# United States Patent [19]

**Hach**

[11] **3,773,423**

[45] **Nov. 20, 1973**


[54] **AUTOMATIC ANALYZER**


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[73] Assignee: **Hach Chemical Company,** Ames, Iowa



[22] Filed: **Aug. 22, 1972**

[21] Appl. No.: **282,729**

[52] **U.S. Cl.**..... **356/181,** 23/253 R, 23/259, 73/244, 250/218, 259/89, 356/36, 356/196

[51] **Int. Cl.**..... **G01j 3/46,** G01n 1/00, G02f 3/04

[58] **Field of Search**..... 356/36, 180, 181, 356/182, 246, 196, 197; 250/218; 259/89; 23/253 R, 259; 73/244



[56] **References Cited**

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|---|---|---|---|
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*Primary Examiner*—David Schonberg
*Assistant Examiner*—V. P. McGraw
*Attorney*—C. Frederick Leydig et al.



[57] **ABSTRACT**

An automatic analyzer which combines a measured volume of a liquid sample with measured volumes of reagents in proper order, mixes and times the reacting liquids, and senses resulting liquid color by pouring the mixture through a colorimeter. The analyzer has only one major moving part — a driven center tube mounting measuring and feeding units, mixing units, and mixing and holding units, with the tube serving as a conduit between units and to the colorimeter. A measuring and feeding unit, upon rotation of the tube, dips a lifting passage into an underlying supply of fluid, lifts a quantity of the fluid by rotation of the passage, pours the liquid into an adjustable measuring pocket with the excess spilling back into the container, and finally pours the measured volume into the tube. The mixing unit receives liquid and spills it through a tortuous path upon rotation before returning the then mixed liquid to the tube. The mixing and holding unit spills liquid along a spiraling passage before returning it to the tube and thus holds the liquid for the number of tube revolutions equaling the coils in the spiral of the passage. The tube itself is slightly inclined so that liquid flows under gravity from unit to unit eventually to the colorimeter.


**11 Claims, 14 Drawing Figures**

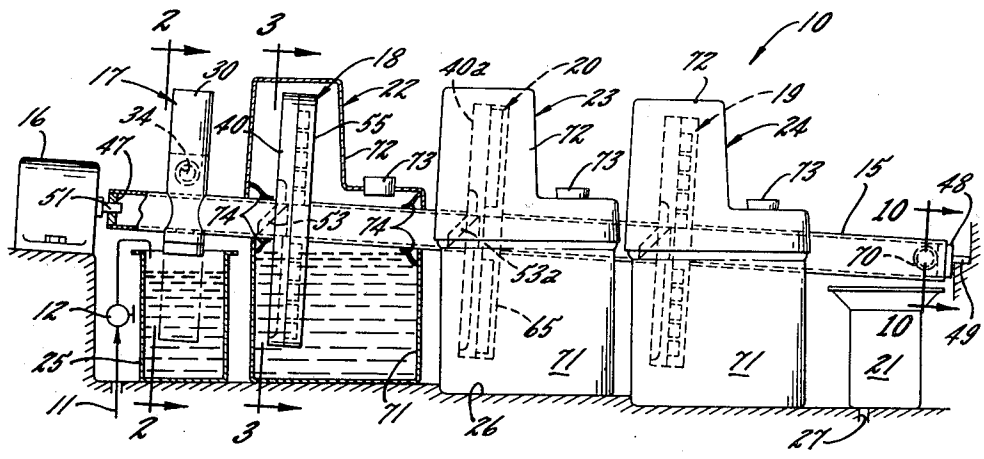
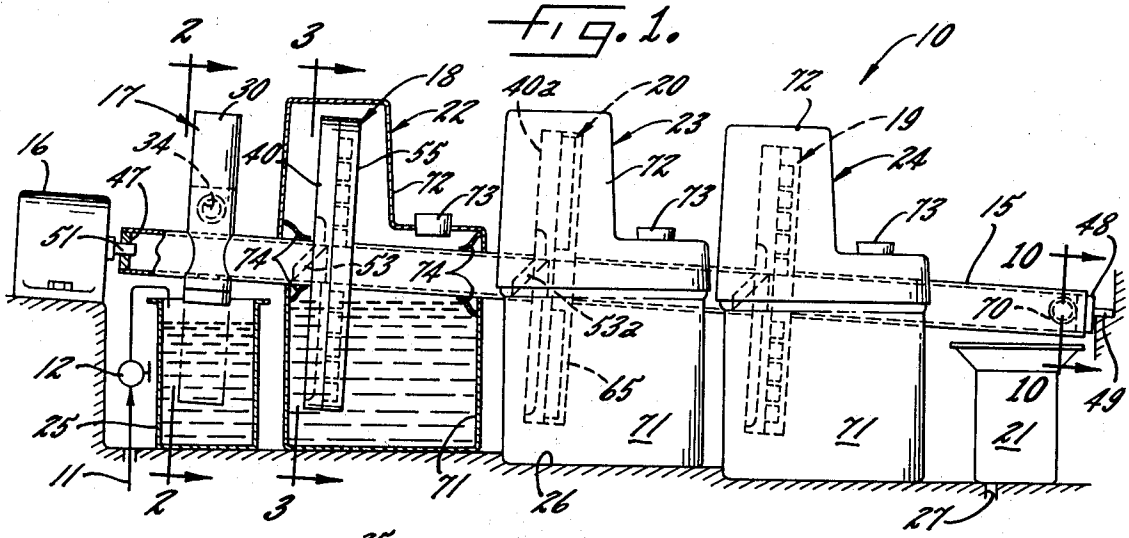


Fig. 1.



