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Description

This invention relates generally to on-line process instruments or systems for monitoring the composition of liquid media in a process plant. More particularly, the invention consists of a chemical analyzer device for determination of a characteristic of a liquid process stream by wet chemical analysis to enable control of the process, said device comprising a sample cell for collection of a predetermined volume of sample to be analyzed and means for performing wet chemical analysis on the sample by progressively adding to the sample a measured flow of liquid reagent to cause progressive reaction with sample while sensing a parameter of the liquid sample as the reaction with the reagent proceeds.

Process instruments are used to perform chemical analyses in multi-stage processes to ensure product quality is maintained and to save energy and raw material. These benefits result from operating within closer tolerances and from the quicker corrective response to inefficient conditions. Process instrument hardware for evaluation of liquid media is typically divided into two general categories based, in part, on whether the sampling of an accurate volume of liquid is important in the measurement process and whether the sample is conditioned. Instruments directly in the process stream, i.e., "in-line", do not condition the sample, nor do they need an accurate volume of sample for testing since they are always subject to the same flow cross-section of liquid. The information supplied by these instruments is continuous, but precision and accuracy are low. Examples of such types of instruments are pH electrodes, ion-selective electrodes, oxidation-reduction potential electrodes, and specific gravity and conductivity instruments.

The second category of instruments consists typically of laboratory-type equipment ruggedized for industrial application. In these special process instruments, often referred to as "on-line", the liquid sample is removed from the process stream, conditioned to standard test conditions by reducing pressure and temperature, filtered to remove contaminants and solids, transferred as a known volume to a second cell in the instrument and reacted with chemicals prior to measurement of a specific component or characteristic. The data from this type of instrument is discrete, being obtained at intervals of from one to twenty minutes, with precision and accuracy comparable to that obtained in a chemical laboratory. The need to make operation automatic and the hardware particularly rugged are the significant differences from instruments designed solely for laboratory use, but these instruments still require a sophisticated operator in order to obtain proper test results. Examples of this type of instrument are titrators and colourimeters. Titrators and their use in chemical determinations are described generally in "Process Instruments and Con-

trols Handbook", Third Edition (1985), Editor-in-Chief, Douglas M. Conkline at p.6.98 et seq. FR-A-2506 453 describes a device for the determination of a quantity of liquid using, amongst other means, a siphon/drain conduit.

Objectives of the present invention include : to provide an on-line instrument capable of capturing a liquid sample from a process stream, for measurement of a characteristic with high repeatability ; to provide an on-line instrument capable of precision, accuracy and reliability without complex interconnected assemblies and delicate precision parts typical of laboratory-type on line instruments ; and to provide an on-line instrument capable of reliable operation while interfacing with process environments with difficult conditions of temperature, chemical composition or contamination.

According to the invention it is realized that increase in precision of repeatedly capturing a small volume of liquid can be achieved by employing a downwardly directed drain inlet precisely located at the desired liquid level of a chamber and applying pressure conditions to cause flow of excess liquid upwardly from the captured volume until the liquid level reaches the inlet and entry of air disrupts the liquid-transfer effect. It is found that, by establishing the level in this way, the wettability of the substance defining the inlet does not substantially affect the accuracy of the level achieved, hence an unusually accurate volume can be repeatedly achieved, despite differences in the character of the liquid from one sample to another. In the case of a 10 ml sample, accuracies of 1% repeatability can be achieved, in which 1% may represent only one small drop.

According to the invention there is provided a chemical analyser device as mentioned before, characterised by the further inclusion in said device of

a siphon cell having a closed volume that serves as said sample cell,
 sample inlet conduit means for delivery of a flow of process liquid into said cell,
 vent means for flow of vent gas into said cell,
 a siphon/drain conduit means having an inlet and an outlet, said conduit means having a first end defining said inlet downwardly disposed within the volume of said cell with said inlet at a predetermined level spaced from the bottom and top of said cell, the partial volume of said cell below said inlet sized to define a predetermined volume of sample to be analyzed, and the partial volume of said cell above the level of the inlet enabling additional liquid to be introduced into said cell during the operation of said device, and said siphon/drain conduit means having a second end defining said outlet downwardly disposed outside said cell with said outlet disposed at a predetermined distance below said inlet,

means for causing flow of process liquid through said sample inlet conduit means into said cell to collect a sample in said cell and establish a level of liquid in said cell above the inlet of said siphon/drain conduit means,

means for establishing flow of excess process liquid out of said cell volume through said siphon/drain conduit means, to cause said siphon/drain conduit means to fill,

means for ceasing flow through said sample inlet conduit means,

means for creating siphoning flow through said siphon/drain conduit means to drain excess process liquid from said cell in the manner that siphoning flow ceases automatically when the level of process liquid in said cell volume reaches the level of said inlet of said siphon/drain conduit means, thereby to define, in said cell, a sample of predetermined repeatable volume, and

said means for performing wet chemical analysis constructed to perform said analysis in situ within said siphon cell by titrating techniques, comprising means for progressively delivering into said siphon cell a measured flow of liquid reagent to cause progressive reaction with sample in situ in said cell, and means for sensing in situ in said siphon cell a parameter of the liquid sample as the reaction with the reagent proceeds.

In a preferred embodiment said means for causing flow of process liquid through said sample inlet conduit means into said cell may be constructed and positioned so that, after collecting a sample in said cell and establishing a level of liquid in said cell above the inlet of said siphon/drain conduit means, by continued flow of liquid into said cell volume via said sample inlet conduit means a flow of excess process liquid out of said cell volume through said siphon/drain conduit means is established to cause said siphon/drain conduit means to fill.

Moreover, said means for creating siphoning flow may comprise means for continuing flow of liquid to establish flow of excess process liquid out of said cell volume through said siphon/drain conduit means. Also, said means for creating siphoning flow may comprise means for applying suction to said outlet.

The means for sensing may comprise an ion sensing probe and/or a temperature sensing probe and/or a conductivity sensing probe. The chemical analyser may further comprise a stir bar positioned within said cell.

According to another aspect of the invention, there is provided a method for determination of a characteristic of a liquid process stream by wet chemical analysis to enable control of said process, comprising the steps of (a) defining a predetermined volume of sample to be analyzed and (b) performing said wet chemical analysis on said sample by progressively adding to said sample a measured flow of

liquid reagent to cause progressive reaction with said sample while sensing a parameter of the liquid sample as said reaction with said reagent proceeds, characterised in that said step (a) of defining said volume of sample to be analyzed comprises providing a siphon cell having a closed volume, sample inlet conduit means for delivery of a flow of process liquid into said cell, vent means for flow of vent gas into said cell, and a siphon/drain conduit means having an inlet and an outlet, said conduit means having a first end defining said inlet downwardly disposed within the volume of said cell with said inlet at a predetermined level spaced from the bottom and top of said cell, the partial volume of said cell below said inlet sized to define a predetermined volume of sample to be analyzed, and the partial volume of said cell above the level of the inlet enabling additional liquid to be introduced into said cell in the performance of said method, and said conduit means having a second end defining said outlet downwardly disposed outside said cell with said outlet disposed at a predetermined distance below said inlet,

causing a flow of process liquid through said sample inlet conduit means into said cell to collect a sample in said cell and establish a level of liquid in said cell above the inlet of said siphon/drain conduit means,

continuing to cause flow of said liquid into said volume via said sample inlet conduit means to establish flow of excess process liquid out of said cell volume through said drain/siphon conduit means, filling said drain/siphon conduit,

after said drain/siphon conduit is filled, ceasing all flow through said sample inlet conduit means and creating siphoning flow through said siphon/drain conduit means to drain excess process liquid from said cell, said siphoning flow ceasing automatically when the level of process liquid in said cell volume reaches the level of said inlet of said siphon/drain conduit, thereby defining, in said cell, a sample of predetermined repeatable volume, and conducting said step (b) of performing said wet chemical analysis in situ within said siphon cell comprising, by titrating techniques, progressively delivering into said siphon cell a measured flow of liquid reagent to cause progressive reaction with said sample in situ in said cell, while sensing in situ in said siphon cell a parameter of the liquid sample as said reaction with said reagent proceeds.

The sample may be taken directly from the liquid process stream of an industrial plant, the pressure of said stream serving to produce said flow of process liquid through said inlet conduit means into said cell and into said drain/siphon conduit.

