liquid after dilution. The optical instrument of this type detects the deflection of the path of a light beam from the source **183** due to the difference between air and the sample (liquid), in terms of ON-OFF signals on the detector **184.** The controller **185** is so adjusted that, when there is a predetermined amount of the sample in the reaction tank **171,** the valve **181** is kept open and the reagent (mere water in this case) is allowed to drop from the bottle **186** into the reaction tank **171** until the liquid level of the sample in the tank comes up to the light path. In this manner the reagent (or water) is added only when there is a predetermined amount of the sample in the reaction tank or, in other words, dilution to a predetermined level is accomplished. In exemplary operations, the errors in dilution were in the range of plus or minus 0.2% per 100 ml of the diluted solution.

The arrangement shown in FIG. **11,** or the electric conductivity type, differs from the type of FIG. **10** in the method of detecting the liquid level after the dilution as specified. The type of FIG. **10** detects the level optically, whereas that of FIG. **11** detects it by means of an electrode that forms a part of an electric circuit. The electrode, indicated at **203,** consists of a glass tube or the like and two wires of platinum or the like insulated and enclosed in the glass. It is vertically movable in the upper part of a reaction tank **191** while hermetically sealing the tank. A controller **204** comprises the electric circuit including the electrode **203** as one of its components, and functions so that, when there is the sample to be diluted in the reaction tank **191,** the controller cooperates with the electric circuit to open a reagent inlet valve **201** and admit the reagent (e.g., water) into the reaction tank and, when the liquid level of the diluted sample has reached the electrode **203,** it closes the reagent inlet valve **201.** The electric circuit is used to detect the difference between the electric conductivities of the air and the sample between the element wires of the electrode **203.** In other words, the circuit is of the electric conductivity type. The components described above are assembled to form a dilution unit **510.**

The electric conductivity system of the dilution unit **510** works in the manner now to be described. It is assumed that the reaction tank **191** is prefilled with a given amount of the sample and that the sample is to be diluted to a certain volume with the addition, for example, of water. The electrode **203** is installed at the height corresponding to the liquid level after the dilution. The controller **204** opens the reagent inlet valve **201** in response to a signal from the outside, so that the reagent (or water in this case) is admitted into the reaction tank **191.** If necessary, the sample may be agitated by an agitator (not shown). Initially the electric conductivity between the electrode wires is zero (because air is an insulator) but, as the liquid surface of the sample having a certain specific conductivity comes into contact with the electrode wires, the controller **204** closes the sample inlet valve **201,** thus completing the dilution. In exemplary experiments, the accuracy of dilution with this unit **510,** as well as with a dilution unit of a high-frequency transmission type, was less than plus or minus 0.2% for the sample volume of 100 ml, where a reagent inlet pipe **200** having an inside diameter of 2.4 mm was employed.

Dropwise introduction of the reagent into the reaction tank **171** may be effected in two ways; either by opening only the atmospheric-pressure line valve **177** and allowing the reagent to flow down by gravity, or by opening only the reduced-pressure line valve **179** and thereby reducing the pressure in the reaction tank **171.**

The fourth example of unit equipment is a washing unit, as schematically shown in FIG. **12.** It is more practical to employ this washing unit as a washer for a reaction tank or container of another unit equipment than to consider it as a unit equipment. However, for the simplicity of explanation, it is taken here as an independent unit equipment. It will be seen from the foregoing description about the three different unit equipment that those units have many parts in common. The illustration and description of the common parts do not appear essential for the explanation of the functional principles of the unit equipments and, therefore, will be omitted hereinafter.

Reference numeral **211** indicates a reaction tank, and a waste-liquid line valve **213** communicates to a sample-drain pipe **212,** which in turn opens in the lower part of the tank. A manifold **214,** open in the upper part of the reaction tank **211,** is communicated also with an atmospheric-pressure line valve **215** and an increased-pressure line valve **216.** Close to the upper end of the chamber inside the tank there is installed a washing nozzle **217,** which has at its lower end a sprinkler **218** and is connected at the other end with a change-over valve **219.** This valve is so designed that when it remains closed as well as other valves, the reaction tank **211** is hermetically sealed. Alternatively, another valve (not shown) may be installed midway the washing nozzle **217** instead of using the change-over valve **219** of the construction just described above. In the arrangement shown, changing over the valve **219** can establish communication between the washing nozzle **217** and either a washing-solution A line **220** or a washing-solution B line **221.** Those lines **220, 221** are connected to respective washing-solution reservoirs (not shown) with or without an additional pressure applied to the liquids therein. These components make up a washing unit **511.**

The function of this washing unit **511** and the washing method adopted will be described below. By way of explanation the inner wall of the reaction tank **211** is assumed to be contaminated. From the viewpoint of introduction of the washing solution, the washing operation can be carried out in a number of ways. In one procedure, the waste-liquid line valve **213** and atmospheric-pressure line valve **215** are opened to allow the contaminant to drain from the reaction tank **211** into the waste-liquid line (not shown) wherein the partial vacuum continues to provide suction as well as in the reaction tank. Next, the change-over valve **219** is manipulated (to the position in FIG. **12**) where it communicates the washing nozzle **217** to the washing-solution A line **220** at an increased pressure or at the prevailing atmospheric pressure. The washing solution A introduced through the washing nozzle **217** is then scattered by the sprinkler **218** to wash the inner wall surface of the reaction tank and flow down into the waste-liquid line (when, if necessary, the atmospheric-pressure line valve **215** may be closed.) Instead of this washing with running liquid, it is also possible to use the washing solution in a retained state. For this purpose the waste-liquid line valve **213** is closed and the atmospheric-pressure line valve **215** is opened so that the washing solution A under pressure or at the atmospheric pressure can be led through the change-over valve **219** and collected in the reaction tank **211.** Following the washing, with agitation where necessary, the washings are allowed to drain in either of two ways. The waste-liquid line valve **213** and atmospheric-pressure line valve **215** are opened and the washing are caused to flow down into the waste-liquid line wherein the suction still prevails. Or, the atmospheric-pressure line valve **215** is closed and the increased-pressure line valve **216** and waste-liquid line valve **213** are opened to flow down the washings. If the washing solution A alone cannot wash well, the change-over valve **219** may be manipulated to use the washing solution B, too. Of course, three or more different washing solutions may be used in this manner. For example, in the case of the hydroxides in river water that precipitate on the alkaline side of pH 10 in a reaction tank capable of treating 100 ml of the sample, mere distilled water cannot thoroughly wash the deposits away. It is customary in such occasion to dissolve the deposits with a dilute acid and then wash away the acidic solution with distilled water. In this manner thorough washing is accomplished.

Still another example, the fifth, of unit equipments is hydrogen-ion-concentration (pH)-adjusting unit. FIG. **13** illustrates the unit schematically. For the pH adjustment, usually a commercially available pH meter equipped with an automatic titrator is used. In order to simplify the construction of the reaction tank a composite glass electrode is advantageously employed. In general, such a glass electrode must not be used in an atmosphere at a positive or negative pressure, because the non-atmospheric pressure can cause undesirable intermixing or mutual contamination of the sample and the aqueous solution of a salt which is a constituent of the glass electrode. For this reason the pH-adjusting unit, as a principle, requires, in addition to the reaction tank in which the glass electrode for pH measurement is inserted, two other reaction tanks, one in front and the other behind. In order that the sample be conveyed into the center tank, the two extra tanks must have active functions whereas the center tank equipped with the glass electrode must function passively.