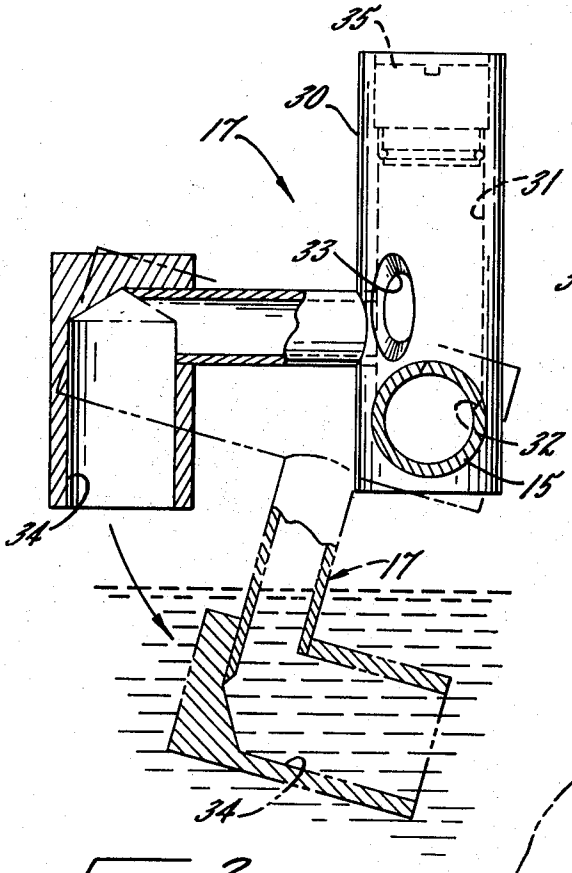




Fig. 2.

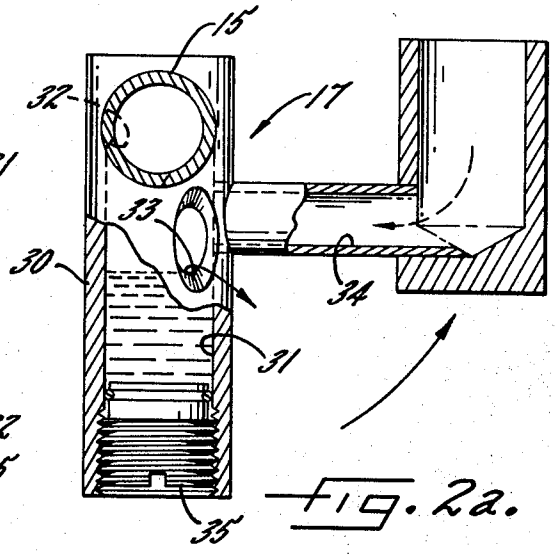



Fig. 2a.

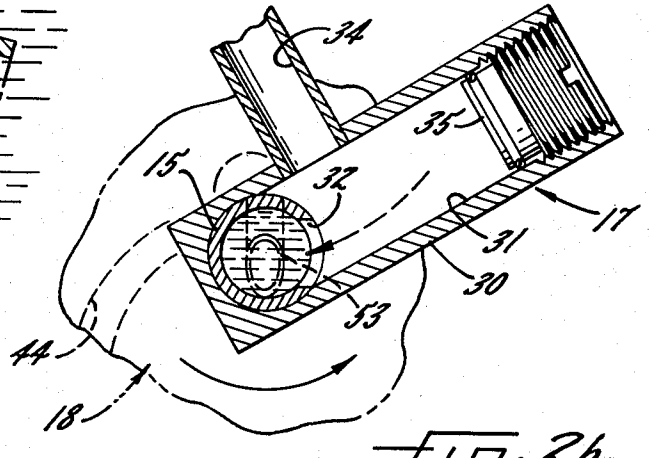



Fig. 2b.

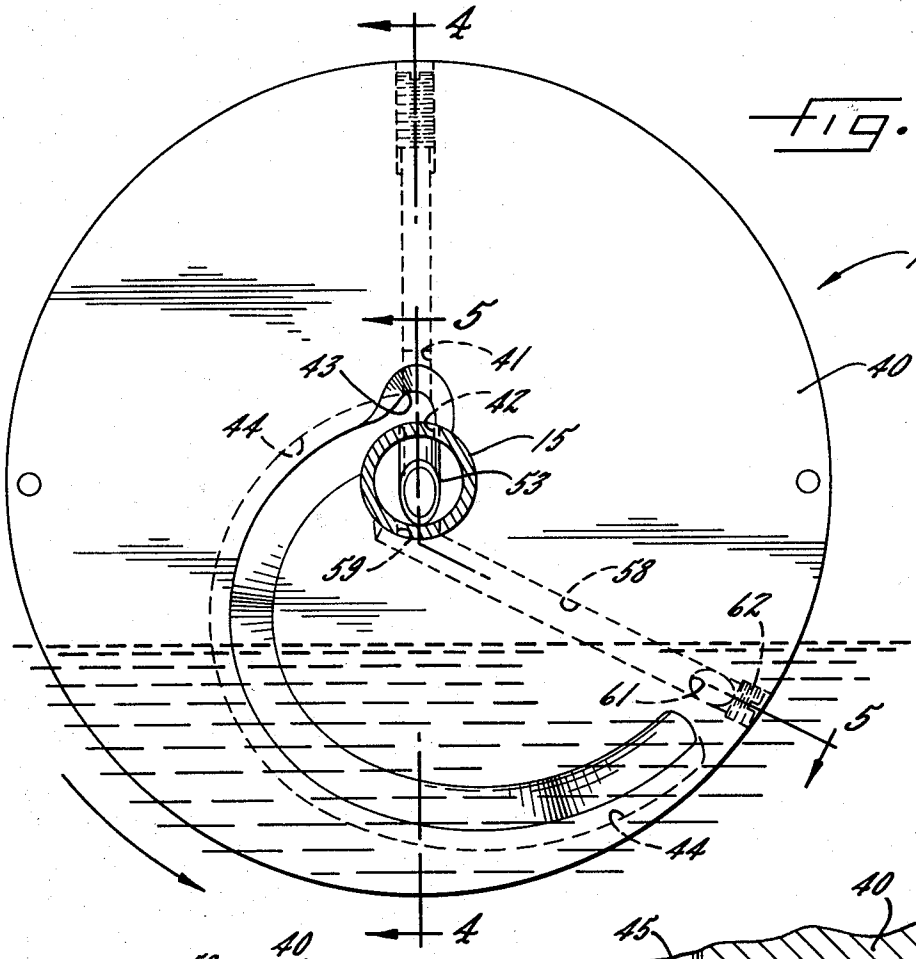



Fig. 3.