The present invention is particularly directed to an improved arrangement of hardware for removing a sample from the process stream, capturing a precise repeatable volume of the sample liquid and allowing

a controlled chemical reaction to occur involving the sample in the same hardware prior to measurements being made on the reacted sample. The design of the device to be used according to the present invention eliminates the need for: (1) accurate and precise sample metering pumps; or (2) valving arrangements or other complex fluid handling equipment to capture a precise volume of the sample. The invention uses a very simple arrangement of a partially pressurized cell and gravity activated siphon and so is a relatively simple system lacking parts which are prone to failure when in contact with a sample stream.

In preferred practice, the parts that are included in the instrument of the present invention include: (1) means for on-line sampling of the process stream in a volumetrically precise and repeatable manner at predetermined intervals; (2) means for introducing reagents to the reaction cell to condition the sample; (3) means for introducing a titrant relevant to the measurement to be made to the reaction cell; and (4) means for introducing a calibrant into the reaction cell in place of the sample in a volumetrically precise and repeatable manner such that it can be analyzed to correct for changes in the measuring instrument and this assembly.

For a better understanding of the invention and to show how the same can be carried into effect, reference will now be made, by way of example only, to the accompanying drawings, wherein:

Figs. 1a to 1c are elevations of sides at right angles to each other viewed in turn of an assembled sampling reaction cell/manifold for a device embodying this invention, with all parts in place; Fig. 2 is an exploded view of the sampling/reaction cell/manifold combination of Figs. 1a to 1c with all relevant parts shown;

Fig. 3 is a side elevation, taken in section, of the assembled sampling reaction cell/manifold of the invention; and

Figs. 3a through 3h are sequential side elevations, taken in section, of the sample capture process of the invention.

Referring now to the drawings, Figs. 1a to 1c show an on-line wet chemical analyzer consisting of a complete sampling/reaction assembly as it would exist in an on-line process installation. The attachment of plumbing lines and tubing to the plurality of connections for introduction of fluids would be all that would be needed to make it ready for use. As shown, a manifold block 1 is the junction point for a plurality of connections for flows of fluid including sample inlet connection 7, siphon/waste connection 6, air vent connection 5, titrant connection 14, standard or calibrant connection 12, and reagent connection 13. Secured to the manifold block through the use of clamp knobs 4 and clamp rods 8 is a sampling reaction cell 2. A plurality of orifices in the manifold block 1 is provided for installing ion sensing probes 9, temperature

sensing probes 10, and conductivity sensing probes 11. A clamp plate 3 is used to compress seals 19 (see Fig. 2) around the previously described probes 9, 10 and 11 to prevent leakage of liquids or air.

In Fig. 2, the remaining parts of the assembly are pictured, including the aforementioned seals 19, additional seals 16, to prevent leakage of liquids or air between the cell 2 and manifold 1, a magnetic stir bar 15 to agitate the captured sample during reaction or measurement, a drain/siphon fitting 17 used to establish the gravity siphon and leave a precise volume of sample in the cell and a titrant fitting 18 to introduce titrant required for the measurement. All of the items described are constructed of materials inert to the sample stream and which are such as to minimize deterioration and clogging and increase service life and reliability.

The operation of this arrangement, which preferably is performed by a CPU microprocessor programmed for the task, is as follows, with reference to Figs. 3 and 3a through 3h.

In Fig. 3, cell 2 and manifold 1 are shown in section, with siphon/waste fitting 17 and titrant fitting 18 extending into the cell. Sample inlet piping 20 extends from a process stream connection (not shown), through valve 21, to sample inlet fitting 7. Siphon/drain piping 22 extends from siphon/waste connection 6, to a distance, D, below the inlet opening to siphon/waste fitting 17 within the cell, D, being selected to establish a pressure differential between the inlet 23 of siphon/drain fitting 17 and the outlet 25 of siphon/drain piping 22 sufficient to start and maintain gravity siphon flow, as will be described below, e.g., a pressure differential of about 6 inches of water. Titrant piping 24 delivers titrating fluid from a source, through a metering pump, and into the cell via titrant connection 14 and fitting 18. The vent line from the cell to fitting 5 (Fig. 1a) lies behind the siphon/drain line and is omitted for clarity. The vent line terminates in vent piping 27 and valve 29, which may be level, as shown, or elevated. The internal lines from standard and reagent fittings 12, 13, and the internal components of probes and sensors 9, 11 are also omitted for clarity.

Referring to Fig. 3a, with the vent valve 29 open, typically to the atmosphere, the sample valve 21 is opened, causing pressurized sample 30 to flow via inlet piping 20 from the liquid process stream. The vent valve 29 is kept open as sample 30 fills the cell from the bottom, displacing entrapped air through the vent piping 27 and valve 29, and also through the siphon/waste piping 22, until the cell is about half full, with the liquid level 32 above the inlet end 23 of the siphon/waste fitting 17 (Fig. 3b). This is typically determined by time, based on the volume flow rate through sample inlet piping 20, as programmed into the CPU microprocessor by operating personnel.

The vent valve 29 is then closed as pressurized

sample continues to flow through inlet piping 20 into cell 2. As the cell volume is now closed, excess sample 30 is forced to flow out of the cell through siphon/drain piping 22 (Fig. 3c). After the siphon/drain piping is filled, the sample valve 21 is closed to stop flow of sample into the cell. The air vent valve 29 is also in closed position at this point, so all flow is stopped (Fig. 3d).

The air vent valve 29 is then reopened, allowing flow of the sample liquid held in the siphon/drain fitting 17 and piping 22 (Fig. 3e). The gravity siphon action continues until the liquid level 32 of sample in cell 2 falls below the inlet end 23 of siphon/waste fitting 17, opening the inlet end of the tube to air in the cell, breaking siphon and leaving a precisely repeatable volume of sample liquid remaining in the cell (Fig. 3f),

The open air vent valve and exposed inlet end of the siphon/drain line in the cell allow the drain line to empty (Fig. 3g), leaving a captured sample of liquid of volume repeatable, e.g., within $\pm 1/2\%$, from sample to sample. (The volume of cell 2 and the sample volume captured are selected on the basis of the process to be monitored, and the nature of the testing to be performed. For example, the cell volume may be 40 ml, and the captured sample volume 20 ml, or the cell volume may be 70 ml, and the captured sample volume 8 ml, e.g., where the process liquid is concentrated, and relatively larger volumes of additives are required.)

At this point, depending on the characteristic or component to be determined and the test to be performed, a measured volume, accurate to about $\pm 1\%$ with a standard titrant pump, of titrant or reagent, or both, are added into the cell. A chemical reaction may be induced, and the desired characteristic or component measured, typically for variation from a standard.

In the process sequence described above, the cell was shown as initially empty. Typically, however, the reacted sample liquid from the previous cycle must be purged from the cell before the next sample is taken. Due to the addition of titrant during testing of the previous sample, the liquid level in the cell is above the inlet of the siphon/drain fitting, e.g., in a system for capturing a sample volume of 8 ml, the final test volume in the cell may be 40 to 50 ml. Flow of liquid through the siphon/drain conduit is established by opening the sample inlet valve 21 with the vent valve 29 closed. Vent valve 29 is then opened and sample inlet valve 21 is closed. Gravity siphon flow through the siphon drain fitting 17 and piping 22 continues until only the capture volume remains in the cell. The condition established in Fig. 3c is maintained to statistically purge the volume of sample remaining in the cell, e.g., six to eight volume exchanges are typically sufficient to provide a captured sample that is better than 95% clean.

At appropriate intervals, e.g., after a predetermined number of process samples are run, a calibrat-

ing liquid is allowed to flow into cell 2. The calibrating liquid is captured in the same manner as the volume of sample described above. The addition of reagent or titrant is carried out in the same manner. Measurement of the calibrating liquid characteristic or component allows for recalibration of the electrodes, sensors and probes to correct for change in the system, as typically will occur over time. It also allows the operator to compare on-line process readings with a periodic reading on a sample of known characteristic. Examples of processes where this is of particular value include :

Steady-state processes, such as maintenance of peroxide at optimum concentration in cotton fabric bleaching. As peroxide is continuously added (solution addition) and depleted (in bleaching action), the concentration changes over a fairly narrow range. At too high a concentration of peroxide, the fabric is damaged, and at too low a concentration, the fabric is inadequately treated. A sample taken at the optimum concentration, prepared to ease sample handling (e.g. filtered), provides a good calibrating solution.

Depletion processes, such as plating copper onto inert medium in the manufacture of printed circuit boards. In this process, the copper concentration is constantly decreasing as the copper is deposited on the board. Monitoring can help prevent excessively low concentrations of copper, which result in unacceptably uneven coverage. For this process, an exact sample of the plating bath, including interfering additives, under conditions slightly above the minimum copper concentration situation gives maximum precision (through standardization) at the critical end of the process range, when additional copper must be added to the bath.

