



EUROPEAN PATENT APPLICATION

Application number : **91311371.8**

Int. Cl.⁵ : **B01F 11/00**

Date of filing : **06.12.91**

Priority : **07.12.90 AU 3753/90**

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Date of publication of application :
17.06.92 Bulletin 92/25

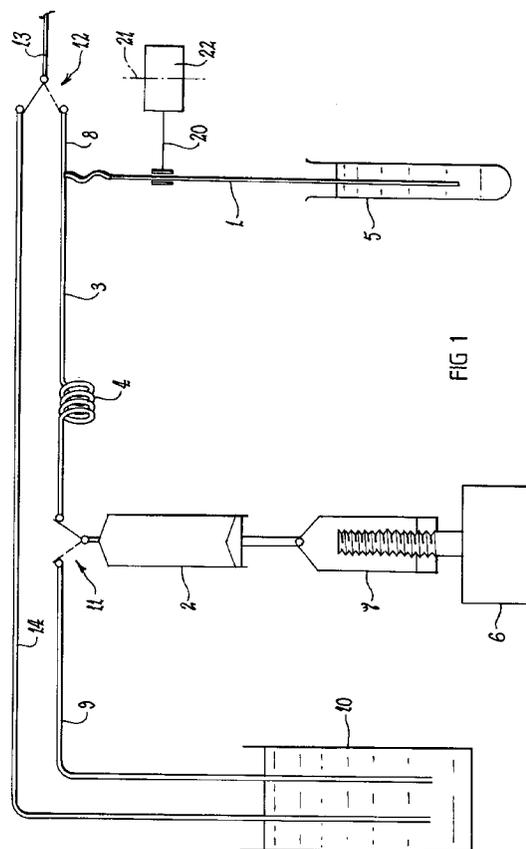
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Designated Contracting States :
DE FR GB IT

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Stirring means.

Apparatus for handling samples for use in chemical analysis, and particularly such analysis by spectroscopic means. The apparatus includes a probe (1) which is insertable into a vessel (5) containing a liquid sample, and is influenced by a pump (2) or other means so as to cause sample liquid to be drawn through the probe and directed to the spectrometer for analysis. Constituents of the sample may be introduced into the vessel through the probe. Drive means (22) is connected to the probe and is operable to cause the probe to move in the manner of a stirrer while submerged in the sample, and in that way the probe functions to thoroughly mix the constituents of the sample. The probe therefore has the dual functions of providing a conduit for the sample, or sample constituents, and providing a stirring device to thoroughly mix the sample.



This invention relates to the handling of liquids, and in particular relates to a method and means for mixing liquids. The invention is particularly concerned with means whereby two or more liquids are stirred so as to mix together. It will be convenient to hereinafter describe the invention with reference to stirring means for use in automated chemical analysis apparatus such as a spectrometer.

There is a demand for spectrometers and similar apparatus to be automated as fully as possible. It is desirable to avoid tedious manual operations in the analysis process because they can lead to errors or inaccuracies and are costly in terms of operator man-hours. Because the need to make up sample mixtures is a common process in chemical analysis, it is desirable that that process be automated to reduce the labor component of sample preparation and reduce the risk of random errors. It is particularly desirable to automate the actual mixing of the constituents which make up the sample mixture. Some constituents of a sample mixture tend to separate or stratify if the mixture is left to stand for any period of time, and in those cases it is desirable to stir the constituents of the mixture just prior to sampling so as to ensure that a truly representative sample is obtained in the sampling process.

One prior automated sample mixing device includes means for passing a gas stream through the body of constituents so as to promote mixing of those constituents. The individual constituents are mixed by the gas bubbling through the body of liquid for a suitable period of time. This approach, it has been found, has three main drawbacks. The first is that the gas is a foreign component which can react with one or more of the constituents of the mixture and thus affect the result of the analysis. This problem can be minimised but not eliminated by using pure and inert gases. The second problem is the additional costs and complexity of the gas plumbing required. The third problem is the cost and inconvenience of a high purity inert gas supply.

A second approach to the problem has been to repeatedly draw up a mixture into the sampling probe or syringe and then redispense it back into the sample container one or more times. The idea behind this approach is that turbulence caused by the fluid movement will result in stirring and consequent mixing. The approach is not satisfactory because of the time taken to repeatedly draw up and re-eject the liquid, and also because of the inadequate degree of uniformity which is achievable.