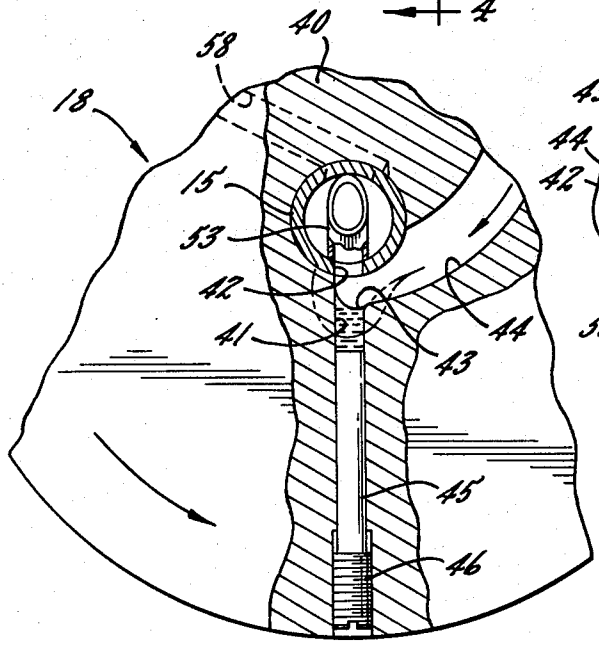



Fig. 3a.

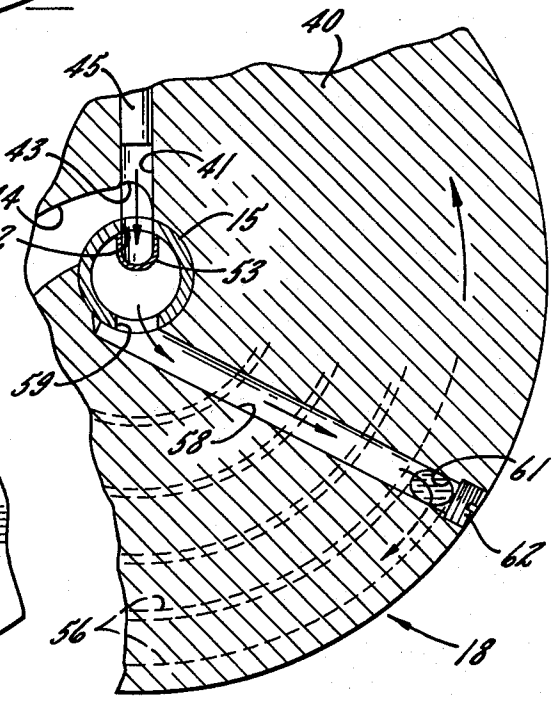



Fig. 3b.

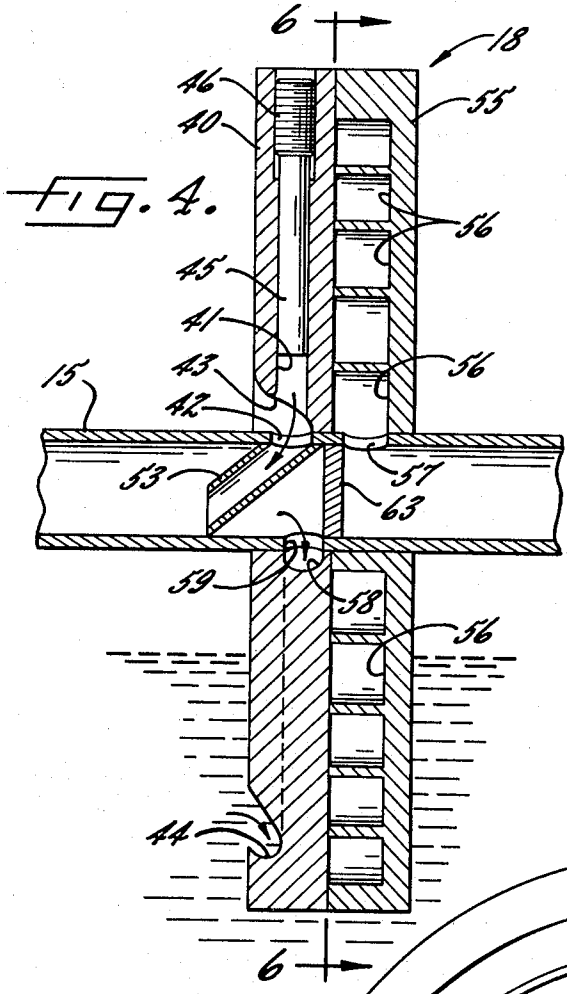



Fig. 4.

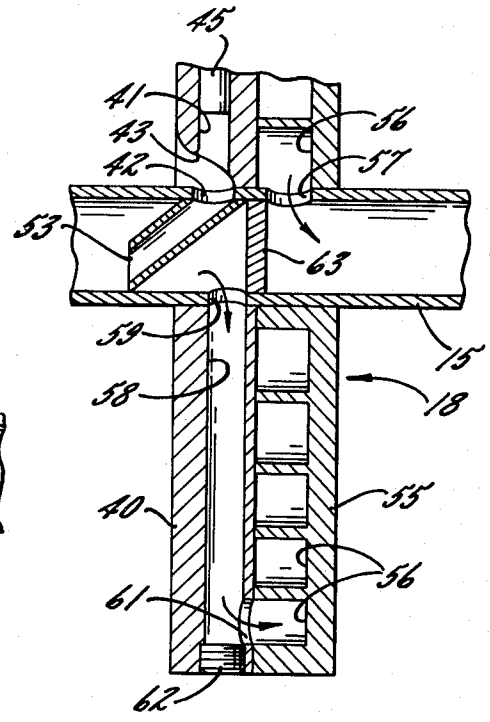



Fig. 5.