Saturation processes, such as waste treatment in which copper ions in solution are precipitated out to prevent their discharge to the general environment. Typically, a chemical is added to cause this to occur, based on an assumed inflow of copper ions. During high-inflow periods, the solution can become overloaded with copper, requiring addition of greater amounts of the treating chemical. A calibrating liquid near this upper limit gives maximum precision.

By way of example only, one specific testing procedure will now be described.

Example

Caustic scrubber, e.g., sodium hydroxide, is pumped from a batch holding tank through pipes in petrochemical plants to remove, i.e., "scrub", dangerous chemicals leaking from pipe valves and fittings. The concentration of caustic solution in the batch tank is monitored to ensure effective and efficient mainte-

nance of a safe operating environment within the plant.

As scrubbing proceeds, the concentration of the caustic solution is reduced due to the intended chemical reaction of the caustic with chemicals in the pipes and the dissolution of additional scrubbed chemicals. The initial concentration of the NaOH is about 20 percent and the operation continues until the NaOH becomes ineffective at some low concentration, e.g., about 2-5 percent. The process is then stopped and the holding tank is replenished with fresh solution. Since scrubbing is carried out continuously, a second holding tank is kept ready for use when the first tank is being recharged.

The concentration of the caustic solution is analyzed by simple acid-based analysis to an endpoint, as sensed by a pH electrode, using the on-line wet chemical analyzer of the invention, as will now be described. With vent valve 29 open, sample valve 21 is opened allowing NaOH to flow through sample inlet piping 20 into the volume of cell 2. After a predetermined time, programmed into the associated CPU microprocessor, when the liquid level in the cell is above the inlet end 23 of siphon/drain fitting 17, vent valve 29 is closed to cause flow of liquid through fitting 17 and siphon/drain piping 22. After a volume of flow calculated to flush the previous sample from the cell and provide a new sample of desired cleanliness, e.g., 160 ml., sample inlet valve 21 is closed and all flow stops.

Vent valve 29 is opened and excess sample fluid flows through siphon/drain piping 22 and fitting 17 from the volume of cell 2 by gravity siphon action until the level of liquid in the cell drops below the inlet end 23 of fitting 17, at which point siphon is interrupted, and the liquid in fitting 17 and siphon/drain piping 22 empties from outlet 25.

There remains within the cell a captured sample of repeatable volume, e.g., 8 ml., for analysis. To the captured sample there is added, via reagent connection 13, 20 ml of barium chloride to counteract the presence of carbonate, usually found in the scrubber solution, which interferes with the acid-based titration analysis of the sample. A titrate of 3N (Normal) hydrochloric acid (HCl) is metered into the cell via titrant piping 24, connection 14 and fitting 18, within the cell, until the predetermined electrochemical potential, i.e., endpoint, of the reaction is reached.

The CPU microprocessor derives the concentration of the NaOH caustic solution and stores the result, as well as sending the result to process display or recorder devices via any of several standard industrial signal devices.

The analysis is thus fully automated and can be repeated on a frequency programmed by the operator.

The arrangement of this invention is further of use, for example, in the power and utility industry, pulp

and paper, food and beverage and chemical/petrochemical industries as well as in the petroleum, plating, dairying, rubber and plastics, primary metals, stone, clay and glass, textile and pharmaceutical industries; in fact, in any industry involving use of liquid media whose composition it is important to monitor in order to determine if a process liquid is used, depleted or changed in composition during an industrial process and/or when it is discharged to the environment.

The arrangement of the present invention may be used, more specifically, for example, in analyses using sensing probes to monitor composition of liquids. The siphon action of the arrangement may also be modified to capture precise sizes of sample for use in instruments where other sensing methods are employed and the applicability of the present invention is independent of the sensing technology used. These methods may include, but are not limited to, amperometric, colourimetric and spectrophotometric methods. The arrangement may be used to condition and/or dilute a sample before analysis, as well as to ensure precision of sample volume.

Other embodiments are within the following claims, for example, the vent may be connected to a source of inert or other gas, rather than being open to the atmosphere, or the vent may be pressurized and the system operated at superatmospheric pressure. The system may include liquid flow and liquid level sensors for controlling operation of valves, and a dump valve may be provided at the bottom of the cell for ease in purging.

Claims

1. A chemical analyzer device for determination of a characteristic of a liquid process stream by wet chemical analysis to enable control of the process, said device comprising a sample cell (2) for collection of a predetermined volume of sample (30) to be analyzed and means for performing wet chemical analysis on the sample by progressively adding to the sample a measured flow of liquid reagent to cause progressive reaction with sample while sensing a parameter of the liquid sample as the reaction with the reagent proceeds, characterised by the further inclusion in said device of

a siphon cell (2) having a closed volume that serves as said sample cell (2),

sample inlet conduit means (7, 20, 21) for delivery of a flow of process liquid into said cell (2), vent means (27, 29) for flow of vent gas into said cell (2),

a siphon/drain conduit means (6, 17, 22) having an inlet (23) and an outlet (25), said conduit means (6, 17, 22) having a first end defining said inlet (23) downwardly disposed within the volume

of said cell (2) with said inlet (23) at a predetermined level spaced from the bottom and top of said cell (2), the partial volume of said cell (2) below said inlet (23) sized to define a predetermined volume of sample (30) to be analyzed, and the partial volume of said cell (2) above the level of the inlet (23) enabling additional liquid to be introduced into said cell (2) during the operation of said device, and said siphon/drain conduit means (6, 17, 22) having a second end defining said outlet (25) downwardly disposed outside said cell (2) with said outlet (25) disposed at a predetermined distance (D) below said inlet (23), means for causing flow of process liquid (7, 20, 21) through said sample inlet conduit means (7, 20, 21) into said cell (2) to collect a sample (30) in said cell (2) and establish a level of liquid (32) in said cell (2) above the inlet (23) of said siphon/drain conduit means (6, 17, 22),

means for establishing flow of excess process liquid out of said cell (2) volume through said siphon/drain conduit means (6, 17, 22), to cause said siphon/drain conduit means (6, 17, 22) to fill, means for ceasing flow (17) through said sample inlet conduit means (7, 20, 21),

means for creating siphoning flow through said siphon/drain conduit means (6, 17, 22) to drain excess process liquid from said cell (2) in the manner that siphoning flow ceases automatically when the level of process liquid in said cell volume reaches the level of said inlet (23) of said siphon/drain conduit means (6, 17, 22), thereby to define, in said cell (2), a sample of predetermined repeatable volume (30), and

said means for performing wet chemical analysis constructed to perform said analysis in situ within said siphon cell (2) by titrating techniques, comprising means (12, 18, 24) for progressively delivering into said siphon cell (2) a measured flow of liquid reagent to cause progressive reaction with sample in situ in said cell (2), and means for sensing (9, 10, 11) in situ in said siphon cell (2) a parameter of the liquid sample as the reaction with the reagent proceeds.

2. The chemical analyzer device of claim 1, wherein said means for causing flow of process liquid through said sample inlet conduit means (7, 20, 21) into said cell (2) is constructed and positioned so that, after collecting a sample (30) in said cell (2) and establishing a level of liquid in said cell (2) above the inlet (23) of said siphon/drain conduit means (6, 17, 22), by continued flow of liquid into said cell volume via said sample inlet conduit means (7, 20, 21) a flow of excess process liquid out of said cell volume through said siphon/drain conduit means (6, 17, 22) is established to cause said siphon/drain conduit means (6, 17, 22) to fill.

3. The chemical analyzer device of claim 1, where-

rein said means for creating siphoning flow comprises means for continuing flow of liquid to establish flow of excess process liquid out of said cell volume through said siphon/drain conduit means (6, 17, 22).

4. The chemical analyzer device of claim 1, wherein said means for creating siphoning flow comprises means for applying suction to said outlet (25).

5. The chemical analyzer device of any preceding claim, wherein said means for sensing comprises an ion sensing probe (9) and/or a temperature sensing probe (10) and/or a conductivity sensing probe (11).

6. The chemical analyzer device of any preceding claim, further comprising a stir bar (15) positioned within said siphon cell (2).