A third approach is to use a separate stirrer element which is caused to move by a rotating magnetic field. There are a number of problems with this approach and in particular it becomes impractical when there is a large number of sample containers in the system. By way of example, there may be up to 500 such containers in any one automatic sample pre-

paration device, and it would be expensive and cumbersome to provide a separate stirrer bar and associated rotating magnetic field for each such container. The alternative of moving a single stirrer from one container to another container is not acceptable because of the inherent problem of cross-contamination of liquid from different containers.

It is an object of the present invention to provide a method and apparatus for stirring liquids which is effective in operation and which at least substantially alleviates the aforementioned problems. A further object of the invention is to provide relatively inexpensive and uncomplicated stirring means which is adapted for use in an automated sampling system. A still further object of the invention is to provide an improved method of handling samples for analysis by spectroscopic means.

According to one aspect of the invention, there is provided liquid handling apparatus including a hollow probe through which liquid can be introduced into or withdrawn from a vessel, flow generating means connected to said probe and being operable to cause liquid to move through said probe, and drive means connected to said probe and being operable to cause movement of the probe relative to a vessel within which the probe is located so that the probe functions to stir the contents of that vessel.

The flow generating means may be of any suitable form. It may be a motor driven syringe, or any other type of pump, or it may be a device such as a nebulizer which is operable to draw liquid out of the vessel through the probe.

Apparatus according to the invention is particularly suited for use as part of an automated sampler of the kind used in spectroscopy. When used in such an application the apparatus has advantage in either of two use situations. In one situation the sample to be handled by the apparatus is composed of two or more liquids which are mixed together. In the other situation, the sample is composed of a body of liquid in which there is a dispersion of solid particulate material.

In the first mentioned situation, the flow generating means will usually be a pump of some form which may be operated to push one liquid constituent through the probe to enter into and mix with another liquid constituent, or which may be operated to withdraw the liquid sample from a vessel through the probe. In either case, the movement of the probe which results from operation of the drive means, causes the probe to function as a stirrer such that the sample is maintained as a homogeneous mixture of liquids.

In the second mentioned situation, the flow generating means may not be a pump as such. By way of example, it may be the nebulizer of a spectrometer to which the apparatus is connected, or it may be some other device which can influence the

contents of the sample vessel so that the sample is withdrawn through the probe. Pump means as referred to in relation to the first mentioned situation may be part of the total system, but operation of such pump means is not necessary for the sample to be withdrawn through the probe. Movement of the probe under the influence of the drive means again causes the probe to act as a stirrer, and it is desirable to stir the sample to ensure regular dispersion of the particulate material immediately before withdrawal of the sample through the probe.

A particular benefit of the invention in both of the described situations is that the device which acts as a stirrer - namely, the probe - is also part of the standard conduit system whereby material is moved into or out of a sample vessel.

According to a further aspect of the invention, there is provided a method of mixing liquids including the steps of, inserting a hollow probe into a liquid body contained in a vessel, introducing a liquid additive into the liquid body through said probe, and causing said probe to move relative to the vessel such as to stir the contents of the vessel and thereby cause the liquid additive to mix with the liquid body.

According to yet another aspect of the invention there is provided a method of handling a sample composed of a body of liquid and solid particulate material dispersed throughout that body, including the steps of introducing a hollow probe into a vessel containing said sample, causing said probe to move relative to the vessel and thereby stir the sample so that said particulate material is maintained in suspension in the liquid body, and removing said sample from the vessel through said probe.

Any suitable means may be used to cause movement of the probe such that it functions as an effective stirrer. For that purpose, the probe may be caused to vibrate or shake, or it may be caused to rotate or oscillate about its longitudinal axis or another axis which is laterally offset from the longitudinal axis. Furthermore, bodily lateral shifting of the probe may be combined with rotary or oscillatory motion. If the probe is rotated, the direction of that rotation may be reversed periodically. In any case, the probe may be also moved longitudinally in a reciprocating fashion to optimize its stirring influence throughout the depth of the liquid body and thereby avoid stratification of the sample. Such longitudinal movement may occur simultaneously with or in alternating fashion with the other movement of the probe.