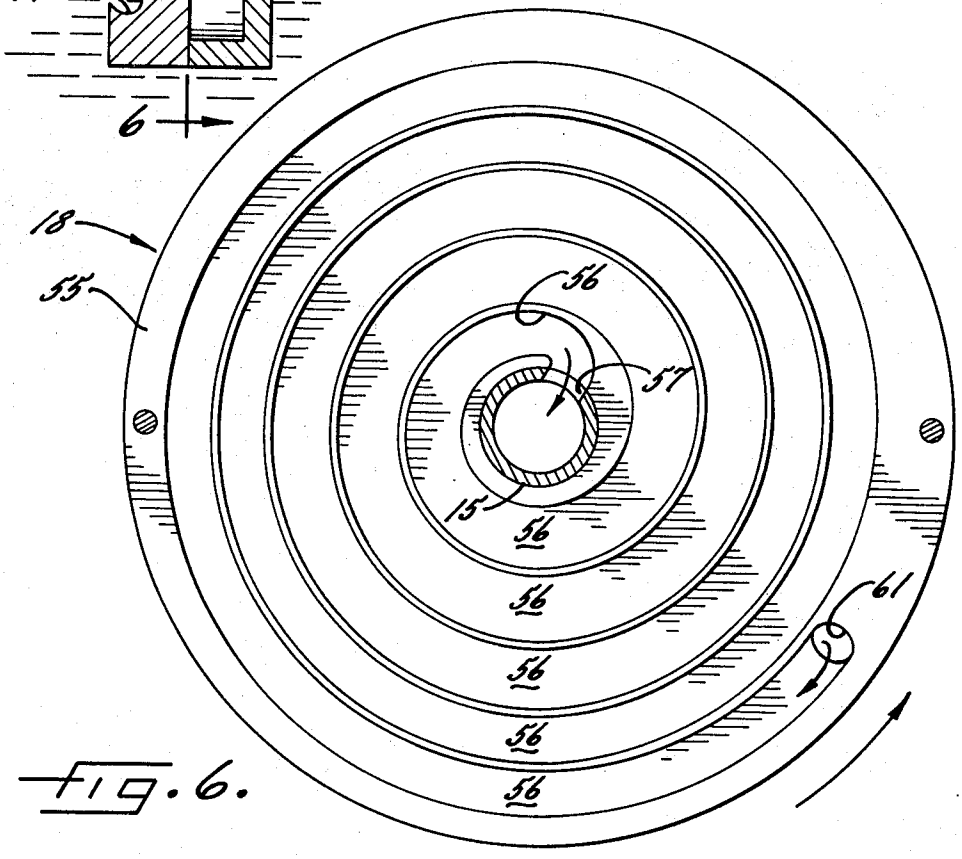



Fig. 6.

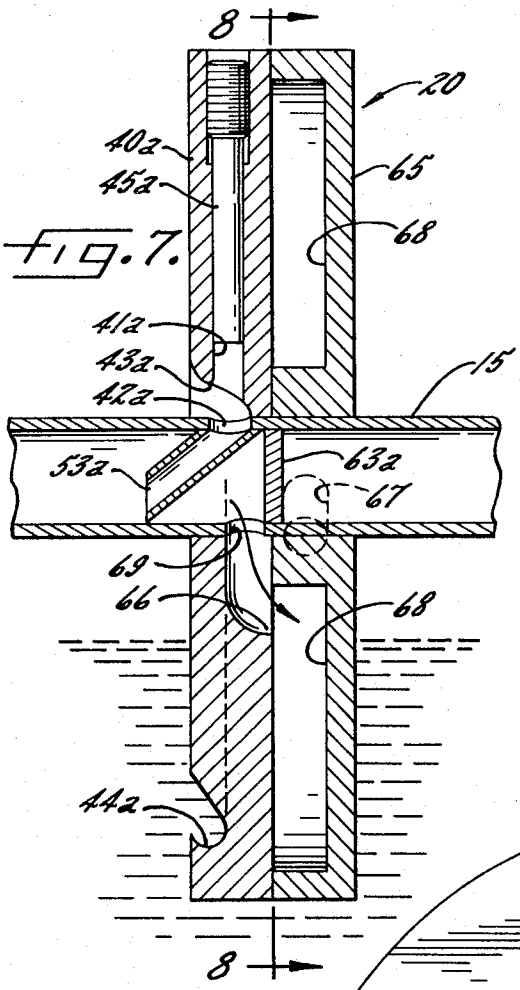



Fig. 7.

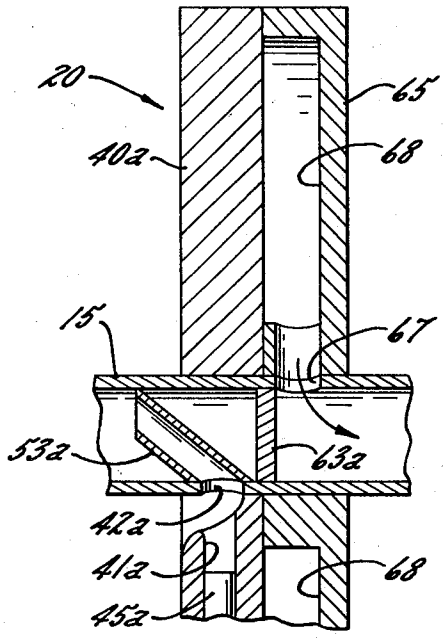



Fig. 9.