7. A method for determination of a characteristic of a liquid process stream by wet chemical analysis to enable control of said process, comprising the steps of (a) defining a predetermined volume of sample (30) to be analyzed and (b) performing said wet chemical analysis on said sample (30) by progressively adding to said sample a measured flow of liquid reagent to cause progressive reaction with said sample (30) while sensing a parameter of the liquid sample (30) as said reaction with said reagent proceeds,

characterised in that said step (a) of defining said volume of sample to be analyzed comprises providing a siphon cell (2) having a closed volume, sample inlet conduit means (7, 20, 21) delivery of a flow of process liquid into said cell (2), vent means (27, 29) for flow of vent gas into said cell, and a siphon/drain conduit means (6, 17, 22) having an inlet (23) and an outlet (25), said conduit means (6, 17, 22) having a first end defining said inlet (23) downwardly disposed within the volume of said cell (2) with said inlet (23) at a predetermined level spaced from the bottom and top of said cell (2), the partial volume of said cell (2) below said inlet (23) sized to define a predetermined volume of sample (30) to be analyzed, and the partial volume of said cell above the level of the inlet (23) enabling additional liquid to be introduced into said cell (2) in the performance of said method, and said conduit means having a second end defining said outlet (25) downwardly disposed outside the said cell (2) with said outlet (25) disposed at a predetermined distance (D) below said inlet (23),

causing a flow of process liquid through said sample inlet conduit means into said cell to collect a sample in said cell and establish a level of liquid in said cell above the inlet of said siphon/drain conduit means,

continuing to cause flow of said liquid into said volume via said sample inlet conduit means to establish flow of excess process liquid out of said cell volume through said drain/siphon conduit means (6, 17, 22) filling said drain/siphon conduit (17),

after said drain/siphon conduit is filled, ceasing all flow through said sample inlet conduit means and creating siphoning flow through said siphon/drain conduit means (6, 17, 22) to drain excess process liquid from said cell (2), said siphoning flow ceasing automatically when the level of process liquid in said cell volume reaches the level of said inlet (23) of said siphon/drain conduit (17), thereby defining, in said cell (2) a sample of predetermined repeatable volume, and conducting said step (b) of performing said wet chemical analysis in situ within said siphon cell (2) comprising, by titrating techniques, progressively delivering into said siphon cell (2) a measured flow of liquid reagent to cause progressive reaction with said sample in situ in said cell (2), while sensing in situ in said siphon cell (2) a parameter of the liquid sample as said reaction with said reagent proceeds.

8. The titration method of claim 7, wherein said sample is taken directly from the liquid process stream of an industrial plant, the pressure of said stream serving to produce said flow of process liquid through said inlet conduit means (7, 20, 21) into said cell (2) and into said drain/siphon conduit (17).

Ansprüche

1. Chemische Analysatorvorrichtung zur Bestimmung einer Charakteristik eines flüssigen Prozeßstromes durch chemische Naßanalyse, um eine Steuerung des Prozesses zu ermöglichen,

wobei die Vorrichtung eine Proben-Zelle (2) zum Sammeln eines bestimmten Volumens einer zu analysierenden Probe (30) und eine Einrichtung umfaßt zur Durchführung einer chemischen Naßanalyse bezüglich der Probe durch fortschreitendes Hinzusetzen eines abgemessenen Stromes eines flüssigen Reagenzes zu der Probe, um eine fortschreitende Reaktion der Probe zu bewirken, während ein Parameter der flüssigen Probe ermittelt wird, wenn die Reaktion mit dem Reagenz fortschreitet, dadurch gekennzeichnet, daß in die Vorrichtung ferner eingeschlossen sind

eine einen geschlossenen Raum aufweisende Siphon-Zelle (2), die als Proben-Zelle (2) dient, eine Proben-Einlaßrohrleitungseinrichtung (7, 20, 21) für die Abgabe eines Stromes der Prozeßflüssigkeit in die betreffende Zelle (2) ;

eine Entlüftungseinrichtung (27, 29) zum Einströmen von Entlüftungsgas in die betreffende Zelle (2) ;

eine Siphon-/Abfluß-Rohrleitungseinrichtung (6, 17, 22) mit einem Einlaß (23) und einem Auslaß (25),

wobei die betreffende Rohrleitungseinrichtung (6,

17, 22) ein erstes Ende aufweist, welches den betreffenden Einlaß (23) festlegt, der innerhalb des genannten Raumes der Zelle (2) nach unten weisend angeordnet ist,

wobei der betreffende Einlaß (23) in einer bestimmten Höhe in Abstand vom Boden und von der Oberseite der Zelle (2) vorgesehen ist,

wobei das Teilvolumen der Zelle (2) unterhalb des Einlasses (23) eine solche Größe hat, daß ein bestimmtes Volumen der zu analysierenden Probe (30) festgelegt ist,

wobei das Teilvolumen der Zelle (2) oberhalb der Höhe des Einlasses (23) die Einführung einer zusätzlichen Flüssigkeit in die betreffende Zelle (2) während des Betriebs der Vorrichtung ermöglicht,

wobei die genannte Siphon-/Abfluß-Rohrleitungseinrichtung (6, 17, 22) ein zweites Ende aufweist, welches den Auslaß (25) festlegt, der außerhalb der betreffenden Zelle (2) nach unten weisend angeordnet ist,

und wobei der betreffende Auslaß (25) in einem bestimmten Abstand (D) unterhalb des genannten Einlasses (23) angeordnet ist ;

eine Einrichtung, die einen Strom der Prozeßflüssigkeit (7, 20, 21) durch die Proben-Einlaßrohrleitungseinrichtung (7, 20, 21) in die betreffende Zelle (2) zum Sammeln einer Probe (30) in der betreffenden Zelle (2) bewirkt und die einen Pegel (32) der Flüssigkeit in der betreffenden Zelle (2) oberhalb des Einlasses (23) der genannten Siphon-/Abfluß-Rohrleitungseinrichtung (6, 17, 22) festlegt ;

eine Einrichtung zur Festlegung eines Stromes überschüssiger Prozeßflüssigkeit aus dem Raum der genannten Zelle (2) heraus durch die Siphon-/Abfluß-Rohrleitungseinrichtung (6, 17, 22) hindurch, um ein Füllen der Siphon-/Abfluß-Rohrleitungseinrichtung (6, 17, 22) zu bewirken ;

eine Einrichtung zur Beendigung des Stromes (17) durch die genannte Proben-Einlaßrohrleitungseinrichtung (7, 20, 21) ;

eine Einrichtung zur Erzeugung eines Entleerungsflusses durch die Siphon-/Abfluß-Rohrleitungseinrichtung (6, 17, 22), um überschüssige Prozeßflüssigkeit aus der betreffenden Zelle (2) in der Weise abzuführen, daß der Entleerungsfluß automatisch aufhört, wenn die Höhe der Prozeßflüssigkeit in dem Zellenraum die Höhe des Einlasses (23) der betreffenden Siphon-/Abfluß-Rohrleitungseinrichtung (6, 17, 22) erreicht, wodurch in der betreffenden Zelle (2) eine Probe bestimmten wiederholbaren Volumens (30) festgelegt ist ;

und wobei die zur Durchführung der chemischen Naßanalyse dienende Einrichtung, die so konstruiert ist, daß die betreffende Analyse an Ort

und Stelle innerhalb der betreffenden Siphon-Zelle (2) durch Titrierungstechniken durchgeführt wird, Einrichtungen (12, 18, 24) zur fortschreitenden Abgabe eines abgemessenen Stromes eines flüssigen Reagenzes in die betreffende Siphon-Zelle (2), um eine fortschreitende Reaktion mit der Probe an Ort und Stelle innerhalb der betreffenden Zelle (2) hervorzurufen, und eine Einrichtung (9, 10, 11) umfaßt, die an Ort und Stelle in der betreffenden Siphon-Zelle (2) einen Parameter der flüssigen Probe ermittelt, wenn die Reaktion mit dem Reagenz fortschreitet.

2. Chemische Analysatorvorrichtung nach Anspruch 1, wobei die Einrichtung, die eine Strömung der Prozessflüssigkeit durch die Proben-Einlaßrohrleitungseinrichtung (7, 20, 21) in die Zelle (2) hinein bewirkt, so konstruiert und positioniert ist, daß nach Sammeln einer Probe (30) in der betreffenden Zelle (2) und Festlegen einer Höhe der Flüssigkeit in der betreffenden Zelle (2) oberhalb des Einlasses (23) der Siphon-/Abfluß-Rohrleitungseinrichtung (6, 17, 22) durch fortgesetztes Fließen der Flüssigkeit in den betreffenden Zellenraum hinein durch die Proben-Einlaßrohrleitungseinrichtung (7, 20, 21) hindurch ein Fluß überschüssiger Prozessflüssigkeit aus dem betreffenden Zellenraum heraus durch die Siphon-/Abfluß-Rohrleitungseinrichtung (6, 17, 22) geschaffen wird, um das Füllen der Siphon-/Abfluß-Rohrleitungseinrichtung (6, 17, 22) zu bewirken.