It will be apparent that there is a wide range of possible movements of the probe which can cause the probe to act as a stirrer. The movement may be lateral, rotational or oscillatory, for example, or a combination of any two or more of those classes of movement. All possibilities are therefore to be understood as being encompassed by the expression "stirring movement", or any other similar expression as used

in the specification.

Apparatus according to the invention is particularly suited for use as part of an automatic sampler for a spectrometer. In such a case, probe positioning means will be operable to move the probe into and out of registry with a plurality of sample vessels. It is preferred that the aforementioned drive means is connected to or forms part of that positioning means.

Embodiments of the invention are described in detail in the following passages of the specification which refer to the accompanying drawings. The drawings, however, are merely illustrative of how the invention might be put into effect, so that the specific form and arrangement of the various features as shown is not to be understood as limiting on the invention.

In the drawings:

Figure 1 is a diagrammatic representation of the essential components of apparatus according to one embodiment of the invention.

Figure 2 is a semi-diagrammatic view showing the probe of Figure 1 connected to positioning and elevating means.

Figure 3 is a semi-diagrammatic view of sample analysis apparatus incorporating an embodiment of the invention.

Figure 1 shows one possible form of apparatus incorporating an embodiment of the invention, and which operates as part of an auto sampler for a spectrometer. The spectrometer can be of any kind including UV, atomic absorption, and inductively coupled plasma spectrometers.

The apparatus of Figure 1 includes a probe 1 which is in the form of an open ended tube made of a suitable material. It is preferred that the probe 1 is relatively rigid so that stirring movement of the probe does not result in one part - e. g., the free end - undergoing significantly greater excursion than any other part of the probe. That is, whatever the excursion of the probe 1, it is preferably substantially regular throughout the length of the probe so that the stirring effect of the probe is substantially constant throughout that length. In some applications however, such regular excursion may not be necessary, and it is possible that greater excursion of the probe at the tip end can be used to advantage in some situations.

In the particular arrangement shown in Figure 1, the probe 1 is connected to a pump 2 through conduit 3. It is preferred that a transitory storage facility for liquid is provided between the probe 1 and the pump 2. In the example shown, that facility is in the form of a tubular coil 4 formed of a suitable material such as of polytetrafluoroethylene (PTFE). The coil 4 is used to store any sample drawn into the conduit 3 from the sample vessel 5, and thereby avoid the sample coming into contact with the pump 2. In the illustrated case, the pump 2 is formed by a syringe having a body of glass construction which could react with some

samples.

The syringe pump 2 is driven by a motor 6 through a suitable drive connection 7, and is preferably operable in either of two modes. In one mode, the pump 2 is operated to produce negative pressure in the conduit 3 and the connected probe 1, and thereby causes sample to be withdrawn from the vessel 5 into the conduit 3. In the other mode of operation, the pump 2 is operated to produce positive pressure in the conduit 3 so as to cause the sample to be expelled through the outlet conduit 8.

In the particular example shown, the syringe pump 2 is connectable through a conduit 9 to a vessel 10 containing diluent, and that connection is controlled by a valve 11 which is preferably solenoid operated. In the position of the valve 11 as shown in Figure 1, the pump 2 is connected to the probe 1 and the outlet 8. In the alternative position shown in broken line, the valve 11 connects the pump 2 to the diluent vessel 10 and disconnects the pump 2 from the probe. Under those circumstances, the pump 2 can be operated to draw diluent into the syringe body for subsequent discharge into the sample vessel 5 when the valve 11 is moved back to the position shown in full line in Figure 1.

The outlet 8 is shown connectable to a spectrometer (not shown in Figure 1) through a valve 12, which may also be solenoid operated. The spectrometer connection is diagrammatically represented by the line 13. When the valve 12 is positioned as shown in Figure 1, the probe is isolated from the spectrometer and sample preparation can be carried out under that condition. The valve 12 however, connects the diluent vessel 10 to the spectrometer through the conduit 14, and that is for a purpose well known in the art and which has no bearing on the present invention.

When the valve 12 is adjusted to the position shown in broken line in Figure 1, the probe 1 is connected to the spectrometer so that sample analysis can be carried out in a known manner.