Referring to FIG. **13**, numeral **241** indicates a reaction tank. A sample pipe **242** is open, via a sample-line valve **243**, in the upper part of the tank. In the lower part of the tank **241** is open a sample-drain pipe **244**, which in turn is communicated with a sample-line valve **245**. Further, a manifold **246** is open in the upper part of the reaction tank **241** and is also communicated with an increased-pressure line valve **247**. The unit constructed in this way is a sample-pressurizing unit **512***a* for transferring a sample to a pH-adjusting tank **512***b* now to be described. The latter unit comprises a reaction tank **248**, having a sample pipe **249** which is open in the upper part of the tank and is communicated at the other end with a sample-line valve **245**. A sample-drain pipe **250** open in the lower part of the reaction tank **248** communicates to a sample-line valve **251**. A manifold **252** open in the upper part of the tank **245** communicates to an atmospheric-pressure line valve **253**. In addition, a composite glass electrode **256** of commerce is inserted into the reaction tank **248** through a vertically movable sealer (not shown) which establishes a gastight seal in the upper part of the tank **245**. This composite electrode communicates to the front end of an automatic titrator of a pH meter (both not shown) equipped with the titrator of which the electrode forms a part. Via a reagent inlet valve **255** a reagent pipe **254** is open in the upper part of the reaction tank **248**. These components constitute the pH-adjusting tank **512***b*. In this tank **512***b* is placed an agitator blade **257**, which is driven by external means, such as a magnetic stirrer (not shown) installed outside, for the agitation of the sample. Another reaction tank **258** has a sample pipe **259** which is open in the upper part of the tank while in communication with the sample-line valve **251**. A sample-line valve **261** is installed in communication with a sample-drain pipe **260**, which in turn opens in the lower part of the reaction tank **258**. A manifold **262** which opens in the upper part of the tank communicates to a reduced-pressure line valve **263**. The unit so constructed is a sample-pressure reducing unit **512***c* for removing the sample from the pH-adjusting tank **512***b*. The sample-pressurizing unit **512***a*, pH-adjusting tank **512***b*, and sample-pressure reducing unit **512***c* are combined to form the pH-adjusting unit. In many cases the sample-pressurizing unit and sample-pressure reducing unit are employed in common with another unit equipment.

The operation of this pH-adjusting unit will now be explained. By way of illustration, it is assumed that the sample-pressurizing unit **512***a* is filled with the sample whose pH is to be adjusted. First, the increased-pressure line valve **247**, sample-line valve **245**, and atmospheric-pressure line valve **253** are opened, so that the pressure on the liquid surface of the sample in the reaction tank **241** is increased and the sample is forced out through the sample-drain pipe **244**, sample-line valve **245**, and sample pipe **249**. By this active transference from the reaction tank **241**, the sample is transferred to the reaction tank **248**. The latter tank, in which the pH-adjusting glass electrode **256** is inserted, does not permit either an increase or decrease in pressure (to positive or negative pressure) as has already been noted. Since the atmospheric-pressure line valve **253** is open, normal atmospheric pressure is maintained in the reaction tank **248**. After the sample has been completely transferred from the reaction tank **241** to **248**, the sample pipe **249** is cleaned with a jet of air (or, if necessary, with a jet of an inert gas). At this time all valves are closed and, if necessary, the atmospheric-pressure line valve **253** is opened to keep the pressure inside the reaction tank **248** atmospheric. Following this, the pH meter is actuated by a signal indicating, for example, that the increased-pressure line valve **247** has been closed. If the pH value of the sample is yet to reach a predetermined level, the titrator automatically works and controls the reagent inlet valve **255**, thus allowing a pH-adjusting reagent to drop from the reagent inlet pipe **254**. During this period the atmospheric-pressure line valve **253** is kept open. If necessary, the agitator blade **257** may be operated by drives located outside so as to agitate the sample. Upon arrival of the pH of the sample at the predetermined value, the titrator stops automatically and the reagent inlet valve **255** closes, thus completing the pH adjustment. In order to transfer the sample whose pH has been adjusted from the reaction tank **248** to **258**, the active transference to the latter tank is resorted to by opening the atmospheric-pressure line valve **253**, sample-line valve **251**, and reduced-pressure line valve **263**. Subsequently the sample pipe **259** is cleaned by a jet of air. As described above, the sample-pressurizing unit **512***a* and sample-pressure reducing unit **512***c* having active functions for the conveyance of the sample are located at the front and rear of the pH-adjusting tank **512***b*, whereby the pressure inside the pH-adjusting tank **512***b* can be kept at the atmospheric level.

A filtration unit is the sixth of the unit equipments that may embody the present invention. Schematically shown in FIG. **14** is a unit of a filter paper type and shown in FIG. **15** is a filter board type. The former type will be detailed first. In principle the filter paper type is so constructed that a sheet of commercially available filter paper, cut to a suitable shape, is kept in close contact with a seat of a suitable shape and, after the filtration of a sample, the paper is abandoned. Reference numeral **271** indicates a container for the sample to be filtered. The container is open at the top and receives the lower end of a sample pipe **272**, which in turn is equipped with a sample-line valve **273**. A drain pipe **274** open in the lower part of the container **271** is equipped with a waste-liquid line valve **275**. A funnel **281** has at its lower end a filter seat **276** of a suitable shape, for example in the form of a cone. One end of a sample pipe **277** is open in this seat **276**. The upper end of the funnel **281** has an annular space wherein a washing sprinkler nozzle **279** formed with a multiplicity of tiny holes along its periphery is provided. Into this annular space is open a washing duct **280**. The filter seat **276** and sprinkler nozzle **279** are connected with the funnel cylinder in such a manner that they can be superposed as intimately as possible. The funnel can be moved into and out of the container **271** by drives not shown which can move vertically and horizontally. The afore-described components constitute a filtration tank unit **513***a*. Another container is indicated at **282.** One end of a sample pipe **277** is open in the upper part of the container, while a sample-drain pipe **283** is open in the bottom of the vessel and is also in communication with a sample-line valve **184.** In addition, a manifold **285** is open in the upper part of the container **282** and is also communicated with an increased-pressure line valve **287** and a reduced-pressure line valve **286.** In this way a filtrate-collecting unit **513***b* is constructed. The filtration unit of the filter paper type thus consists of the filtration tank unit **513***a* and filtratecollecting unit **513***b*. The filtrate-collecting unit may also serve as such for any other unit equipment.

The operation of this filtration unit will now be described. A predetermined amount of the sample is fed to the container **271** through the sample pipe **272** either under pressure through the sample-line valve **273** opened or by gravity. A sheet of commercially available filter paper having a suitable shape is attached closely to the underside of the filter seat **276** of the funnel **281** that was taken out of the container **271** prior to the filtration. The close attachment is attained, for example, by opening the reduced-pressure line valve **287** of the sampling unit **513***b* and maintaining a reduced (negative) pressure in the container **282** as well as in the sample pipe **277** in communication therewith. The funnel loaded with the filter paper is then slowly introduced into the container **271** and kept in a position where a necessary amount of the sample can be filtered out. The sample filtered through the filter paper is drawn up into the adjacent container **282** wherein a reduced pressure is maintained. Conveyance of this sample is effected by the active transference from the filtrate-collecting unit **513***b*. The used filter paper is abandoned by taking the funnel **281** out of the container and opening the increased-pressure line valve **286** thereby blowing off the filter paper from the seat. The residues of the sample deposited on the outer cylinder wall of the funnel **281** and on the inner wall of the container **271** are washed away by placing the funnel **281** into the container **271** and spraying a washing solution under pressure through the washing duct **280** and sprinkler nozzle **279.** Where two or more washing solutions are used, the afore-described procedure of washing with the washing unit **511** may be adopted. In that event, the waste-liquid line valve **275** may be opened to drain off the waste liquid and washings into the waste liquid line (not shown) which is ready for suction at all times.