3. Chemische Analysatorvorrichtung nach Anspruch 1, wobei die Einrichtung zur Erzeugung eines Entleerungsflusses eine Einrichtung umfaßt, die das Fließen der Flüssigkeit fortsetzt, um das Fließen einer überschüssigen Prozessflüssigkeit aus dem Zellenraum heraus durch die betreffende Siphon-/Abfluß-Rohrleitungseinrichtung (6, 17, 22) hervorzurufen,

4. Chemische Analysatorvorrichtung nach Anspruch 1, wobei die Einrichtung zur Erzeugung eines Entleerungsflusses eine Einrichtung zur Ausübung einer Saugwirkung auf den Auslaß (25) umfaßt.

5. Chemische Analysatorvorrichtung nach irgendeinem vorhergehenden Anspruch, wobei die Einrichtung zur Ermittlung eine Ionen-Meßsonde (9) und/oder eine Temperatur-Meßsonde (10) und/oder eine Leitfähigkeits-Meßsonde (11) umfaßt.

6. Chemische Analysatorvorrichtung nach irgendeinem vorhergehenden Anspruch, umfassend ferner einen innerhalb der genannten Siphon-Zelle (2) positionierten Rührstab (15).

7. Verfahren zur Bestimmung einer Charakteristik eines flüssigen Prozessstromes durch chemische Naßanalyse, um eine Steuerung des betreffenden Prozesses zu ermöglichen, umfassend die Schritte (a) Festlegen eines bestimmten Volumens der zu analysierenden Probe (30) und (b) Ausführen der

betreffenden chemischen Naßanalyse anhand der Probe (30) durch fortschreitendes Hinzusetzen eines abgemessenen Stromes eines flüssigen Reagenzes zu der betreffenden Probe (30), um eine fortschreitende Reaktion mit der betreffenden Probe (30) zu bewirken, während ein Parameter der flüssigen Probe ermittelt wird, wenn die Reaktion mit dem Reagenz fortschreitet, dadurch gekennzeichnet, daß der genannte Schritt (a) des Festlegens des Volumens einer zu analysierenden Probe die Bereitstellung einer Siphon-Zelle (2) mit einem geschlossenen Raum, einer Proben-Einlaßrohrleitungseinrichtung (7, 20, 21), die einen Strom der Prozessflüssigkeit in die betreffende Zelle (2) abgibt, einer Entlüftungseinrichtung (27, 29) für das Einströmen eines Entlüftungsgases in die betreffende Zelle und einer Siphon-/Abfluß-Rohrleitungseinrichtung (6, 17, 22) mit einem Einlaß (23) und einem Auslaß (25) umfaßt,

wobei die betreffende Rohrleitungseinrichtung (6, 17, 22) ein erstes Ende aufweist, welches den genannten Einlaß (23) festlegt, der innerhalb des Raumes der betreffenden Zelle (2) nach unten weisend angeordnet ist,

wobei der Einlaß (23) in einer bestimmten Höhe in Abstand vom Boden und der Oberseite der Zelle (2) vorgesehen ist, wobei das Teilvolumen der Zelle (23) unterhalb des Einlasses (23) so groß ist, daß ein bestimmtes Volumen der zu analysierenden Probe (30) festgelegt ist, wobei das Teilvolumen der Zelle oberhalb der Höhe des Einlasses (23) die Einführung einer zusätzlichen Flüssigkeit in die betreffende Zelle (2) im Zuge der Ausführung des Verfahrens ermöglicht,

wobei die genannte Rohrleitungseinrichtung ein zweites Ende aufweist, welches den Auslaß (25) festlegt, der außerhalb der betreffenden Zelle (2) nach unten weisend angeordnet ist, und wobei der Auslaß (25) in einem bestimmten Abstand (D) unterhalb des Einlasses (23) angeordnet ist;

daß ein Fließen der Prozessflüssigkeit durch die betreffende Proben-Einlaßrohrleitungseinrichtung in die genannte Zelle bewirkt wird, um eine Probe in der Zelle zu sammeln und um einen Flüssigkeitspegel der Flüssigkeit in der Zelle oberhalb des Einlasses der Siphon-/Abfluß-Rohrleitungseinrichtung hervorzurufen,

daß das Fließen der betreffenden Flüssigkeit in den genannten Raum durch die Proben-Einlaßrohrleitungseinrichtung fortgesetzt bewirkt wird, um ein Herausfließen überschüssiger Prozessflüssigkeit aus dem Zellenraum durch die Abfluß-/Siphon-Rohrleitungseinrichtung (6, 17, 22) hervorzurufen, wobei die betreffende Abfluß-/Siphonrohrleitung (17) gefüllt wird,

daß nach Füllen der Abfluß-/Siphonrohrleitung der Gesamtfluß durch die Proben-Einlaßrohrleitung beendet und ein Entleerungsfluß durch die

Siphon-/Abfluß-Rohrleitungseinrichtung (6, 17, 22) hervorgerufen wird, um überschüssige Prozessflüssigkeit aus der Zelle (2) abzuführen, wobei der betreffende Entleerungsfluß automatisch aufhört, wenn der Pegel der Prozessflüssigkeit innerhalb des Zellenraumes die Höhe des Einlasses (23) der Siphon-/Abflußrohrleitung (17) erreicht, wodurch in der betreffenden Zelle (2) eine Probe eines bestimmten wiederholbaren Volumens festgelegt ist, und daß die Durchführung des Schrittes (b), der Ausführung der chemischen Naßanalyse an Ort und Stelle innerhalb der Siphon-Zelle (2) durch Titrierungsverfahren die fortschreitende Abgabe eines abgemessenen Flüssigkeitsstromes eines flüssigen Reagenzes in die betreffende Siphon-Zelle (2) umfaßt, um eine fortschreitende Reaktion mit der betreffenden Probe an Ort und Stelle in der betreffenden Zelle (2) zu bewirken, während an Ort und Stelle in der Siphon-Zelle (2) ein Parameter der flüssigen Probe ermittelt wird, wenn die Reaktion mit dem Reagenz fortgeschritten ist.

8. Titrierungsverfahren nach Anspruch 7, wobei die Probe direkt aus dem flüssigen Prozessstrom einer Industrieanlage entnommen wird, wobei der Druck des betreffenden Stromes dazu dient, das Fließen der Prozessflüssigkeit durch die Einlaß-Rohrleitungseinrichtung (7, 20, 21) in die Zelle (2) und in die Abfluß-/Siphon-Rohrleitung (17) hervorzurufen.

Revendications

1. Dispositif d'analyse chimique pour la détermination d'une caractéristique d'un courant de processus liquide par analyse chimique par voie humide pour permettre la régulation des processus, le dispositif comprenant une cellule d'échantillon (2) destinée à recueillir un volume prédéterminé d'échantillon (30) à analyser et des moyens pour effectuer l'analyse chimique par voie humide sur l'échantillon en ajoutant progressivement à l'échantillon un flux mesuré de réactif liquide pour provoquer la réaction progressive avec l'échantillon tout en captant un paramètre de l'échantillon liquide à mesure que se déroule la réaction avec le réactif, caractérisé par l'incorporation supplémentaire dans le dispositif :

d'une cellule de siphon (2) comportant un volume fermé qui sert de cellule d'échantillon (2),
des moyens de conduite d'admission d'échantillon (7, 20, 21) pour amener un flux de liquide de processus dans la cellule (2),
des moyens de purge (27, 29) pour le flux des gaz de purge dans la cellule (2),
une conduite de siphon/évacuation (6, 17, 22) comportant une entrée (23) et une sortie (25), les conduites (6, 17, 22) ayant une première extrémité définissant l'entrée (23) disposée vers le bas

dans le volume de la cellule (2) avec l'entrée (23) à un niveau prédéterminé espacé du fond et du dessus de la cellule (2), le volume partiel de la cellule (2) au-dessous de l'entrée (23) dimensionnée pour définir un volume prédéterminé d'échantillon (30) à analyser, et le volume partiel de la cellule (2) au-dessus du niveau de l'entrée (23) permettant l'introduction de liquide supplémentaire dans la cellule (2) pendant le fonctionnement du dispositif, et les conduites de siphon/évacuation (6, 17, 22) ayant une seconde extrémité définissant la sortie (25) disposée vers le bas à l'extérieur de la cellule (2) avec la sortie (25) disposée à une distance prédéterminée (D) au-dessous de l'entrée (23),

des moyens pour provoquer l'écoulement du liquide de processus (7, 20, 21) à travers les conduites d'admission d'échantillon (7, 20, 21) dans la cellule (2) pour recueillir un échantillon (30) dans la cellule (2) et établir un niveau de liquide (32) dans la cellule (2) au-dessus de l'entrée (23) des conduites de siphon/vidange (6, 17, 22),