Figure 2 shows one possible arrangement for positioning the probe 1 in registry with the sample vessel 5, and for moving the probe 1 into and out of that vessel. Other arrangements could be adopted for the same purpose. In the arrangement shown, the probe 1 is mounted on the outer end of an articulated arm assembly 15, and the outer end of that assembly 15 is mounted on a post 16 such that it is rotatable about a primary axis 17. The post 16 is connected to elevating means 18 which is operable to raise and lower the arm assembly 15 as required. The assembly 15 comprises an inner or primary positioning arm 19, and an outer or secondary positioning arm 20. The two arms 19 and 20 are connected for relative movement about a secondary axis 21 which is substantially parallel to the primary axis 17.

It is a feature of the present invention that the probe 1 is subjected to the influence of drive means

22 such that it can be caused to undergo stirring movement as previously defined. In the particular arrangement shown, that drive means 22 includes a stepper motor or similar device which is connected to the arm 20 and is operable to cause that arm to oscillate about the axis 21. The extent and speed of the oscillation can be determined according to individual requirements. Furthermore, the extent and/or speed of oscillation may be varied during a stirring operation.

In practice, the drive means 22 may be operated to cause the probe 1 to undergo stirring movement immediately prior to the pump 2 being operated to direct sample into an associated spectrometer. Under some circumstances, it may be desirable to simultaneously operate the elevating means 18 so that the probe 1 is moved longitudinally while undergoing the stirring movement. Such longitudinal movement may serve to avoid stratification of the sample constituents and ensure that the consistency of the sample is regular throughout the depth of the vessel 5. The degree of such longitudinal movement is preferably regulated so that the tip of the probe does not leave the sample during stirring movement of the probe.

After the sample has been withdrawn from the vessel 5, the probe 1 may be lifted out of that vessel by appropriate operation of the elevating means 18. After that removal, the drive means 22 may be operated to cause the probe 1 to move and thereby promote separation of any droplets of sample which have remained resident on the outside of the probe 1. It may be desirable to effect any such droplet removal under conditions such that the droplets do not contaminate other samples, or sample constituents, in the vicinity of the probe 1.

Figure 3 shows sample analysis apparatus incorporating the invention. The main components of the apparatus shown are an auto-sampler 23, a spectrometer 24 and control means 25. The control means is typically a computer which is connected to both the sampler 23 and the spectrometer 24 so as to control and coordinate the operation of both of those instruments.

The sampler 23 as shown includes a plurality of racks 26, each of which can hold a plurality of vessels (e. g., tubes) for containing samples and constituents intended to form a sample mixture. In general there will be a large number of vessels into which the probe 1 can be inserted and these may contain for example, samples, standard solutions, and blank solutions, and some vessels may be empty so as to be used as the target for mixtures being prepared.

The arm assembly 15 is driven through a stepper motor (not shown) or other suitable drive mechanism such as to position the probe 1 in registry with a selected vessel in the racks 26. In that regard, the aforementioned drive mechanism will control the rotational position of the primary arm 19, whereas the drive motor 22 is operable to move the secondary arm

20 relative to the primary arm 19. The drive motor 22 may therefore subject the arm 20 to different movement according to whether it is being operated for stirring or probe positioning purposes.

A particular advantage of the arrangement described is that the probe positioning means in effect adopts the further function of driving the probe through stirring movement. Consequently, modification of existing apparatus to function in the manner required by the invention, is a relatively simple procedure.

Operation of the elevating means 18 enables the probe 1 to be removed from or located in a selected vessel.

It is usually important that the probe 1 not contain any liquid prior to it being inserted into a vessel, since that liquid may be shaken out of the probe 1 as it is vibrated. The possibility of the liquid becoming discharged in this manner can be eliminated by filling the probe 1 with air prior to commencing a mixing operation. The difference in specific weights between the air in the probe 1 and the liquid in the associated vessel prevents the air being mixed with the sample solution. The probe 1 may be filled with air by drawing up a volume of air equal to the internal volume of the probe whilst the end of the probe is open to the air.

It will be appreciated that, since the probe 1 will in any event need to move from one sample vessel to another in order to pick up the samples from each vessel, there will be no additional source of contamination from one sample container to the next as has been the problem with other prior sample stirring devices. It is relevant that the mixing device is in fact the probe which must in any event be moved from one vessel to the next, because as a consequence there is no additional source of contamination beyond that which would otherwise be the case. Thus, the mixing process adds no further carry over problem. Generally the apparatus will be programmed so that the operator has the option of automatically washing the probe in a rinse solution between each sample container.