Next, a filtration unit of the filter board type will be explained with reference to FIG. **15.** The principle of its operation is that the filtration is carried out using a stationary filter board, for example, of glass, and, after each cycle of filtration, the filter board is washed by a washing solution capable of dissolving the filtration residues, which are mostly solids, while, for example, the filtrate is flown contrariwise over the board. In the upper part of a container **291** a sample pipe **292** is open via a sample-line valve **293.** A drain pipe **294,** open in the lower part of the container, is also communicated with a waste-liquid line valve **295.** A manifold **296,** open in the upper part of the container **291,** is provided with an atmospheric-pressure line valve **297,** an increased-pressure line valve **298,** and a reduced-pressure line valve **299.** Moreover, a nozzle **300** extends downwardly from the top of the container **291** and is open at a suitable point just clear of the bottom of the container. The nozzle **300** communicates to a sample line **301,** filter **303,** and a tee **304** that leads to a change-over valve **305** and also to a sample-line valve **308.** These components combinedly form a filtration tank unit **514***a*. The filter **303** has a filter board, e.g., of glass, in the center. The change-over valve **305,** like the one described in relation to the washing unit, is designed to establish alternative communication between the tee **304** and either a washing-solution A line **306** or a washing-solution B line **307,** or some other line. In the upper part of another container **310** is open a sample pipe **309** which also communicates to the sample-line valve **308.** A sample-drain pipe **311,** open in the lower part of the container, is also communicated with a sample-line valve **312.** A manifold **313,** open in the upper part of the container **310,** communicates to an increased-pressure line valve **314** and a reduced-pressure line valve **315.** Such is the construction of a filtrate-collecting unit **514***b*. The filtration unit of the filter board type thus comprises the filtration tank unit **514***a* and filtrate-collecting unit **514***b*.

This filtration unit operates in the manner now to be described. A predetermined amount of the sample is admitted into the container **291** through the sample pipe **292** either under pressure via the sample-line valve **293** or gravitationally. Next, the atmospheric-pressure line valve **297,** sample-line valve **308,** and reduced-pressure line valve **315** are opened. This establishes communication between the containers **291, 310** through the sample line and the associated fittings, thus enabling a reduced (negative) pressure to prevail in the container **310.** Consequently, the sample from the container **291** is drawn up by suction through the nozzle **300** and sample line **301** into the filter **303,** where the solid contents are removed and the filtrate alone is admitted into the container **310** by way of the tee **304,** sample-line valve **308,** and sample pipe **309.** After a necessary amount of the sample has been filtered, all the valves are closed. When the filtrate in the container **310** is to be transferred to some other place, the increased-pressure line valve **314** and sample-line valve **312** are opened to effect the transference. Solids and other residues deposited on the walls of the filter **303** and filter board **302** are washed away with the washing solution A under pressure that can dissolve those residues, through communication between the washing-solution A line **306** and tee **304.** At this time it is only necessary in the filtration tank unit to open the atmospheric-pressure line valve **297** or, alternatively, the waste-liquid line valve is opened to drain off the washings into the waste-liquid line wherein suction is provided at all times. If the washing solution of one type alone is found inadequate for the washing purpose, the change-over valve **305** may be manipulated for communication with the line **307** for supplying the washing solution B under pressure. Desirably, after the necessary amounts of such washing solutions have flowed down, the change-over valve **305** is turned to introduce a jet of air (or other inert gas) under pressure through the tee **304,** filter **303,** sample line **301,** and nozzle **300,** thereby to clean the inner walls of those lines. In order to wash the containers **291, 310,** it is generally desirable to apply the method of washing with the washing unit that has already been described.

It should be obvious to one skilled in the art that the filter incorporated in this filtration unit may use, if necessary, a dialyzing membrane in place of the ordinary filter board so that it can serve as an ultrafilter.

The seventh example is an extraction unit as schematically illustrated in FIGS. **16** and **17**. The technical concept of the extraction resides in mixing with agitation a sample and an extracting solvent in an agitation tank, thereby extracting the objective (extractive) ingredients from the sample, transferring the extracts into a settler (stationary separation tank) and keeping them stationary for a certain period of time to separate them gravitationally into light and heavy layers, and then taking out the light or heavy layer under an increased or reduced pressure. FIG. **16** is a schematic arrangement for taking out a light layer, and FIG. **17** for taking out a heavy layer. The former arrangement will now be detailed first. In the upper part of a container **321** is open a sample pipe **322** that extends via a sample-line valve **323**. A sample-drain pipe **324**, open in the bottom of the container, is in turn communicated with a sample-line valve **325** and a waste-liquid line valve **330**. A manifold **326**, open in the upper part of the container, is equipped at the other part with an atmospheric-pressure line valve **327**, an increased-pressure line valve **328**, and a reduced-pressure line valve **329**. A reagent inlet pipe **331** opens in the upper part of the container and is connected, at the other end, with a change-over valve **332** that can alternatively communicate the pipe **331** with a washing-solution A line **333** or a washing-solution B line **334** for selective supply of the washing solutions under pressure. Inside the container **321** there is placed an agitator blade **335** for agitating the sample therein, and, outside the vessel there is a drive, e.g., a magnetic stirrer **336**, for driving the blade **335**. These components constitute an agitation unit **515**. It should be construed possible, though not shown, that the change-over valve **332** can be stopped in a position where it does not establish any connection between the pipe **331** and either washing-solution line, or where the valve itself is closed. Another container **337** is so shaped as to comprise an upper part or a light-layer compartment E that has a suitable contour and a suitable capacity, a lower part or a heavy-layer compartment G also having a suitable contour and a suitable capacity, and an intermediate compartment F having the same or smaller diameter than those of the other compartments. The expression "suitable contour" as used herein means a contour suited for the transference of the sample or the like to be described later and also suited for washing of the container to be described later. In the upper part of the container **337** enters one end of a sample pipe **338** that communicates at the other end to the above-mentioned sample-line valve **325**. A sample-drain pipe **339**, open in the lower part of the container, is associated at the other end with a sample-line valve **340** and a waste-liquid line valve **352**. A manifold **341** that opens in the top of the container **337** is in communication with an atmospheric-pressure line valve **342**, an increased-pressure line valve **343**, and a reduced-pressure line valve **344**. A light-layer-conveying valve **346** is installed on a nozzle **345** which, in turn, extends into the upper part of the container **337**. Also open in the upper part of the vessel is a pipe **348** equipped with a change-over valve **349** for its selective communication with washing-solution lines **350, 351** in the same manner as has been described with the agitation unit **515**. In the manner described a settler unit **516** is built. The lower end of the sample pipe **338** is preferably open in the center of the intermediate compartment F of the container **337**, while the nozzle **345** is preferably open in the lower part of the light-layer compartment E. Thus, the agitation unit **515** and settler unit **516** are combined to form an extraction unit for the removal of the light layer.

The operation of this extraction unit will now be explained. It is assumed that the sample to be handled amounts to 100 ml and the extractive ingredients contained therein are to be extracted with 10 ml of an extracting solvent lighter in specific gravity than the sample. Here a "suitable capacity" for the heavy-layer compartment G is such that the sum of the capacity of the compartment G and one half of the capacity of the intermediate compartment F amounts to 100 ml. Stated differently, 100 ml of the sample to constitute the heavy layer, when placed in the container **337**, forms a liquid level in the vicinity of the open end of the sample pipe **338**. A "suitable capacity" for the light-layer compartment E is such that when a light layer overlies the heavy layer its liquid level reaches approximately the center height of the light-layer compartment E (the volume being about 20 cm^3 in this embodiment).