des moyens pour établir le passage de liquide de processus excédentaire s'écoulant hors du volume de cellule (2) par les conduites de siphon/vidange (6, 17, 22) pour entraîner le remplissage des conduites de siphon/vidange (6, 17, 22),

des moyens pour interrompre le flux (17) à travers les conduites d'admission d'échantillon (7, 20, 21),

des moyens pour créer le flux de siphonnage à travers les conduites de siphon/vidange (6, 17, 22) pour évacuer le liquide de processus excédentaire à partir de la cellule (2) de telle manière que le flux de siphonnage cesse automatiquement lorsque le niveau de liquide de processus dans le volume de la cellule atteint le niveau de l'entrée (23) des conduites de siphon/vidange (6, 17, 22), définissant ainsi dans la cellule (2) un échantillon de volume prédéterminé répétable (30), et

des moyens pour effectuer l'analyse chimique par voie humide, construits pour effectuer l'analyse in situ à l'intérieur de la cellule de siphon (2) par des techniques de titrage, comprenant des moyens (12, 18, 24) pour amener progressivement dans la cellule de siphon (2) un flux mesuré de réactif liquide pour provoquer la réaction progressive avec l'échantillon in situ dans la cellule (2) et des moyens pour détecter (9, 10, 11) in situ dans la cellule de siphon (2) un paramètre de l'échantillon liquide à mesure que se déroule la réaction avec le réactif.

2. Dispositif d'analyse chimique selon la revendication 1, dans lequel les moyens destinés à entraîner l'écoulement du liquide de processus à travers les

conduites d'admission d'échantillon (7, 20, 21) dans la cellule (2) est construit et positionné de façon qu'après avoir recueilli un échantillon (30) dans la cellule (2) et après avoir établi un niveau de liquide dans la cellule (2) au-dessus de l'admission (23) des conduites de siphon/vidange (6, 17, 22) par le flux continu de liquide dans le volume de cellule par l'intermédiaire des conduites d'admission d'échantillon (7, 20, 21) un flux de liquide de processus excédentaire s'écoulant de la cellule par les conduites de siphon/vidange (6, 17, 22) est établi pour provoquer le remplissage de conduite de siphon/vidange (6, 17, 22).

3. Dispositif d'analyse chimique selon la revendication 1, dans lequel les moyens destinés à créer le flux de siphonnage comprennent des moyens aptes à faire poursuivre le flux de liquide pour établir un flux de liquide de processus excédentaire s'écoulant de la cellule par l'intermédiaire des conduites de siphon/vidange (6, 17, 22).

4. Dispositif d'analyse selon la revendication 1, dans lequel des moyens destinés à créer le flux de siphonnage comprennent des moyens aptes à appliquer une aspiration à l'orifice de sortie (25),

5. Dispositif d'analyse chimique selon l'une quelconque des revendications précédentes, dans lequel les moyens de détection comprennent une sonde de détection ionique (9) et/ou une sonde de détection de température (10) et/ou une sonde de détection de conductivité (11).

6. Dispositif d'analyse chimique selon l'une quelconque des revendications précédentes, comprenant de plus une barre d'agitation (15) positionnée à l'intérieur de la cellule de siphonnage (2).

7. Procédé pour la détermination d'une caractéristique d'un courant de processus liquide par analyse chimique par voie humide pour permettre la régulation de ces processus, comprenant les étapes consistant à (a) définir un volume prédéterminé d'échantillon (30) à analyser et (b) effectuer l'analyse chimique par voie humide sur l'échantillon (30) en ajoutant progressivement à l'échantillon un flux mesuré de réactif liquide pour provoquer la réaction progressive avec l'échantillon (30) tout en détectant un paramètre de l'échantillon liquide (30) à mesure que se déroule la réaction avec le réactif,

caractérisé en ce que l'étape consistant à (a) définir le volume d'échantillon analysé comprend la mise en oeuvre d'une cellule de siphon (2) comportant un volume fermé, les conduites d'admission d'échantillon (7, 20, 21) pour l'amenée d'un flux de liquide de processus dans la cellule (2), des moyens de purge (27, 29) pour l'écoulement des gaz de purge dans la cellule, et des conduites de siphon/vidange (6, 17, 22) comportant une admission (23) et une sortie (25), les conduites (6, 17, 22) présentant une première extrémité définissant l'orifice d'admission (23)

disposée vers le bas à l'intérieur du volume de la cellule (2) avec l'orifice d'admission (23) à un niveau prédéterminé espacé du fond et du dessus de la cellule (2), le volume partiel de la cellule (2) au-dessous de l'orifice d'admission (23) dimensionné pour définir un volume prédéterminé d'échantillon (30) à analyser, et le volume partiel de la cellule au-dessus du niveau de l'orifice d'admission (23) permettant d'introduire du liquide supplémentaire dans la cellule (2) pour l'exécution du procédé, et les conduites présentant une seconde extrémité définissant l'orifice de sortie (25) disposée vers le bas à l'extérieur de la cellule (2) avec l'orifice de sortie (25) disposé à une distance prédéterminée (D) au-dessous de l'orifice d'admission (23),

provoquer un flux de liquide de processus à travers les conduites d'admission d'échantillon dans la cellule pour recueillir un échantillon dans celle-ci et établir un niveau de liquide dans la cellule au-dessus de l'orifice de l'admission des conduites de siphon/vidange,

poursuivre l'écoulement du liquide dans le volume par l'intermédiaire des conduites d'admission d'échantillon pour établir le flux de liquide de processus excédentaire s'écoulant hors de la cellule à travers les conduites de vidange/siphon (6, 17, 22) remplissant la conduite de vidange/siphon (17),

après avoir rempli la conduite vidange/siphon, interrompre tout flux à travers les conduites d'admission d'échantillon et créer un passage de siphonnage à travers les conduites de siphon/vidange (6, 17, 22) pour vidanger tout liquide de processus excédentaire de la cellule (2), ce flux de siphonnage s'interrompant automatiquement lorsque le niveau du liquide de processus dans la cellule atteint le niveau d'admission (23) de la conduite siphon/vidange (17), définissant ainsi dans chaque cellule (2) un échantillon de volume prédéterminé répétable, et conduire l'étape (b) d'exécution de l'analyse chimique par voie humide in situ à l'intérieur de la cellule de siphon (2) comprenant, par des techniques de titrage, l'amenée progressive dans la cellule de siphon (2) d'un flux mesuré de réactif liquide pour provoquer la réaction progressive avec l'échantillon in situ dans la cellule (2) tout en captant in situ dans la cellule de siphon (2) un paramètre de l'échantillon de liquide à mesure que se déroule la réaction avec le réactif.

8. Procédé de titrage selon la revendication 7, dans lequel l'échantillon est pris directement du courant de processus liquide d'une usine industrielle la pression du courant servant à produire le flux de liquide de processus à travers les conduites d'admission (7, 20, 21) dans la cellule (2) et dans la conduite vidange/siphon (17).

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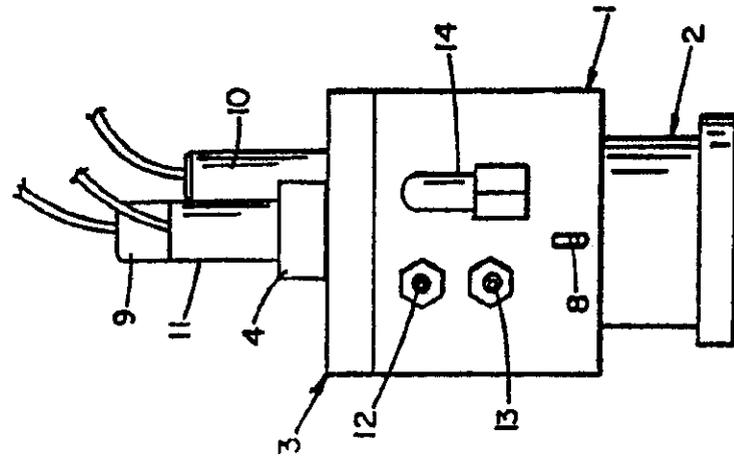