Various alterations, modifications and/or additions may be introduced into the constructions and arrangements of parts previously described without departing from the spirit or ambit of the invention as defined by the appended claims.

Claims

1. Liquid handling apparatus including, a hollow probe through which liquid can be introduced into or withdrawn from a vessel, and flow generating means connected to said probe and being operable to cause liquid to move through said probe, characterised in that drive means (22) is connected to said probe (1) and is operable to cause movement of the probe (1) relative to a vessel (5) within which the probe (1) is located so that the probe (1) functions to stir the contents of that vessel (5).
2. Apparatus according to claim 1, wherein said drive means (22) includes a shaft which is caused to oscillate when said drive means (22) is operated, and a connecting arm (20) extends laterally from said shaft and interconnects the shaft and the probe (1) so that said probe movement occurs as a result of said shaft oscillation.
3. Apparatus according to claim 1 or 2, wherein said drive means (22) includes a stepper motor connected to said shaft and which is operable to cause said shaft oscillation.
4. Apparatus according to any preceding claim, wherein elevating means (18) is connected to said probe (1) and is operable to raise or lower the probe (1) so that the probe (1) can be lifted out of or inserted into a said vessel (5).
5. Apparatus according to claim 4, wherein said elevating means (18) is operable to raise and lower said probe (1) through a predetermined distance while said probe (1) is being moved by said drive means (22).
6. Apparatus according to any preceding claim, wherein positioning means (15) is connected to said probe (1) and is operable to move said probe (1) into and out of registry with a station at which said vessel (5) is located.
7. Apparatus according to claim 6, wherein said positioning means (15) is operable to move said probe (1) between a plurality of said stations, and a respective said vessel (5) is locatable at each said station.
8. Apparatus according to claim 6 when appended to claim 4, wherein said positioning means (15) is operable to move said probe (1) out of registry when said probe (1) is lifted out of a said vessel by said elevating means (18).
9. Apparatus according to any one of claims 6 to 8, wherein said positioning means (18) includes a primary arm which is rotatable about a primary axis located adjacent one end of the arm, a secondary arm is connected to the other end of said primary arm and is rotatable relative to that arm about a secondary axis which is substantially parallel to said primary axis, and said probe is connected to an end of said secondary arm remote from said primary arm.

10. Apparatus according to any preceding claim, wherein said flow generating means is in the form of a pump (2).
11. Apparatus according to claim 10, wherein said pump (2) includes a motor driven syringe. 5
12. Apparatus according to claim 10 or 11, wherein said pump (2) is operable in a first mode to produce positive pressure at an outlet thereof, and is operable in a second mode to produce negative pressure at said outlet. 10
13. Apparatus according to any one of claims 10 to 12, wherein transitory storage means (4) for liquid is included in the connection between said pump (2) and said probe (1). 15
14. Apparatus according to any preceding claim, wherein said probe (1) is relatively rigid so as to resist flexing during a said stirring operation. 20
15. A sampler for use with a spectrometer, including apparatus according to any preceding claim. 25
16. Sample analysis apparatus including a sampler according to claim 15, a spectrometer (24) connected to said sampler (23), and control means 25 connected to both said sampler (23) and said spectrometer (24) and controlling the operation thereof. 30
17. A method of mixing liquids including the steps of, inserting a hollow probe into a liquid body contained in a vessel, and introducing a liquid additive into the liquid body through said probe, characterised in that said probe (1) is caused to move relative to the vessel (5) such as to stir the contents of the vessel (5) and thereby cause the liquid additive to mix with the liquid body. 35 40
18. A method according to claim 17, wherein said probe movement includes lateral movement of the probe (1) relative to said vessel (5). 45
19. A method according to claim 17 or 18, wherein said probe movement includes longitudinal movement of said probe (1) relative to said vessel (5). 50
20. A method according to any one of claims 17 to 19, wherein said probe (1) forms part of sample analysis apparatus which includes a spectrometer (24), and at least part of the mixture comprising said liquid body and said liquid additive is withdrawn from said vessel (5) through said probe (1) and is delivered to said spectrometer (24). 55
21. A method according to claim 20, wherein said probe (1) is removed from said vessel (5) after said mixing is complete, and is then caused to vibrate to remove droplets of the mixture resident on the outside of said probe (1).
22. A method of handling a sample composed of a body of liquid and solid particulate material dispersed throughout that body, including the steps of introducing a hollow probe into a vessel containing said sample, and removing said sample from the vessel through said probe; characterised in that said probe (1) is caused to move relative to the vessel (5) and thereby stir the sample so that said particulate material is maintained in suspension in the liquid body.