First, the sample-line valve **323** and reduced-pressure line valve **329** are opened to convey the sample into the container **321** through the sample pipe **322**. The extracting solvent may be premixed with the sample or may be separately introduced into the container by means not shown but already explained in relation to the reagent-addition unit. After the sample and extracting solvent have been fed to the container **321**, all of the valves may be closed or, if necessary, the atmospheric-pressure line valve **327** is opened and the charge is mixed with agitation by the agitator blade **335** driven, for example, by the magnetic stirrer **336**. The container **327** and agitator blade **335** are, of course, so shaped as to suit extraction. Following the agitation for a sufficient period for extraction, the agitation is discontinued, the atmospheric-pressure line valve **327** is closed, and the increased-pressure line valve **328**, sample-line valve **327**, and atmospheric-pressure line valve **342** are opened. By this procedure of active transference from the agitation unit **515** the sample-solvent mixture is conveyed to the container **337**. Because an extracting solvent is often volatile, the passive transference from the agitation unit **515** is not advisable. Following the transference of the sample-solvent mixture to the settler unit **516**, all valves are reclosed and quiescense is maintained for a sufficient period to effect the separation of the liquid into heavy and light layers. The light layer so separated is taken out by opening the light-layer-conveying valve **346** and increased-pressure line valve **343** and forcing the layer out through the nozzle **345** open in the lower part of the light-layer compartment E. At this time, care must be exerted to use a pressure (positive pressure) source that will not disturb the boundary between the light and heavy layers. If the heavy layer of the sample-solvent mixture left behind is to be examined by a subsequent chemical analysis, only the increased-pressure line valve **343** and sample-line valve **340** are opened to take out the heavy layer from the container **337**. The portion of the residual sample-solvent mixture close to the inter-layer boundary must be left intact for subsequent abandonment through the waste-liquid line valve **352**. Washing of the interior of the container **321** is carried out in the same manner as described in connection with the washing unit **511**. It may be accompanied by agitation by the blade **335**. The inside of the container **337** may be washed again by the same procedure as with the washing unit **511**.

As regards the extraction unit for selectively taking out a heavy layer, it is noted that the agitation unit to be employed is the same as the one for the removal of the light layer and, therefore, the settler unit alone will now be explained in detail by reference to FIG. **17.** A container is indicated at **361.** A nozzle **362** is sealed in the lower part of the container and is open at a point therein to be described later. At its lower end the nozzle is connected to a sample-line valve **363** and a sample line not shown (corresponding to the sample line **338** of FIG. **16** if this settler unit is to be communicated to the agitation unit). A sample-drain pipe **364** is open in the lower part of the container **361** and has, at the other end, a sample-line valve **365** and a waste-liquid line valve **370.** In communication with a manifold **366** which opens in the upper part of the container, there are installed an atmospheric-pressure line valve **367,** an increased-pressure line valve **368,** and a reduced-pressure line valve **369.** Also provided are a washing-solution C line **373,** a washing-solution D line **374,** a change-over valve **372** for the respective lines, and a reagent inlet pipe **371** communicated with those lines and change-over valve and is open in the upper part of the container. These components are assembled to form a settler unit **517** for taking out a heavy layer. The shape of the container **361** is suited for washing. It is desirable that, when the volume of the sample to be treated is 100 ml and that of the extracting solvent is 20 ml, the capacity of the heavy-layer compartment J in the lower part of the container **361** is slightly less than 20 cm^3, say 18 cm^3, while the capacity of the upper light-layer compartment H of the container **361** is about 120 cm^3. The open end of the nozzle preferably is held near the boundary between the heavy and light layers, or, in this embodiment, at a point corresponding to the surface level of the liquid in an amount of 20 cm^3 filled in the lower part of the container **361.**

The settler unit **517** is operated for selective removal of a heavy layer therefrom in the following way.

The sample-solvent mixture agitated by the agitation unit **515** is conveyed to the container **361** through the nozzle **362** by the active transference from the unit **515.** The sample mixture separated into heavy and light layers before the transference is taken out from the lower part of the container of the agitation unit, and initially the heavy layer is conveyed and, immediately after the liquid level of the layer has reached the open end of the nozzle **362,** the conveyance of the light layer is started. Consequently there is no possibility of the layers being disturbed by the flow of the sample mixture in the settler. The liquid is allowed to stand for a period of time enough to effect its thorough separation into the heavy and light layers. Then, if the heavy layer alone is to be taken out, the sample-line valve **365** and increased-pressure line valve **368** are opened. Care must be used to discontinue the transference leaving a part of the heavy layer behind. If, immediately after this, the light layer is to be taken out for chemical analysis, it is possible to open the waste-liquid line valve **370** and increased-pressure line valve **368** to abondon the residual heavy layer and a lower portion of the light layer, and thereafter open the sample-line valve **365** and increased-pressure line valve **368** to take out the rest. Washing of the interior of the container **361** may be performed generally in conformity with the procedure described in connection with the washing unit **511.**

The eighth example of unit equipments is an incubator unit as schematically illustrated in FIG. **18.** Since the rate of a chemical reaction generally depends upon the temperature, it is required to maintain a constant ambient temperature for the reaction vessel. The method employed in this embodiment is, for example, to circulate a thermal medium such as water at a constant temperature around the reaction vessel. A container is indicated at **381.** A sample pipe **382** provided with a sample-line valve **383** is open in the upper part of the container. A sample-drain pipe **384** which opens in the lower part of the vessel is equipped with a sample-line valve **385** and waste-liquid line valve **390.** A manifold **386** also connected to the upper part of the container is communicated with an atmospheric-pressure line valve **387,** an increased-pressure line valve **388,** and a reduced-pressure line valve **389.** All around the container except for its top wall, a jacket **391** is provided in the form of an enclosed vessel open only at a constant-temperature water inlet K and a constant-temperature water outlet L, and through which the sample-drain pipe **384** extends from the container downward. These components form an incubator unit **518.**

The function of this incubator unit will now be explained. First, a thermal medium such as, for example, water at a given temperature is led into the jacket through the constant-temperature water inlet K and is overflown out of the outlet L, so that the temperature of the container **381** can be kept constant at a preset level. A sample is fed into the container **381** by the active transference into the incubator unit by use of the sample-line valve **383** and reduced-pressure line valve **389.** After the sampling, the atmospheric-pressure line valve **387** is opened to maintain the sample at the atmospheric pressure. If necessary, the sample is agitated while the atmospheric-pressure line valve is kept open and, where necessary, by means of an agitator such as a magnetic stirrer. In the manner described, the sample will attain the preset temperature. It is then retained in the container for a period of time necessary for the chemical reaction desired. Thereafter, the sample-line valve **385** and increased-pressure line valve **388** are opened, and the sample is transfererd to some other place by the active transference from the incubator unit **518.** While water is used in this embodiment as a thermal medium for keeping the temperature constant, it is possible, of course, to replace the thermal medium by an electric heater.