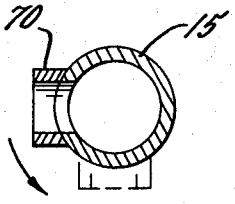



Fig. 10.

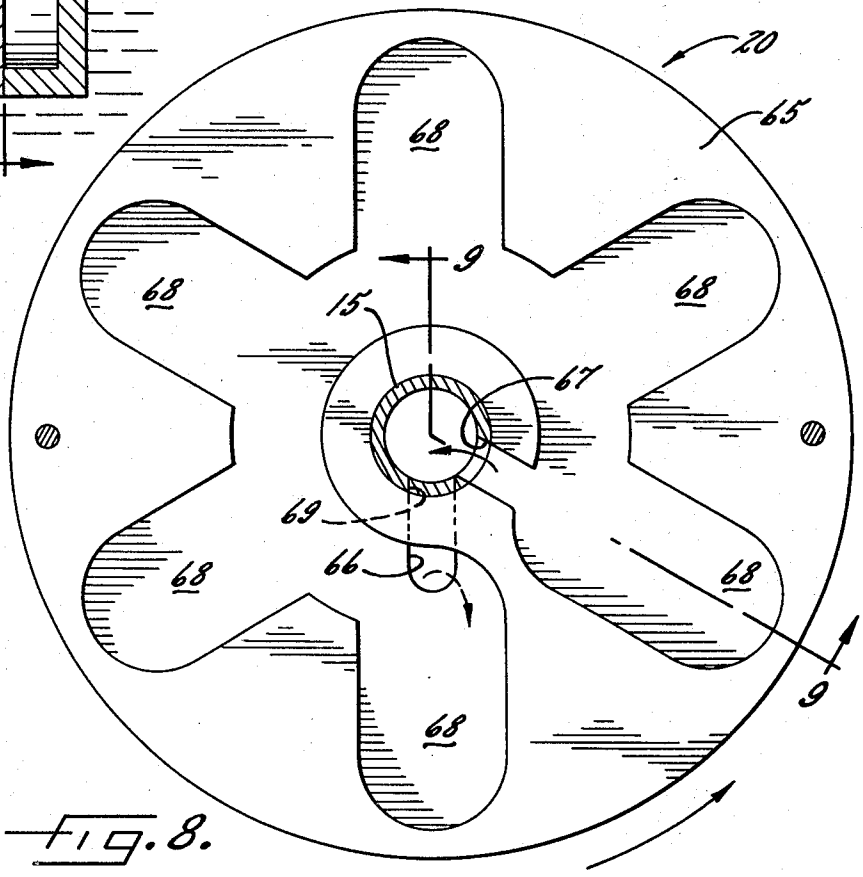



Fig. 8.

# AUTOMATIC ANALYZER

This invention relates generally to automatic chemical analyzers and more particularly concerns a continuous analyzer for colorimetrically monitoring a given characteristic of a flowing liquid sample over long periods of time.

Chemical analyzers which react to a color change in the sample under investigation upon the addition of one or more reagents normally depend for accuracy upon bringing together closely controlled amounts of reagent and sample. Such accurate metering has, in the past, been achieved with precision pumps or with capillary passages. However, pumps for this purpose are usually intricate and expensive, and capillary metering is subject to clogging problems and is dependent upon viscosity which, in turn, is a function of temperature which must therefore be controlled. Despite such problems, however, continuous automatic testing, particularly of water intended for any one of a variety of uses, has become an increasingly sought-after objective. Continuous monitoring of a flowing water supply for acidity, chlorine or fluoride content, hardness, and/or iron or other metallic concentrations, to name just a few characteristics, is of value in water treatment plants, power stations and other industrial and agricultural situations.

The general aim of the invention is to provide an improved analyzer that is economical to manufacture and operate, requiring virtually no maintenance, and which functions accurately and reliably without viscosity, i.e. temperature, control.

It is also an object of this invention to provide an analyzer as characterized above which is rugged and damage-resistant in that measuring, mixing, and aging or timing functions are carried out by a solid, single assembly, so that even relatively complex tests are automatically and repeatedly run with what is virtually a single moving part.

Another object is to provide an analyzer of the above described type which is made up of components that can be assembled in groups, arrangements and proportions to perform a wide variety of tests varying in number and quantity of reagents employed, and in timing or aging of the reaction steps.

A further object is to provide an analyzer as referred to above which, for accuracy and reliability, mechanically measures and mixes, and mechanically times or ages under the control of an ordinary synchronous motor.

Other objects and advantages of the invention will become apparent upon reading the following detailed description and upon reference to the drawings, in which:

FIG. 1 is an elevation, partially in section and partially diagrammatic, of an analyzer embodying the invention;

FIG. 2 is an enlarged fragmentary section taken approximately along the line 2—2 in FIG. 1;

FIGS. 2*a* and 2*b* are similar to FIG. 2 but show the parts in alternate operating positions;

FIG. 3 is an enlarged fragmentary section taken approximately along the line 3—3 in FIG. 1;

FIGS. 3*a* and 3*b* are fragmentary sections corresponding to FIG. 3 but showing the parts in alternate operating positions;



FIG. 4 is a fragmentary section taken approximately along the line 4—4 in FIG. 3;

FIG. 5 is a fragmentary section corresponding to FIG. 4 but showing the unit in an alternate operating position;

FIG. 6 is a section taken approximately along the line 6—6 in FIG. 4;

FIG. 7 is an enlarged fragmentary longitudinal section of another one of the units shown in FIG. 1;

FIG. 8 is a section taken approximately along the line 8—8 in FIG. 7;

FIG. 9 is a fragmentary section taken approximately along the line 9—9 in FIG. 8; and

FIG. 10 is an enlarged fragmentary section taken along the line 10—10 in FIG. 1.

While the invention will be described in connection with a preferred embodiment, it will be understood that I do not intend to limit the invention to that embodiment. On the contrary, I intend to cover all alternatives, modifications and equivalents as may be included within the spirit and scope of the invention as defined by the appended claims.

