

[54] TAG ION CELL
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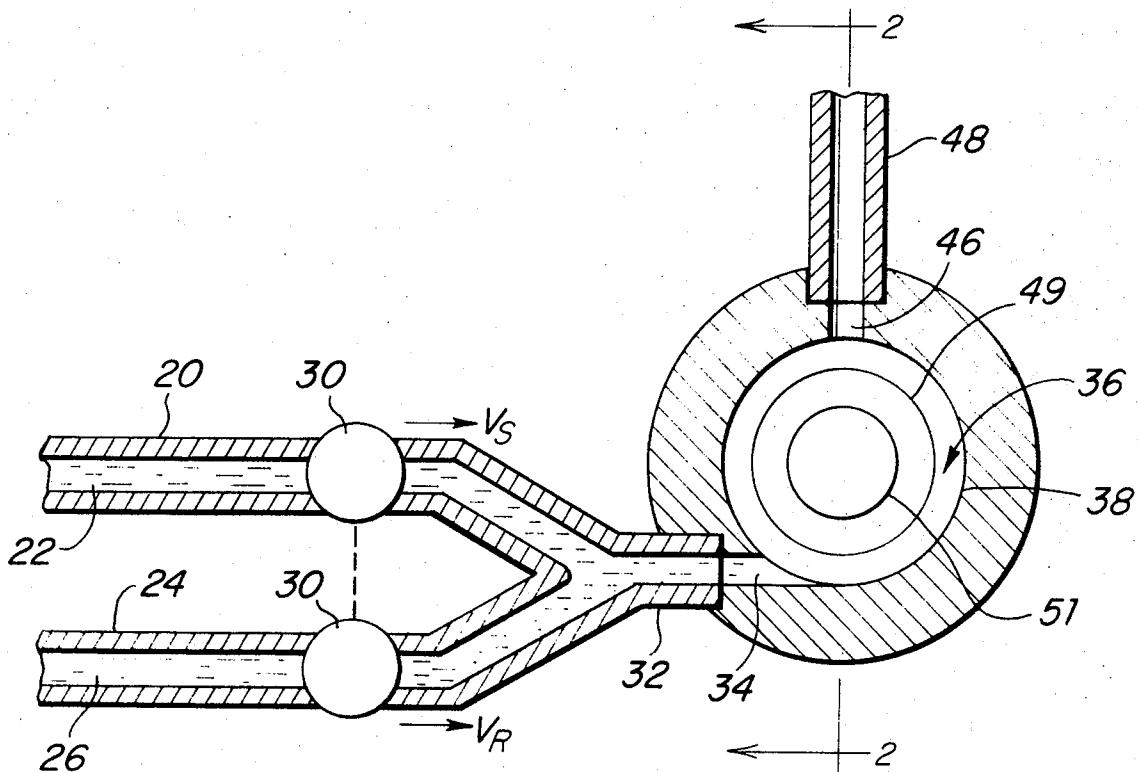
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[57] ABSTRACT

A system for making electrochemical measurements in a flow stream, which system employs reagent addition to a sample stream and a pair of ion-sensing electrodes responsive respectively to the ion of interest and the tag ion in the mixed stream. The electrodes are so disposed in an electrode chamber that the system is unaffected by the presence of any air bubbles in the mixed stream, or variations in flow rate of the mixed stream.