FIG 1A

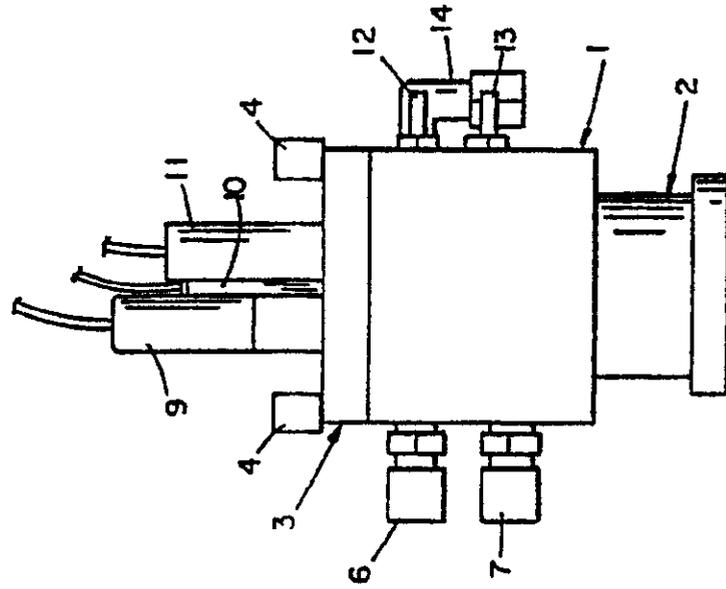


FIG 1B

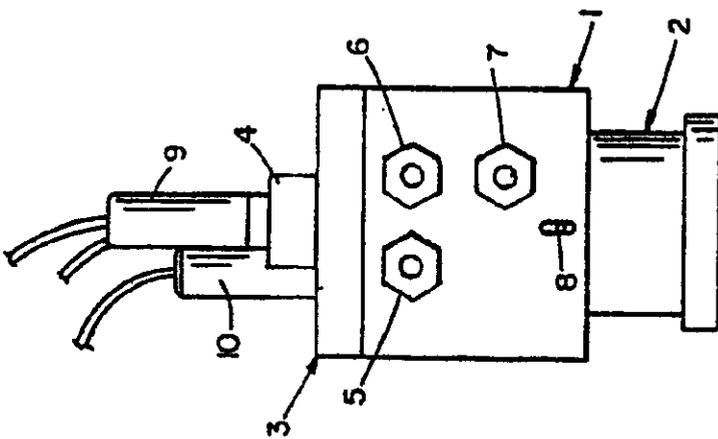


FIG 1C

FIG 2

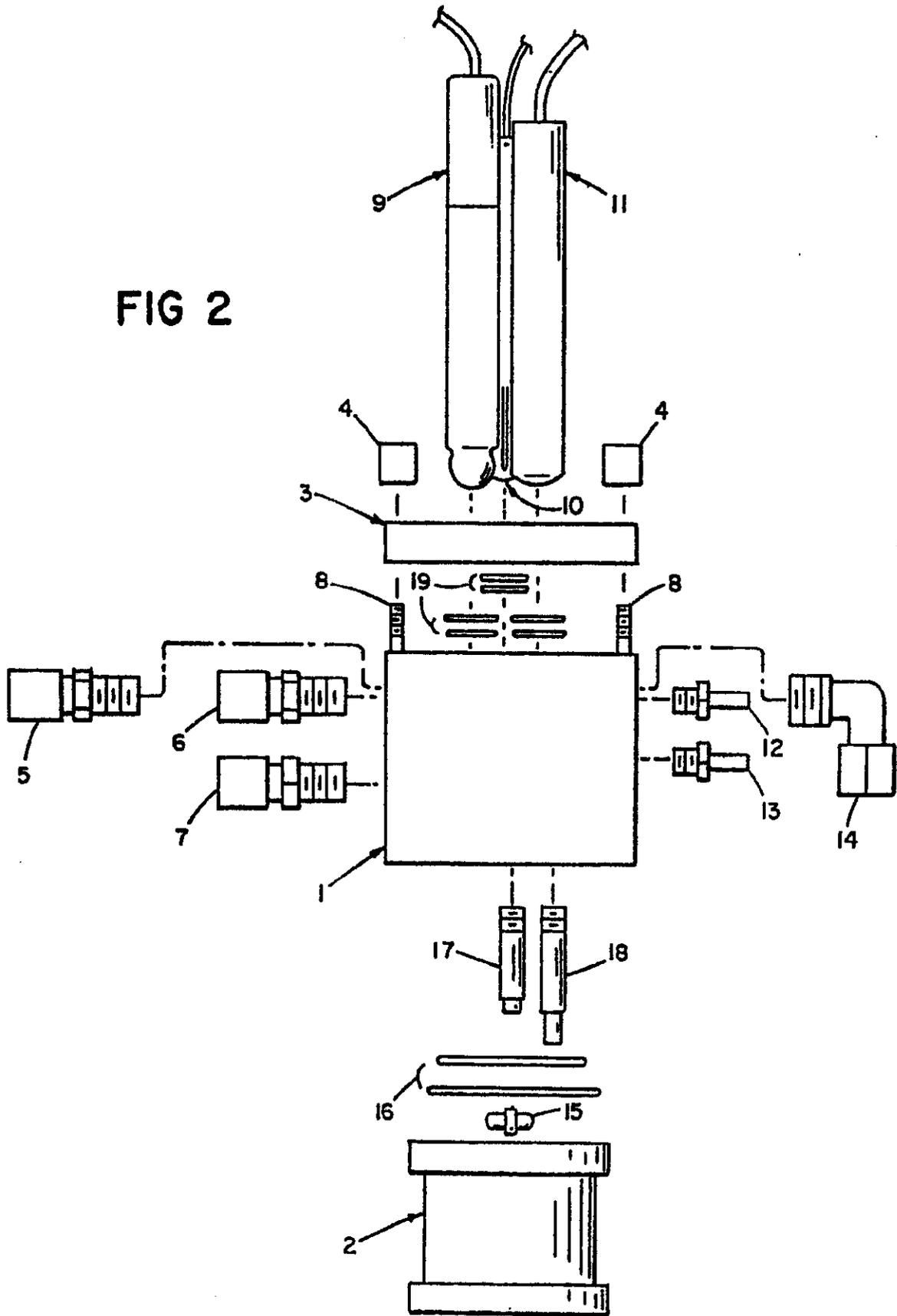
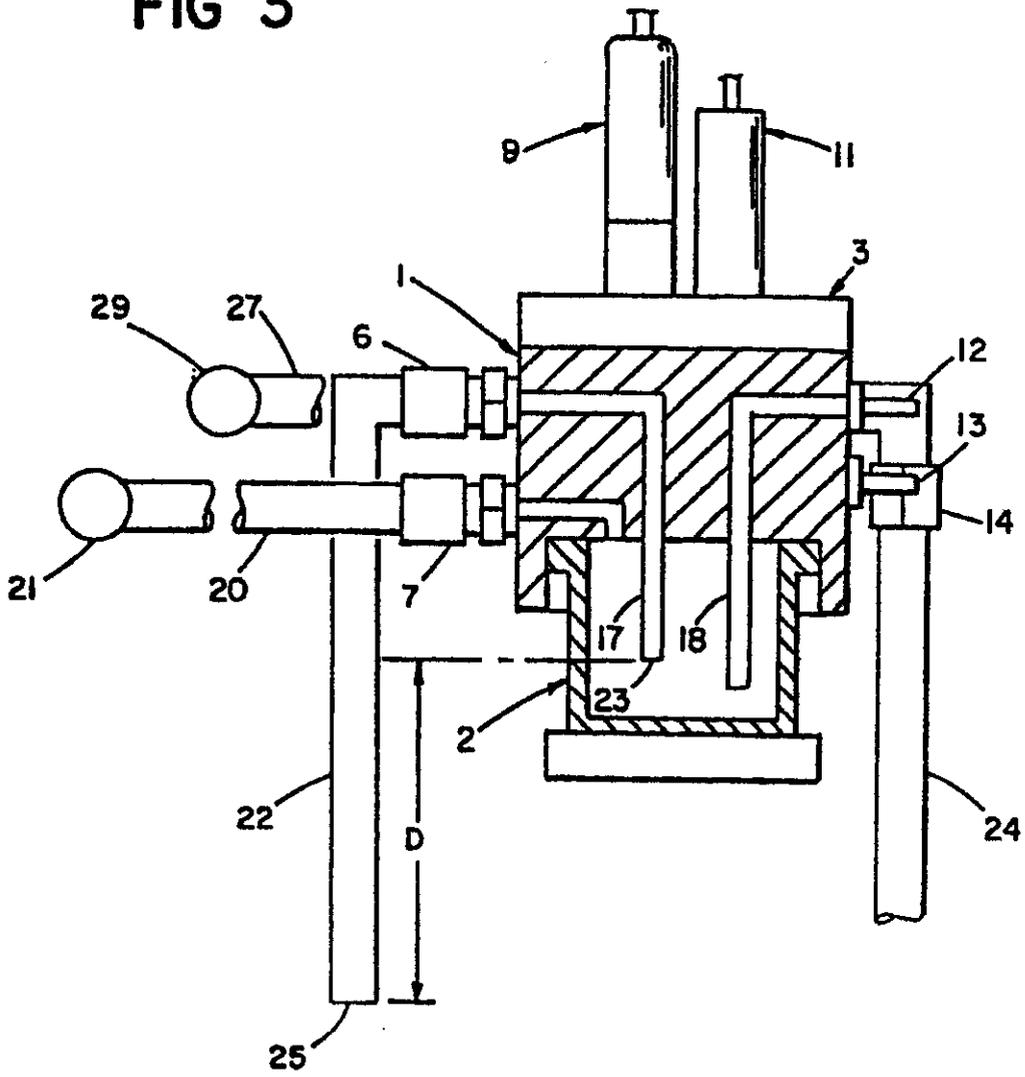
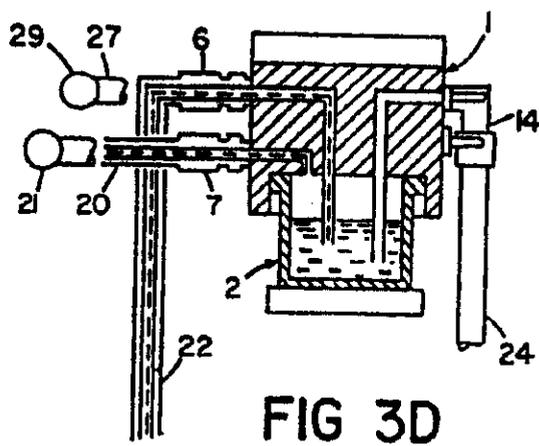
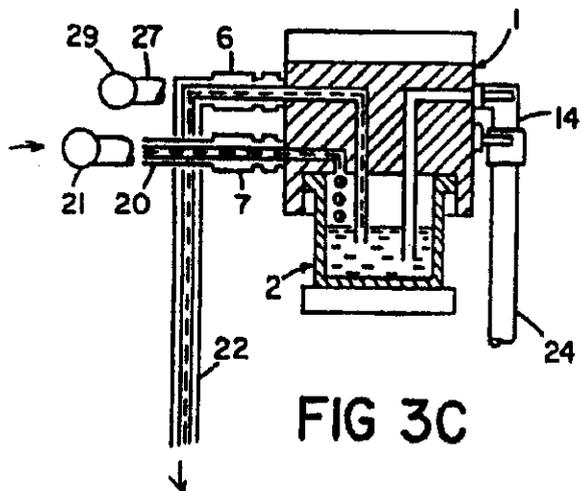
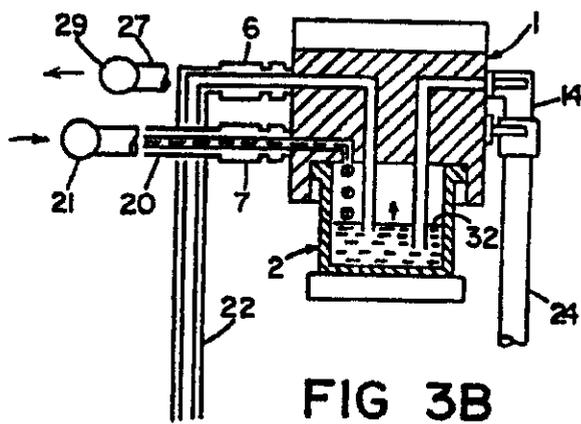
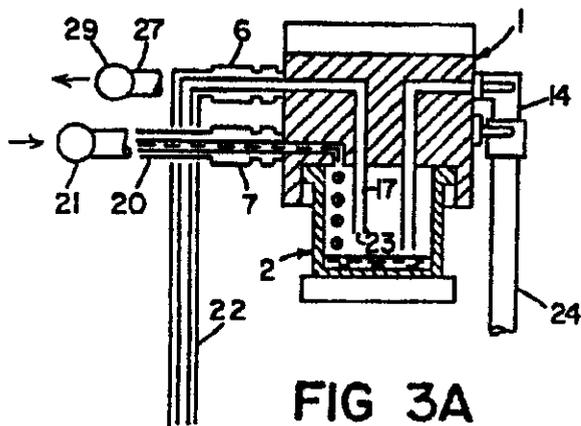