The ninth exemplary unit equipment is an aeration unit schematically shown in FIG. **19.** There is shown a container **401,** in the upper part of which is open a sample pipe **402** equipped with a sample-line valve **403.** A sample-drain pipe **404** is open in the bottom of the container **401** and is equipped with a sample-line valve **405.** A manifold **406** opens in the upper part of the container and is communicated with an increased-pressure line valve **407** and a reduced-pressure line valve **408.** Also open in the upper part of the container is a gas-collecting pipe **409** which, in turn, communicates to a trap **410** and a gas-collecting valve **411.** From above the container **401** comes down an aerating pipe **413,** which terminates with a nozzle **414** at the lower end. The other end of the aerating pipe **413** is provided with an aerating valve **412.** Constructed in this way is an aeration unit **519.**

The operation of this aeration unit **519** will be described in detail below. Because the sample to be handled often contains volatile matter, it is desirable that the sample be kept under pressure and that it be transferred by the passive function of the aeration unit **519** with both the sample-line valve **403** and atmospheric-pressure line valve **407** opened. Next, the gas-collecting valve **411** connected to a gas-collecting container not shown is opened, while the aerating valve **412** is opened to admit an aerating gas under pressure into the sample. The nozzle **414** has a shape suited for the aeration purpose; for example, it may take the form of a perforated disc, ball or tube, or a finely perforated pipe directed against the inner wall of the container **401**. Since the gas after the aeration (which has taken over the volatile matter from the sample) contains fine particles of the liquid, the trap **410** for gas-liquid separation is provided on the gas-collecting pipe **409**, preferably close to the container **401**. The aerated sample is conveyed elsewhere by the active transference from the aeration unit **519**, with the sample-line valve **405** and increased pressure line valve **408** opened.

The tenth example of unit equipments is a thermal concentration unit as schematically shown in FIG. **20**, which will now be described in detail. In the upper part of reaction tank **421** is open a sample pipe **422**, which in turn communicates to a sample-line valve **423**. In the lower part of the tank is open a sample-drain pipe **424** which is connected to a sample-line valve **425** and a waste-liquid line valve **430**. A manifold **426**, also open in the upper part of the tank, is provided with an atmospheric-pressure line valve **427**, increased-pressure line valve **428**, and a reduced-pressure line valve **429**. A vapor pipe **431** in communication with the upper center of the reaction tank **421** is partially covered with a cooling jacket **432**, which in turn has a cooling-water inlet **433** and a cooling-water outlet **434**. Near the upper end of the jacket, a vapor valve **435** is installed. A capillary tube **436** extends from above the reaction tank **421** downward and is open in the lower part of the vessel, whereas the upper end of the tube **436** is connected to a line **438** via a valve **437**. An oil bath **444** to be described later surrounds the reaction tank **421** except for its top portion, the sample-drain pipe **424** extending downward through the bath. In this way a thermal concentration unit **520** is constructed. A jacket **439** containing the oil bath is provided with a reflux tube **441** in the upper part which is integrally formed with an air condenser **442** and an open port **443**. An electric heater **440** is liquidtightly sealed in the lower part of the bath. The jacket **439** is filled with a type of oil (not shown) having a high boiling point and a low vapor pressure.

The operational function of this unit is as follows. The oil in the jacket **439** is heated by the electric heater **440** and is partly evaporated. The oil vapor is cooled by the air condenser **442** (which may be replaced by a water condenser, if necessary), and is returned to the bath through the reflux tube **441**. The open port **443** permits the jacket **439** to maintain the prevailing atmospheric pressure inside. The oil temperature can be kept at a predetermined level by controlling the power supply to the electric heater **440**.

Now it is assumed that the sample-line valve **423** has been turned open, the sample fed to the reaction tank **421**, and the vapor valve **425** opened. The oil bath **444** preheated to a suitable temperature is further heated to a predetermined temperature by the electric heater **440**. If the sample is to be heated up to its boiling point, it is a desirable practice to introduce clean air or inert gas under slight pressure into the line **438** and open the valve **437**, so that the gas is gradually blown out of the capillary tube at a rate low enough to avoid bumping. The cooling jacket **432** provided on the intermediate part of the vapor pipe **431** is designed to condense high-boiling-point ingredients of the sample and return the condensate to the container. For this purpose cooling water is admitted into the jacket through the inlet **433** and is overflown through the outlet **434**. If low-boiling-point ingredients are to be recovered, a recovery tank (not shown) may be located on the other end of the vapor valve **435**. If the unit is intended for mere heating, a cooling jacket having a suitably chosen length may be used to reflux every drop of the condensate. After the thermal concentration to a predetermined value, the heating is discontinued. The valve **437** and vapor valve **435** are closed, while the sample-line valve **425** and atmospheric-pressure line valve **427** or increased-pressure line valve **428** are manipulated to effect transference, either passively or actively, of the concentrated matter elsewhere from the thermal concentration unit **520**.

The eleventh example is a distillation unit. FIG. **21** is a schematic view of the arrangement. This unit consists of three major components, i.e., a heating tank, a cooling jacket, and a distillate tank. The heating tank is analogous to the thermal concentration unit just described above. The tank **451** is connected at its upper part to a sample pipe **452** for the supply of the sample through a sample-line valve **453**. In the lower part of the tank is open a sample-drain pipe **454**, which in turn is connected to a waste-liquid-line valve **459**. A manifold **455** opens, too, in the upper part of the heating tank and is provided, on the other hand, with an atmospheric-pressure line valve **456**, an increased-pressure line valve **457**, and a reduced-pressure line valve **458**. The heating tank **451** is further connected to a vapor pipe **466** through its top wall. An oil bath **465** to be described later surrounds the heating tank **451** except for its top portion, the sample-drain pipe **454** extending downward through the bath. These components form a heating tank unit **467**. The oil bath **465** comprises: a jacket **460** which surrounds the heating tank **451** except for the top portion and allows the sample-drain pipe **454** to penetrate therethrough; a reflux tube **461** which opens in the upper part of the jacket and is formed with an air condenser **462** and terminates at its upper end with a port **463** open in the atmosphere; an electric heater **464** sealed in the bath on the bottom of the jacket **460**; and a chemically stable oil or heat medium having a high boiling point and a low vapor pressure filled in the jacket **460**. The cooler **471** comprises a cooling jacket **468** having a cooling water inlet **469** and an outlet **470**, which jacket is connected at one end to the vapor pipe **466** and at the other end to a check valve **472** that contains a float **473**. The distillate tank unit **483** comprises: a receiving tank **474** in which a nozzle **482** connected to the check valve **472** extends downward; a sample-drain pipe **477** which opens in the lower part of the receiving tank **474** and is connected to a sample-line valve **478**; a manifold **479** which opens in the upper part of the tank and is provided with an atmospheric-pressure line valve **480** and an increased-pressure line valve **481**; and a reagent inlet pipe **475** which opens in the upper part of the tank **474** and is communicated with a reagent inlet valve **476**. The heating tank unit **467**, cooler **471**, and distillate tank unit **483** are combined to form the distillation unit.

The operational function of this distillation unit will now be explained. The oil in the jacket is heated by the electric heater **464** and is partly evaporated. The oil vapor is cooled by the air condenser **462** (or, if necessary, by a water condenser) and is returned to the jacket through the reflux tube **461.** The open port **463** permits the maintenance of atmospheric pressure in the jacket **460,** and control of the power supply to the electric heater **464** makes it possible to keep the oil temperature at a predetermined level. The check valve **472** works in such a manner that, if there is no liquid therein, it does not function as a valve, but if there is, the float **473** rises to close the path for an upward flow but provide no obstruction to a downward flow. It follows that, when the check valve **472** is not filled with a liquid (or when all other valves of the distillation unit are closed), the heating tank **451** and receiving tank **474** are in communication with each other through the cooler **471,** thus forming a closed system independent of the outside. The sample to be distilled may be fed to the heating tank **451** in four different ways. One (A) is by passive transference to the distillation unit with both the sample-line valve **453** and the atmospheric-pressure line valve **456** opened. Another (B) is by passive transference to the distillation unit with the sample-line valve **453** and atmospheric-pressure line valve **480** opened. The third procedure (C) is to open the sample-line valve **453** and reduced-pressure line valve **458** and effect active transference to the distillation unit. The fourth (D) is by opening the sample-line valve **453** and a reduced-pressure line valve not shown which is communicated with the manifold **479** and thereby effecting active transference to the distillation unit. One of these procedures may be chosen in consideration of the unit's combination with another unit or units intended.