Turning to the drawing, there is shown an analyzer 10 embodying the invention and including a number of sub-components arranged to test water introduced through a line 11 at a rate determined by the setting of a valve 12. To illustrate the construction and operation of the invention, the analyzer 10 is set up to test for silica in the water sample using the "heteropoly blue method" in which a water sample is taken; ammonium molybdate in an amount equaling a 50th part of the water volume is added, mixed and held for 5 minutes; oxalic acid in an amount equaling a 50th part of the water sample volume is next added and mixed; and finally an amino acid solution in an amount equaling a 50th part of the water sample volume is added, mixed and held for another 5 minutes. A blue color developed in the solution is indicative of the presence of silica in the water sample. The analyzer 10 performs this test automatically and repeatedly on water flowing in from the line 11. It will be apparent, once the analyzer 10 is understood, that other arrangements of the analyzer components can be assembled to perform a wide variety of other test procedures involving measuring, mixing, holding and color checking of the sample and test reagents.

The components of the analyzer 10 include a center tube 15 rotatably driven by a synchronous motor 16, a sample measuring and feeding unit 17, a pair of reagent measuring, mixing and holding units 18 and 19, a reagent measuring and mixing unit 20, and a colorimeter 21 of the flow-through type. The units 17–20 are all fixed on the tube 15 for simultaneous rotation with the tube, and the reagent units 18–20 are enclosed in tanks 22, 23 and 24 containing, respectively, ammonium molybdate, oxalic acid and a solution of amino acid. The sample unit 17 also rotates on the tube 15 into a container 25 which receives water for testing from the line 11 through the valve 12. All of the components of the analyzer 10 are supported in a suitable frame 26, schematically indicated, which includes a discharge line 27 for draining the water and reagent solution from the analyzer following testing.

Considering first the measuring and feeding of the water sample, the unit 17 includes a body 30 having a liquid receiving core fitted tightly around the tube 15 which defines the axis about which the body 30 rotates.

The body **30** defines a measuring pocket **31** adjacent the core and having an open top leading to an opening **32** in the tube **15.** The pocket **31** also has a spill wall side whose edge **33** defines the top of the pocket **31** and thus the upper level of liquid in the pocket when the pocket is disposed beneath the axis of the tube **15** (see FIG. **2***a*).

The body **30** also includes a cup and tube defining a lifting passage **34** leading from the top of the pocket **31** to a point well spaced from the axis of the tube **15,** with the passage **34** having a bottom surface generally facing the axis of the tube so that rotation of the body on the tube with the tube axis generally parallel to the water in the container **25** will sequentially cause the bottom of the passage **34** to dip into the liquid, raise a quantity of liquid from the supply and pour the raised liquid quantity into the pocket **31** — the sequence illustrated in FIGS. **2** and **2***a*. The passage **34,** particularly the cup portion thereof, is proportioned to raise and pour into the pocket **31** a volume of liquid significantly greater than that retained by the pocket spill wall side. Preferably, the passage **34** is also sufficiently large in diameter that the liquid flows smoothly without bridging across the passage. The edge **33** of the spill wall is rounded and made hydrophilic so that liquid spills smoothly thereover with a minimum capillary effect from surface tension, and the edge **33** is also curved about the axis of the tube **15** so as to maintain a substantially fixed wall height through a range of rotation of the body **30** about that axis. In the illustrated embodiment, the hydrophilic property is imparted to the spill wall edge **33** by forming the body of polyvinyl chloride and slightly roughening that edge, as by sanding or chemical etching.

As a result of the spill wall configuration, a precise volume of liquid is retained in the pocket **31,** the excess spilling over the spill wall edge **33,** with the top of the retained liquid being almost exactly at the spill wall edge when the pocket is beneath the tube **15** (see FIG. **2***a*). To adjust this precisely measured volume, a member **35** is adjustably mounted, in this case by a threaded connection, for movement into and out of the pocket **31** so as to permit selective variation of the pocket volume. Once having been measured, the liquid content of the pocket **31** is poured into the tube **15** through the opening **32** upon continuing rotation of the tube (see FIG. **2***b*). In keeping with the analysis performed by the analyzer **10,** the unit **17** measures and feeds into the tube 5 ml. of water sample upon each tube revolution.

The measuring portions of the units **18–20** are structurally virtually alike and conceptually similar to the structure and operation of the unit **17.** Taking the unit **18** as representative, it includes a body **40** in the form of a disk having a liquid receiving core tightly fitted on the tube **15** which defines the axis about which the body **40** rotates (see also FIG. **3**). The body **40** defines a measuring pocket **41** adjacent the core and having an open top leading to an opening **42** in the tube **15** (see also FIG. **4**). The pocket **41** also has a spill wall side whose edge **43** defines the top of the pocket and thus the upper level of liquid in the pocket when the pocket is beneath the axis of the tube **15** (see FIG. **3***a*).

The body **40** is formed with a spiral groove in its outer face defining a lifting passage **44** leading from the top of the pocket **41** to a point well spaced from the axis of the tube **15,** with the passage **44** having a bottom surface generally facing the tube axis so that rotation of the body on the tube with the tube axis generally parallel to the surface of the reagent in the container **22** will sequentially cause the surface to dip into the liquid, raise a quantity of liquid from the supply, and pour the raised liquid quantity to the pocket **41** — the sequence shown in FIGS. **3, 4** and **3***a*. The passage **44** is proportioned to raise and pour into the pocket **41** a volume of reagent greater than that retained by the spill wall side **43.** Preferably, the groove forming the passage is sufficiently large that the liquid flows smoothly without bridging across. The edge **43** of the spill wall is rounded and made hydrophilic so that liquid spills smoothly thereover with a minumum capillary effect, and the edge **43** is also curved about the axis of the tube **15** to maintain a substantially fixed wall height through a range of body rotation about that axis. As was the case in the unit **17,** the hydrophilic property can preferably be imparted to the spill wall edge **43** by forming the body **40** of PVC and slightly roughening the edge **43** as by sanding or chemical etching.