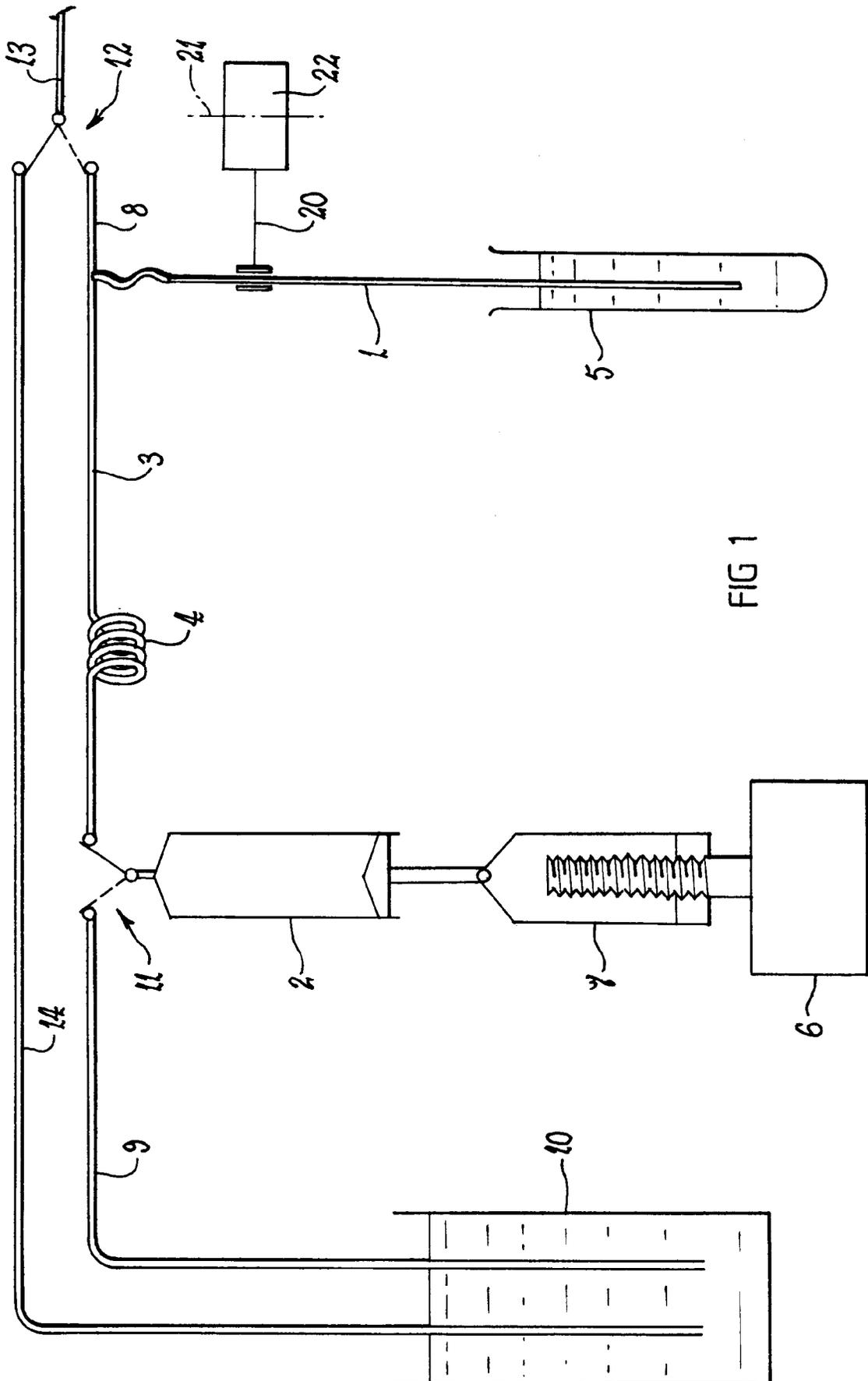


FIG 1

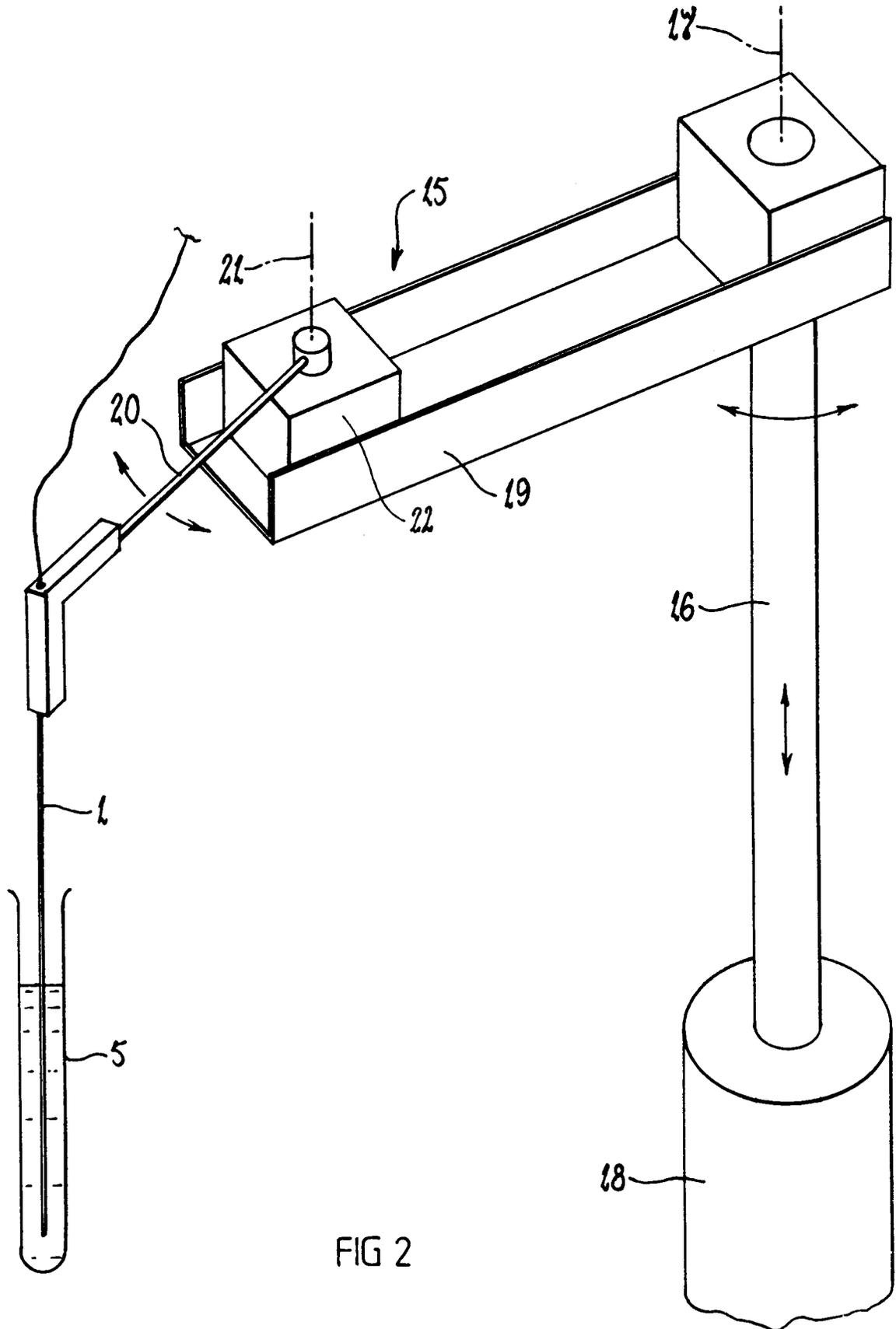


FIG 2

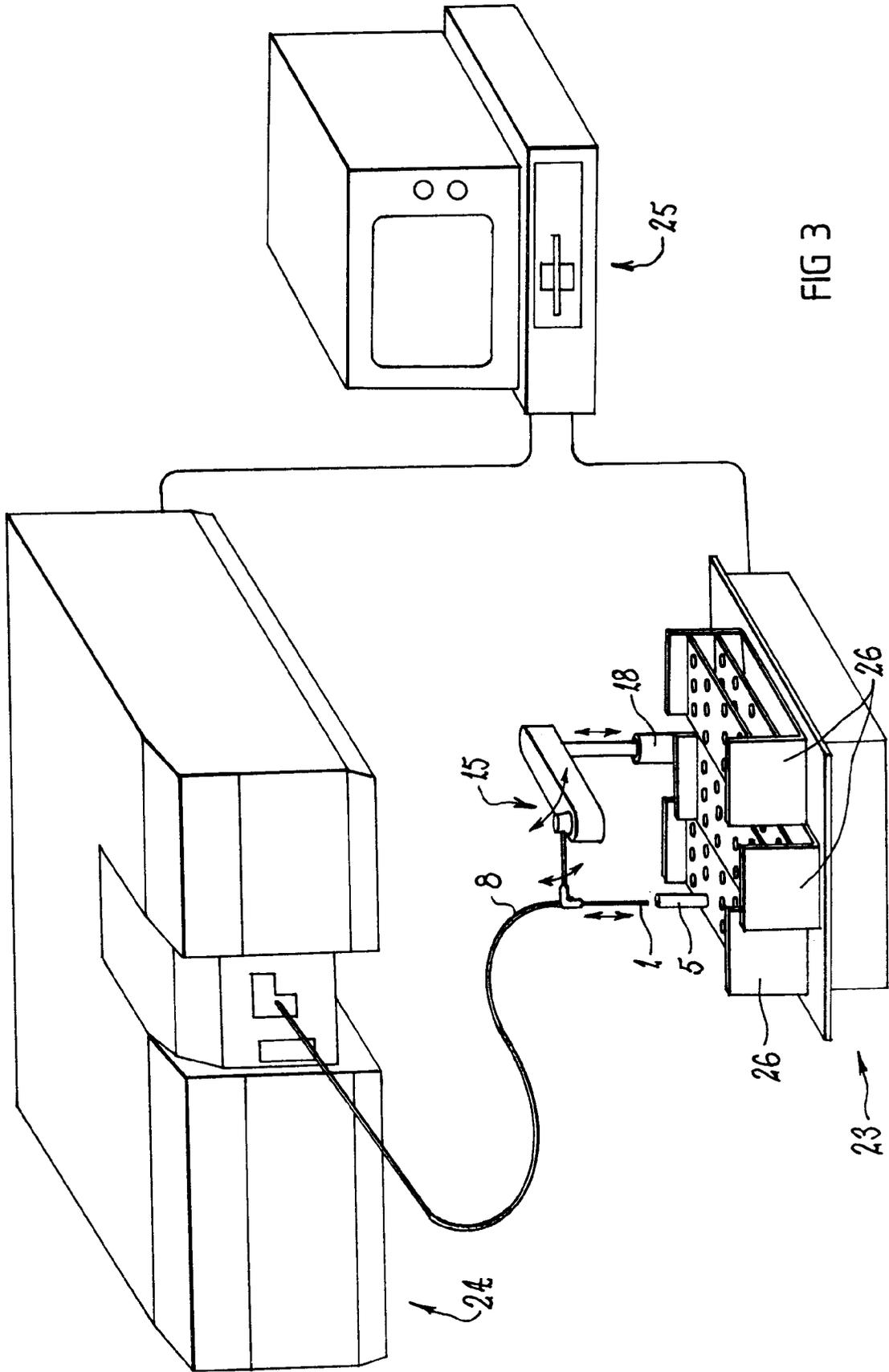


FIG 3



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 31 1371

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	US-A-4 341 736 (DRBAL) * column 6, line 46 - column 7, line 6; figures 2,5,6 *	1-22	B01F11/00
A	DE-A-2 651 903 (THOMAE)		
A	US-A-3 347 531 (STRONG)		
A	FR-A-2 469 953 (SEROTHERAPIE)		

The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			B01F G01N
Place of search THE HAGUE		Date of completion of the search 27 FEBRUARY 1992	Examiner PEETERS S.
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			

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