With power supply to the electric heater **464,** the oil bath preheated to a suitable temperature is further heated to a desired temperature, and distillation is started. At this time the atmospheric-pressure line valve **480** must be kept open. If bumping of the sample is to be prevented, the method as used with the thermal concentration unit should be adopted, too. The vapor of the sample is condensed by the cooler **471,** dropped through the nozzle **482,** and is collected in the receiving tank **474.** If it is desired to stabilize the distilled sample by having the same absorbed by an absorbent, the absorbent is supplied beforehand to the tank **474** through the reagent inlet valve **476.** Judicious choice of the open end position of the nozzle relative to the reagent level is an important consideration. This may necessitate a modification to the bottom contour of the receiving tank. Should the open nozzle end be immersed in the distilled sample during the distillation, the heating container would form a closed system. In such case a pressure change may lead to a backward flow of the distilled sample from the nozzle **482** up to the cooler **471.** When this happens, the float **473** rises up and forms a check valve that keeps the distilled sample from flowing back to the cooler **471,** in the manner already explained. After distillation for a predetermined period of time, or after a predetermined amount of distillate has been obtained (as determined by the liquid level detection methods with the dilution unit, although no such means is shown here), the electric heater **464** is switched off, the atmospheric-pressure line valve **456** (or, if necessary, the increased-pressure line valve **457**) is opened and, after the pressure inside the system has returned to the atmospheric level, all valves are closed. The atmospheric-pressure line valve **456** may have to be kept open depending on the condition of the oil bath **465.** Residues from the heating tank are drained off by opening the waste-liquid line valve **459,** and the sample in the distillate tank unit **483** is transferred elsewhere by opening the sample-line valve **478.** Washing of the heating tank **451** and receiving tank **474** may be carried out in the manner already described in connection with the washing unit. If the cooler has to be cleaned, it may be either washed with the washing solution distilled in the way above described or cleaned with a jet of air or inert gas.

So far a total of eleven typical unit equipments having separate functions for chemical operations have been described in detail. As noted in the early paragraphs dealing with the fundamental principle of the invention, these units may be freely combined to meet the particular requirements for various chemical analyses and, in that way, fully automatized analytical operations will be made possible.

As a preferred embodiment of the present invention, an automatic analyzer built in conformity with the invention for conducting Testing Method B (indophenol test) for the analysis of ammonium ions according to JIS K-102 will now be described.

The indophenol test will be briefly explained first. One hundred milliliters of test water (usually adjusted to about pH 2 by the addition of hydrochloric acid for the preservation purpose) is neutralized to about pH 7 by dropping a sodium hydroxide solution. With the addition of one milliliter of a zinc sulfate solution, the mixed solution is thoroughly mixed with stirring. The pH is adjusted to about 10.5 by the addition of a mixed solution of sodium hydroxide and sodium carbonate (usually in an amount of 0.3 to 0.5 ml). The mixture is again throughly mixed with stirring, allowed to stand for some time, and the supernatant fluid is separated or filtered out to obtain a clear solution. A suitable amount of this test water is neutralized to about pH 7 with hydrochloric acid, and water is added to give a total amount of about 10 ml. One milliliter of an EDTA (disodium ethylene diamine tetraacetate) solution and 4 ml of a sodium phenolate solution are added and the mixture is shaken well. Finally 3 ml of a sodium hypochlorite solution and water are added to obtain a total amount of 25 ml, and the mixture is mixed with shaking. The mixture is allowed to stand at 20°–25°C for about 20 minutes. After the standing, it is transferred to a 10 mm absorption cell of a spectrophotometer, and the absorbance is determined in the vicinity of the wave-length of 625 nm, and the amount of ammonium ions is found from a calibration curve prepared beforehand.

FIG. **22** is a schematic diagram of this automatic ammonium ion analyzer embodying the present invention. The component units will now be detailed. Reference numeral **601** indicates a fixed-quantity sampling unit, the construction and function of which have already been described separately. The unit is equipped with a metering nozzle **602** and outgoing and incoming sample-line valves **603** and **671.** A reagent-addition unit **611** is associated with a pH-adjusting unit. The structures and operational functions of these units have already been clarified. A sample line **612** extends between the sample-line valve **603** and the upper part of the container for the reagent-addition unit **611.** A pH electrode **613** is operatively connected to an automatic titrator located outside but not shown, so that the reagent can be dropped from a sodium hydroxide solution line for the pH adjustment of the sample. The reagent-addition unit is also equipped with a magnetic stirrer **614** and a sample line **615.** Settler tank units **621, 621'** are constructed and designed for functioning as have been explained in the early paragraphs dealing with the fixed-quantity sampling unit. In the upper parts of these settler tanks are open, respectively, sample lines **623, 623'** which in turn communicates to the sample line **615** via sample-line valves **622, 622'**. Nozzles **624, 624'** which extend through the top walls of the settler tanks and open near the bottoms of those tanks are provided with sample-line valves **625, 625'** above the tanks. The settler tanks **621, 621'** are arranged in parallel with the reagent-addition unit **611** and a filtration unit **631** now to be described. The filtration unit, the construction and function of which have already been detailed separately, has a sample line **632** open in the vessel and also in communication with the above-mentioned sample-line valves **625, 625'**. The unit is equipped, moreover, with a vertically and horizontally movable funnel **633** and a sample line **634** communicated with the funnel. A fixed-quantity collecting unit **641,** which in effect serves as a filtrate-collecting unit for the filtration unit **631,** has the structure and function of the fixed-quantity sampling unit already described as a unit equipment. A sample line **634** provided with a sample-line valve **635** is open in the upper part of the vessel of this unit. In addition, a nozzle **643** and a sample-line valve **642** are installed. A reagent-addition unit **651** is associated with a pH-adjusting unit. In this unit **651** is open a sample line **652** in communication with the sample-line valve **642.** The unit is also equipped with a pH electrode **653,** a magnetic stirrer **654,** etc. An incubator unit **661** is built and functions in the manner described separately as a unit equipment. It is communicated to the reagent-addition unit **651** with a sample line **663** open in the bottom of that unit and extended to this unit **661** via a sample-line valve **662.** On the other hand, the unit **661** is communicated to a sample line **672** through a sample-line valve **664.** Although two such incubator units are shown, actually five units are connected in parallel with the reagent-addition unit **651** and sample line **672.** An atmospheric-pressure line **681,** an increased-pressure line **682,** a reduced-pressure line **683,** and a waste-liquid line **686** in which suction is provided at all times are all connected to the above-mentioned units through valves, as illustrated. The functions of those valves have already been explained in connection with the individual unit equipments. The atmospheric-pressure and increased-pressure lines are in communication with reservoirs of clean air or inert gas free of impurities such as carbonic acid gas. Also provided are a zinc sulfate solution line **692,** an alkaline mixed solution line **693,** a hydrochloric acid line **694,** an EDTA solution line **695,** a sodium phenolate solution line **696,** and a sodium hypochlorite solution line **697,** through which predetermined amounts of a zinc sulfate solution, mixed solution of sodium hydroxide and sodium carbonate, aqueous solution of hydrochloric acid, EDTA solution, sodium phenolate solution, and sodium hypochlorite solution can be forced into the system. The forced introduction of these solutions may be accomplished, for example, by a combination of an injector and a valve motion which can be automatically operated, or a commercially available reagent-pipetting device.