As a result of the spill wall configuration, a precise volume of liquid is retained in the pocket **41** upon rotation of the tube **15,** the excess falling over the spill wall with the top of the liquid retained being almost exactly at the spill edge **43** when the pocket is beneath the tube **15** (see FIG. 3a). To adjust this measured volume, a member **45** is adjustably mounted, in this case by a threaded connection **46,** in the body **40** for movement into or out of the pocket **41** so as to permit selective variation of the pocket volume. Once measured, the fluid reagent in the pocket **41** is poured into the tube **15** through the opening **42** upon continuing rotation of the tube. Again, following through with the analysis performed by the analyzer **10,** the unit **18** measures and feeds into the tube 0.1 ml. of ammonium molybdate upon each tube revolution.

The center tube **15** is slightly inclined (see FIG. **1**) so that there is gravity flow of liquid from the high end, on which the sample unit **17** is fixed, to the low end, under which the colorimeter **21** is mounted. The ends of the tube are sealed by plugs **47** and **48,** the plug **48** carrying a pin **49** rotatably seated in the frame **26** so as to define a bearing and the plug **47** being formed to slide over an irregularly shaped output shaft **51** forming part of the motor **16.** The tube **15** is thus drivingly connected to the motor, although it can be easily removed from the analyzer frame for cleaning or other servicing.

The units **17** and **18** are angularly phased on the tube **15** so that the lower, or downstream, unit **18** pours its reagent into the tube **15** just ahead of the upstream water sample being received into the tube so that the sample, in effect, washes all of the reagent along. To insure that liquid in the center tube **15** will not spill back into the unit **18,** an introduction tube **53,**fitted into the center tube **15,** opens from the tube opening **42** to the opposite side of the center tube **15.** Thus, with the pocket **41** above the axis of the tube **15,** liquid spills through the opening **42** and through the introduction tube **53** directly into the path of the onflowing water sample at the bottom of the center tube. Further rotation of the center tube places the introduction tube opening above the then bottom of the center tube (see FIG. 3a) so that, in the event that there is some residual liquid in the tube, that liquid will not flow back into the pocket **41** to disturb the accuracy of the next reagent measurement.

It will be recalled that the unit **18** in the illustrated analyzer **10** is a measuring, mixing and holding unit intended to mix 0.1 ml. of ammonium molybdate with 5.0 ml. of water and to hold that mixture for 5 minutes. The mixing and holding portion of the unit **18** comprises a body **55** in the form of a disk having a liquid receiving core fitted tightly on the center tube **15** and a spiraling passage **56** leading from the periphery of the body **55** to an opening **57** in the tube **15.** Preferably, the passage **56** is milled into one face of the disk body **55** and is closed by the bodies **40, 55** being sealed to one another. The liquid solution is introduced to the outer end of the spiraling passage **56** through a generally radial passage **58** formed in the body **40** which connects a pair of openings **59** and **61** and is sealed by a plug **62** adjacent the opening **61.** A wall **63** within the tube **15** provides a fluid-tight block to fluid flow down the tube so that liquid introduced by the units **17** and **18** is forced into the opening **59** and through the passage **58** to the opening **61** and the spiraling passage **56** (see FIGS. **3***b* and **5**).

In the illustrated analyzer, the synchronous motor **16** rotates the tube **15,** and thus the units **17–20,** at the rate of one revolution per minute. Thus, the passage **56** is spiraled five times about the axis of the tube **15** with the result that five revolutions, and five minutes, are required to have fluid flow along the passage **56** from the opening **61** to the opening **57** which leads back into the center tube **15** on the downstream side of the blocking wall **63.**

To avoid having the liquid in the passage **56** bridge that passage and possibly develop a blocking bubble, the passage **56** is formed with an increasing cross section as the radius of the spiral increases (see FIG. **4**).

The measuring and mixing unit **20** includes measuring structure virtually identical to that found in the unit **18** and therefore it will be identified with the same reference numerals having the distinguishing suffix "*a*" added. Thus, the measuring portion of the unit **20** includes a body **40***a* defining a pocket **41***a* whose volume is adjusted by a member **45***a* and whose upper edge is defined by a spill wall edge **43***a*. The pocket is filled by a lifting passage **44***a*, and the pocket pours that reagent, upon continued rotation of the tube **15,** into an opening **42***a* in the tube and through an introduction tube **53***a*. The units **18** and **20** are angularly phased on the tube **15** so that, in the illustrated analyzer 10, 0.1 ml. of oxalic acid from the container **23** is poured into the center tube through the introduction tube **53***a* just as the 5.1 ml. of solution is poured from the body **55** so that the further reagent is washed along.

The mixing portion of the unit **20** includes a body **65** in the form of a disk having a liquid receiving core fitted tightly on the center tube **15,** a pair of openings **66** and **67** angularly spaced about the axis of the tube **15** which serve as inlet and outlet openings, and a tortuous serpentine path **68** defined by spoke-like recesses connecting the openings **66, 67.** The path **68** is preferably formed by milling the recesses into the face of the body **65** with the passage being closed by the bodies **65** and **40***a* being sealed to one another. A passage **69** is formed in the body **40***a* adjacent a wall **63***a* in the tube **15** (see FIG. **7**) which leads to and defines the opening **66.** As will be apparent, solution poured through the opening **66** will, upon rotation of the unit **20,** spill from one spoke of the recess into the next along the serpentine passage **68** so as to thoroughly mix the solution.