FIG 3





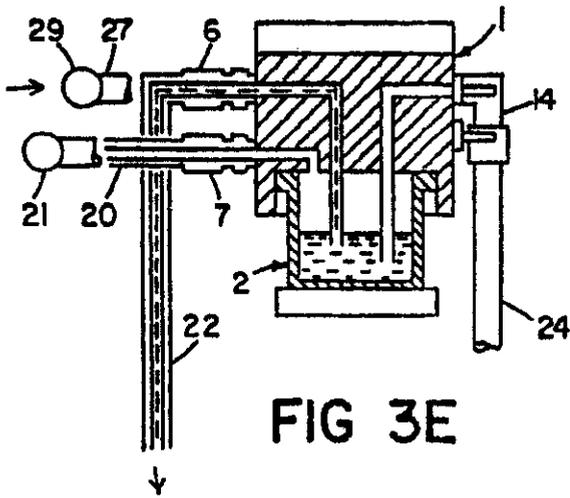


FIG 3E

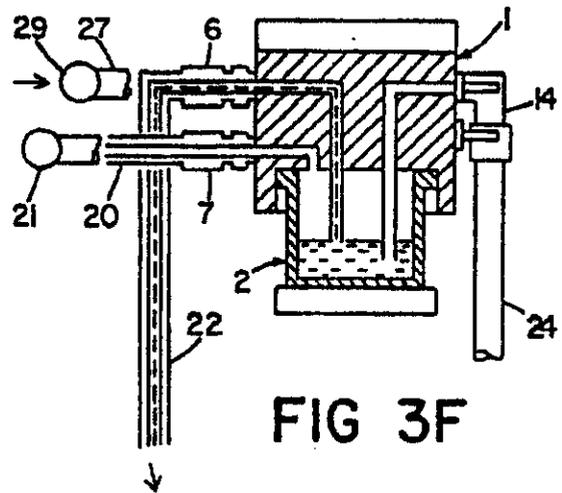


FIG 3F

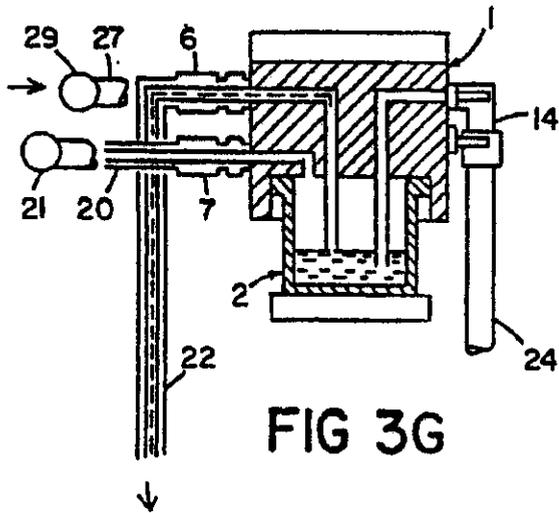


FIG 3G

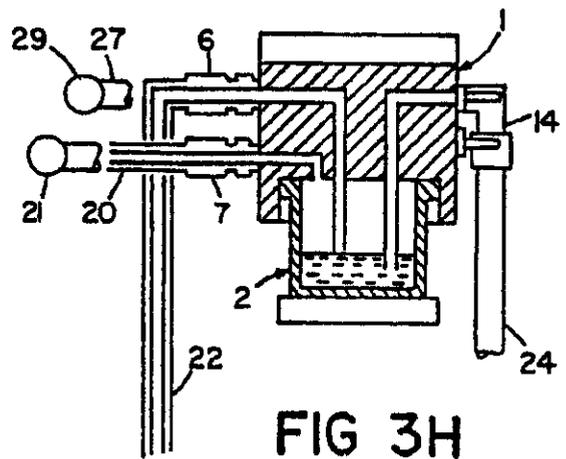


FIG 3H

REGISTER ENTRY FOR EP0214846

European Application No EP86306855.7 filing date 04.09.1986

Priority claimed:

06.09.1985 in United Kingdom - doc: 8522126

Designated States BE CH DE FR GB IT LI LU NL SE AT

Title SAMPLE MONITORING INSTRUMENT FOR ON-LINE APPLICATION

Applicant/Proprietor

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