The operation of this ammonium ion analyzer will be described below in the order of the procedural steps involved. It is to be understood that all of the surface to contact the sample and other liquids to be handled are made of chemically resistant material, e.g., glass, fluorocarbon resin, polyvinyl chloride or the like, and that, unless otherwise specified, all valves are normally closed. The sample line (not shown) in communication with the sample-line valve **671** is immersed in water to be tested, and the sample-line valve **671** and a suction valve communicated to the nozzle **602** is opened, so that the test water is sampled by the active transference to the fixed-quantity sampling unit **601.** At this time the open end position of the nozzle **602** should be equal to the liquid level of 100 ml of the sample in the vessel. After the sampling, the sample line immersed in the test water is taken out and the sample deposited on the inner wall of the sample line and the associated parts is blown away cleanly with a jet of air. The sample portion overflown from the nozzle is drained into the waste-liquid line wherein the suction prevails. The atmospheric-pressure line valve is opened and the pressure inside the tank is made atmospheric. Next, the increased-pressure line valve and sample-line valve **603** of the fixed-quantity sampling unit **601,** and the atmospheric-pressure line valve of the reagent-addition unit **611** are opened to convey the sample by active transference from the fixed-quantity sampling unit **601** to the reagent-addition unit **611.** After the transference the interior of the sample line **612** is cleaned with a jet of air. As already noted in connection with the pH-adjusting unit, a reaction unit equipped with a pH electrode must at all times be kept at the atmospheric pressure. The 100 ml portion of the test water fed to the reagent-addition unit is adjusted to pH 7 by the addition of a sodium hydroxide solution supplied from the line **691** by means of an automatic titrator cooperative with the pH electrode **613,** while the sample is being agitated, for example, by the magnetic stirrer **614.** Next, one milliliter of a zinc sulfate solution and 0.5 ml of a sodium hydroxide-sodium carbonate solution are added, respectively, from the zinc sulfate solution line **692** and alkaline mixed solution line **693.** Desirably the sample is continuously agitated during this course of addition. Then, a white precipitate will result. Manipulation for the opening and closing of the solenoid valves for the above operation is performed by a programmer that produces a working program of the control sequence with the aid of electric pulse generators which give 3-, 8- and 16-second pulses at intervals of 30 seconds or thereabouts. All of the foregoing steps of chemical operation and the washing to be described later are carried out in a period of five minutes. The sample that has yielded the white precipitate is conveyed to the settler tank unit **621** by the active transference with the sample-line valve **622** and reduced-pressure line valve opened. In about 7 minutes the precipitate aggregates to form sufficiently coarse particles to settle down on the bottom of the tank, and the liquid portion becomes almost clear in the portion of the settler tank unit where the lower end of the nozzle **624** opens. In the meantime, the fixed-quantity sampling unit **601** and reagent-addition unit **611** are thoroughly washed by the method of the washing in the washing unit **511** already described and by means of a washing nozzle or the like not shown, using a dilute acid and pure water. Following the washing, untreated test water is again sampled and chemically treated in the manner above described.

Then, the sample-line valve **622'** and reduced-pressure line valve are opened and the treated sample is transferred to the settler tank unit **621'**. After the lapse of a predetermined period of time, the increased-pressure line valve and sample-line valve **625** are opened and only the supernatant fluid of the sample in the settler tank unit **621** is forced by the active transference therefrom to the adjacent filtration unit **631** through the nozzle **624.** The sample residues containing the white precipitate are abandoned into the waste-liquid line **686** through the waste-liquid line valve and atmospheric-pressure line valves both opened for the draining purpose. The emptied vessel is washed with a solution from a washing nozzle not shown. Since this step requires about 10 minutes, the pair of settler tank units **621, 621'** are connected in parallel. The sample fed to the filtration unit **631** still contains fine particles of the precipitate. A sheet of filter paper cut to a suitable size and shape is applied to the funnel **633** taken out in advance from the vessel, and the valve communicated to the nozzle **643** of the fixed-quantity collecting unit and the sample-line valve **635** are opened so that the filter paper can be sucked up by the funnel, and then the funnel is lowered and immersed into the sample to admit the sample into the fixed-quantity collecting unit **641** through the funnel and the sample line **634.** The open end of the nozzle **643** is preadjusted to the position equivalent to the liquid level that 10 ml of the sample produces. Next, the sample-line valve **642** and the increased-pressure line valve of the fixed-quantity collecting unit are opened to force the sample into the adjacent tank of the reagent-addition unit. The used filter paper of the filtration unit is abandoned, and the unit is washed, together with the fixed-quantity collecting unit, by means of washing nozzles not shown. The combined period of time required for these two steps is about **5** minutes. Inside the reagent-addition unit **651,** the sample is adjusted to pH 7 by the addition of an aqueous solution of hydrochloric acid from the line **694** and with the use of the pH electrode **653,** while being agitated by the magnetic stirrer **654** in the manner described in relation to the reagent-addition unit **611.** Next, 1 ml of an EDTA solution, 4 ml of sodium phenolate solution, and 3 ml of sodium hypochlorite are added, respectively, from the lines **695, 696, 697.** The mixture is thoroughly agitated and is diluted with pure water to a total volume of 25 ml in a dilution unit of the electric conductivity type, which is not shown but has already been described as a unit equipment. The sample is transferred actively to the incubator unit **661** by use of the sample-line valve **662** and reduced-pressure line valve. The reagent-addition unit **651** is subsequently washed. The above step requires about 5 minutes. The sample in the incubator unit **661** is kept at 25°C by water at that temperature circulated through the jacket. Because the time required for this step of color development and stabilization is about 20 minutes, and also because the ensuing samples arrive at this station at intervals of 5 minutes, five such incubator units are connected in parallel and the samples are temporarily stored in succession in these units. This means that, when the fifth incubator unit is supplied with a sample, the sample in the first unit **661** has been kept at 25°C for about 20 minutes and the color developed has stabilized. Therefore, the increased-pressure line valve and sample-line valve **664** are opened, and the sample is conveyed through the sample line **672** to the flow cell in the visible range of a spectrophotometer not shown, so that its absorbance is determined. After each sample has been transferred in this way, the sample line **672** and flow cell are cleaned with a jet of air. The time required for the above-described step is 5 minutes. From the foregoing it follows that the results of analysis of the first water sample by this automatic analyzer are made known about 45 minutes after its introduction into the apparatus, and thenceforth the results of the following samples are revealed at intervals of 5 minutes. The results are subjected to data processing by an electronic apparatus on the basis of calibration curves obtained in advance from tests on controls, and are converted into ratios by weight of ammonia contents or the like, and then are recorded together with the sample numbers and other information. In a typical test with this analyzer, the following results were obtained. The calibration curve attained linearity with 0–3 ppm, the reproducibility was three percent in terms of the Cv value, the sensitivity was one percent of the full scale, and the degree of contamination was three percent. These values indicate that the apparatus is of great value as a fully automatic analyzer.

While the programmer for the sequential procedure of opening and closing solenoid valves is of the electronic type in this embodiment, genuine fluid elements may be employed instead. In the latter case pneumatically driven valves are advantageously used in place of the solenoid valves.