The unit **19,** a measuring, mixing and holding unit, is identical to the unit **18** and will not therefore be described in greater detail. In the illustrated analyzer **10,** the unit **19** functions to add 0.1 ml. of amino acid solution from the container **24** to the previously mixed solution already traveling down the tube **15.** Unit **19** is angularly phased with respect to the unit **20** so that the reagent is poured into the tube **15** from the unit **19** just as the solution flows down from the upstream unit **20.** Following the 5-minute holding and mixing cycle developed by the unit **19,** the solution is poured from that unit back into the tube **15,** from which it flows through a collar **70** (see FIG. **10**) into the colorimeter **21.** Appropriate filters and light sensors in the colorimeter respond to the development of the test color, blue in this case, so as to indicate the presence or absence of silica in the water sample under test.

It will be appreciated that the analyzer **10** is a continuously cycling apparatus, and that a number of samples will be simultaneously in the process of passing through the various units **17–20.** Once all of the units are, in effect, full then successive checks will be made every revolution of the tube **15,** i.e., every minute. Upon start-up, it is desirable to allow several samples to pass completely through the analyzer **10** so that proportioning of the reagents can become stabilized. It will be noted that, for example, the unit **20** will deposit about six measured amounts of the reagent associated with that unit in the tube **15** before the first water sample reaches that unit so that, until a few samples have passed through the entire analyzer, the possibility of inaccurate proportioning in the solution exists.

The tanks **22–24** are preferably formed in two pieces, having spacious bottom portions **71** to contain a long-lasting quantity of reagent, and tops **72** which enclose the respective units as well as the tank bottoms so as to avoid contamination. Filler holes and plugs **73** permit convenient replenishing of the reagent contents, and the openings through which the center tube **15** passes are preferably closed by annular flap valves **74.**

Those skilled in this art will appreciate that the analyzer **10** can be manufactured quite economically, particularly when it is compared with those analyzers requiring expensive pumps and valving. The analyzer **10** also operates accurately and reliably while requiring virtually no maintenance. The analyzer is quite temperature stable since there are no critical flow rates which might be affected by a change in the viscosity of the liquids being handled.

It can also be seen that the components of the analyzer **10** are quite rugged and, indeed, there is virtually but a single moving part which can be quite solidly made. This rugged, simple construction has been achieved despite the relatively sophisticated nature of the analysis being carried out.

It has already been pointed out that a wide variety of tests can be set up by arranging the components of the analyzer **10** so as to produce a desired sequence of measuring, mixing and holding virtually any number of reagents with the sample under investigation.

I claim as my invention:

**1.** A liquid measuring and feeding unit for automatic analyzers comprising a body having a liquid receiving core at an axis about which the body rotates, said body defining a measuring pocket adjacent said core and having an open top open to the core, said pocket also having a spill wall side for defining the top of the

pocket and thus the upper level of liquid in the pocket when the pocket is beneath said axis, said body also defining a lifting passage leading from the top of said pocket to a point well spaced from said axis, said passage including a bottom surface generally facing said axis so that rotation of the body thereon with the axis generally parallel to a supply of liquid will sequentially cause the surface to dip into the liquid, raise a quantity of liquid from said supply and pour the raised liquid quantity into said pocket, and said passage being proportioned to raise and pour into said pocket a volume of liquid greater than that retained by said spill wall side.

**2.** The unit of claim **1** in which the edge of said spill wall adjacent said core is rounded and hydrophilic so that liquid spills smoothly thereover with minimum capillary effect, and said edge is curved about said axis to maintain a substantially fixed wall height through a range of body rotation about said axis.

**3.** The unit of claim **1** including, in combination, a member adjustably mounted in said body for movement into or out of said pocket so as to selectively vary the volume of the pocket.

**4.** The unit of claim **1** in which said passage has a cross section sufficiently large so as not to be bridged by liquid being conveyed to said pocket.

**5.** A liquid holding and mixing unit for automatic analyzers comprising a body having a liquid receiving core and an axis about which the body rotates, said body defining a spiraling passage leading from the body periphery to an opening at said core, and said body also having a liquid introduction opening for allowing liquid to flow into the peripheral end of said passage whereby the liquid will flow into said core after a predetermined number of body revolutions about said axis.

**6.** The combination of claim **5** in which said spiraling passage is formed with an increasing cross section as the radius of the spiral decreases so as to avoid having the liquid volume bridge the passage.

**7.** A liquid mixing unit for automatic analyzers comprising a body having a liquid receiving core at an axis about which the body rotates, said body having a pair of openings angularly spaced about said axis for serving as inlet and outlet openings, and said body also having a tortuous serpentine path connecting said pair of openings so that, upon rotation of said body, liquid introduced through one opening is mixing by spilling along said passage before exiting through the other opening.

**8.** An analyzer comprising, in combination, a frame, a center tube mounted for rotation in said frame and being disposed at an angle with respect to the horizontal so as to have a high end and a low end, a colorimeter in said frame having a liquid receiving passage beneath the lower end of said tube, a plurality of liquid containers in said frame spaced beneath said tube, a plurality of liquid measuring and feeding units mounted on said tube for rotation into respective ones of said containers upon rotation of the tube, and means in said frame for rotating said tube so that said units lift liquid from said containers, spill back all but a measured volume and pour that volume into said tube, said tube having an opening above said colorimeter so that the total of said measured liquid volumes flows into the colorimeter.

**9.** The combination of claim **8** including an introduction tube fitted into said center tube and opening from one of said units to the opposite side of the center tube on which the unit is mounted so that liquid in the center tube will not spill back into said one unit.

**10.** The combination of claim **8** including a mixing unit mounted on said center tube at a lower tube portion than where a pair of said measuring and feeding units are mounted, said mixing unit being open to the tube for receiving liquid and having a path for spilling the liquid through a tortuous path upon rotation of the center tube before allowing the liquid to flow to said colorimeter.

**11.** The combination of claim **8** including a mixing and holding unit mounted on said center tube at a lower tube portion than where a pair of said measuring and feeding units are mounted, said mixing and holding unit being open to the tube for receiving liquid and having a path for spilling the liquid through a spiraling path upon rotation of the center tube through a predetermined number of revolutions before allowing the liquid to flow to said colorimeter.

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