In addition to those embodiments of the invention so far described, a few other embodiments as unit equipments will now be illustrated. One of them concerns the method of agitation with an agitation unit for an extracting operation. The agitation is accomplished not merely by the use of remote force as by the magnetic stirrer shown in FIG. **16,** but equally by mechanical means as in FIG. **23.** The latter comprises a glass vessel **701** having a neck **702** on its top, a shaft **703** of glass, fluorine-contained resin or other chemically stable material which fits in the neck to form a labyrinth seal, a bladed rotor **704** of glass or other chemically stable member supported at the lower end of the shaft **703** and located in a suitable part of the vessel, and a motor **705** for driving the shaft and rotor at a suitable speed. Although not shown, valves for the transport of samples are, of course, installed on the vessel. Of those valves, an increased-pressure line valve **706** may be partly opened to supply at all times a very small amount of gas under pressure to the vessel in order to avoid seizing of the labyrinth seal.

Another method pertains to heating, and an arrangement for heating in accordance with the present invention is shown in FIGS. **24*a*** and **24*b*** which are, respectively, a vertical sectional view and a transverse sectional view as seen in the direction of arrows in the former figure. As compared with the heating means in the embodiment described earlier which use an oil bath, this arrangement is designed to hold an electric heater in the vessel. A vessel **711,** equipped with sample lines and valves not shown, is formed with a ring **713** having a circular cross section and supported near the bottom of the vessel by a connecting part **714** for integral connection with the surrounding wall of the vessel. An electric heating wire is inserted into the ring through holes **713** communicating the circular space and the outside.

With regard to valves, those to be used for contact with liquids (corresponding to the sample-line valves already described) are pinch valves, small switching valves, and change-over valves. In addition, check valves may be employed for other embodiments. With the sample-conveying system using check valves, it is not always possible to adopt both the active and passive transference procedures as with the units so far described. Nevertheless, the limitation that only one of the two procedures have to be resorted to is offset by the advantage of simplified construction of the valves.

Among possible combinations of unit equipments according to this invention are, in addition to the ammonia analyzer described above, metal analyzers equipped with extractors, cyanide monitors incorporating heating and distilling means, and various other automatic analyzers perfected by automatizing analytical operations which have hitherto been done manually.

As has been described hereinbefore, the present invention offers the following advantages:

1. Where a number of samples are to be chemically analyzed in the usual manner, the volume of each sample that can be handled is limited to at most about 10 milliliters. Under the invention, by contrast, many samples can be handled in much larger unit volumes, say between 25 and 200 ml.

2. Means for various operations involved in chemical analyses, e.g., filtration, aeration, thermal distillation, thermal concentration, addition of reagent, agitation, pH adjustment, extraction, centrifugal separation, and dissolution, can be selectively incorporated in any part of a series of analytical means of an automatic analyzer. Moreover, sampling, pretreatment of samples, analysis and recording on instruments can be automatically controlled.

3. Of the chemical operations, those which usually take long periods of time, e.g., thermal distillation and thermostatic control, are performed efficiently with increased capacities because a plurality of treating units may be arranged in parallel with the rest of unit equipments.

4. Since mutual interference of analytical steps is eliminated and the units for the chemical analysis are designed for independent operations, the overall analytical procedure may be readily modified with ease.

What is claimed is:

1. An apparatus for successively transferring a plurality of different liquid samples to a plurality of different treatment stations in an analytical system comprising:

a first treatment unit including a first enclosed vessel, a sample inlet connected to an upper part of said first vessel and a first valve connected to said sample inlet;

a second treatment unit including a second enclosed vessel, a sample outlet connected to the lowermost portion of said second vessel and a second valve connected to said sample outlet;

first conduit means fluidly communicating the lowermost portion of said first vessel with an upper portion of said second vessel;

a third valve connected to said first conduit means;

sources of gasses at an increased pressure, reduced pressure and atmospheric pressure fluidly communicating with upper portions of said first and second vessesl through respective valves; and

control means for controlling the gas sources so that a pressure differential is maintained between the interiors of said first vessel and said second vessel for transferring a sample in said first vessel to said second vessel, said control means maintaining a pressure differential between the interiors of said first vessel and said second vessel after all of the sample is transferred from said first vessel to said second vessel so that sample deposited on the walls of said conduit means is blown away cleanly by a jet of gas, said control means thereafter causing another sample to be introduced into said first treatment station.

2. The apparatus of claim **1**, further comprising a third treatment unit including a third enclosed vessel; second conduit means fluidly communicating the lowermost portion of said first vessel with an upper portion of said third vessel; a fourth valve connected to said second conduit means; a sample outlet connected to the lowermost portion of said third vessel; a fifth valve connected to said sample outlet; said source of gas under pressure fluidly communicating with an upper portion of said first vessel through a valve.

3. A method for successively transferring a plurality of liquid samples to a plurality of different treatment stations in an analytical system, each treatment station including a hermetically sealed vessel, inlet means located in the upper portion of the vessel and outlet means located in the lowermost portion of the vessel, said method comprising transferring a first liquid sample to a first treatment station, establishing by means of a conduit a fluid communication between the outlet means of said first treatment station and the inlet means of a second treatment station, establishing a pressure differential between the vessel interiors of the first and second treatment stations so that said first sample is transferred by means of said pressure differential from said first treatment station to said second treatment station, and maintaining the pressure differential between said first and second treatment stations after all of said first sample has been transferred to said second treatment station so that portions of said first sample deposited on the walls of the vessel of said first treatment station and said conduit are blown away cleanly with a jet of gas.

4. The method of claim **3**, wherein the pressure differential is established by maintaining the pressure in said second treatment station at substantially 1 atmosphere and increasing the pressure in said first treatment station above 1 atmosphere.

5. The method of claim **3**, wherein the pressure differential is established by maintaining the pressure in said first treatment station about 1 atmosphere and reducing the pressure in said second treatment station below 1 atmosphere.

6. The method of claim **3**, further comprising transferring said first sample from said second treatment station to a third treatment station by means of a pressure differential established between said second treatment station and said third treatment station.

7. The method of claim **6**, wherein a second sample is transferred to said first treatment station prior to the exiting of said first sample from said analytical system.

8. The method of claim **3**, further comprising transferring a second sample to said first treatment station after the first sample has been removed therefrom, and transferring said second sample from said first treatment station to a third treatment station by establishing a fluid communication between the outlet means of said first treatment station and the inlet means of said third treatment station and establishing a pressure differential between the vessel interiors of the first and third treatment stations.

9. The method of claim 8, further comprising transferring said first sample from said second treatment station to a fourth treatment station arranged in series with respect to both said second treatment station and said third treatment station, and thereafter transferring said second sample from said third treatment station to said fourth treatment station.

10. The method of claim 9, wherein each sample is transferred from one of the treatment stations to a successive downstream treatment station by establishing a fluid communication between the outlet means of said one treatment station and the inlet means of said successive downstream treatment station and by establishing a pressure differential between the vessel interiors of said one treatment station and said successive downstream treatment station.

11. The method of claim 9, wherein the residence times of the samples in said second treatment station and said third treatment station are approximately twice the residence time of the samples in said first treatment station.

12. The method of claim 11, wherein successive samples passing out of said first treatment station are alternately transferred to said second treatment station and said third treatment station.

13. The method of claim 3, wherein said apparatus is arranged so that said treatment stations define at least one flow path for each sample, each sample travelling down its respective flow path in the forward direction only.

14. The method of claim 3, wherein said first sample is transferred from said first treatment station to said second treatment station by maintaining the pressure in said second treatment station approximately 1 atmosphere and increasing the pressure in said first treatment station to above 1 atmosphere, said process further comprising transferring a second sample from said first treatment station to said second treatment station by maintaining the pressure in said first treatment station about 1 atmosphere and decreasing the pressure in said second treatment station to below 1 atmosphere.

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