11 Claims, 2 Drawing Figures



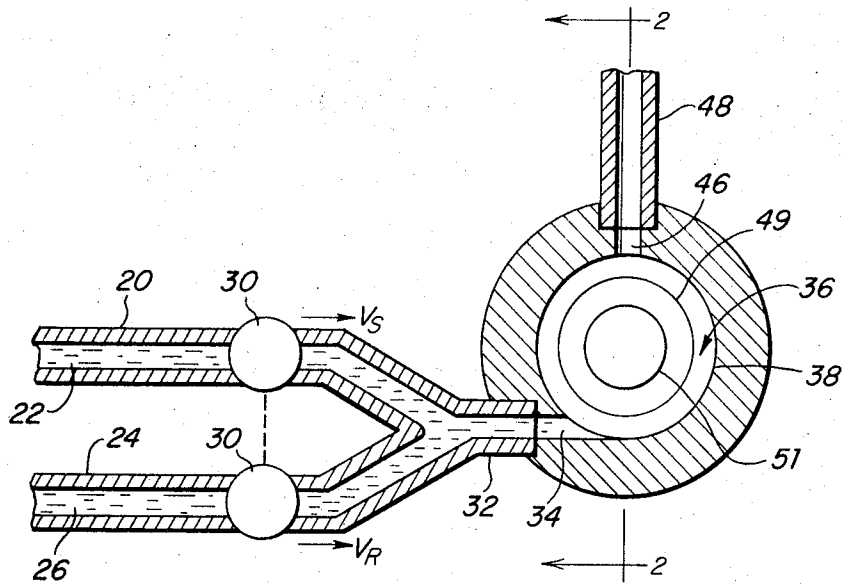


FIG. 1.

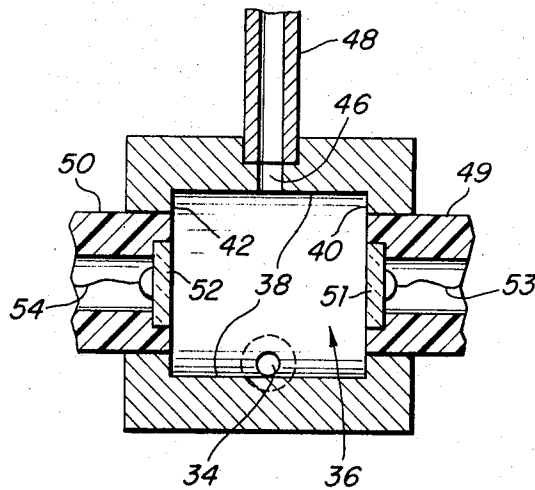


FIG. 2.

This invention relates to electro-chemical analytical systems, and more particularly to substantially continuously monitoring of fluid streams for ionic constituents with ion-sensitive electrodes.

Various continuous monitoring or sensing systems using ion-sensitive electrodes are known in the art for providing information relating to the activity of an ionic species of interest, or to the concentration thereof. Such systems generally comprise a reference electrode and an electrode sensitive to the ion of interest. The reference function may be served by adding a constant level of a reagent of "tag" ion to the sample. The reference and ion-sensitive electrodes are then placed in the mixture of sample and tag ion. The reference and ion-sensitive electrodes typically provide an electrical signal which is a function of the logarithm of the activity in the stream of the ionic species to which each electrode is sensitive.

In cases which involve the addition of a reagent, it is desirable to have a low flow rate in order to reduce reagent costs for long-term monitoring. However, opposed to the preference for keeping the flow rate low is the desirability of having high velocity of solution through the device to obtain a short response time and to minimize time lapse for "on-time" monitoring. One can reconcile these two objectives by keeping the flow volumes through the device as small as possible. Accordingly, it has been proposed to use relatively small diameter tubing, and small mixing and sample chambers.

In practice it is often very difficult, if not impossible, to remove all traces of air bubbles in the mixed stream, without taking fairly elaborate procedures, and such procedures may be adversely affected by temperature fluctuations and variations in the nature of the incoming samples, particularly when using relatively small diameter tubing or small chambers and low flow rates. For example, if an air bubble is carried by a solution into a piece of small diameter tubing or a small chamber separating a sensing electrode and reference electrode, there may be a large increase in electrical resistance and this may result in displacement of the meter reading or recording. Thus, air bubbles may cause erratic and unstable performance which is particularly severe in monitoring systems which operate with relatively low flow rates and small volumes.

A principal object of the present invention is to provide a system for monitoring with ion-sensitive electrodes, which system is basically unaffected by air bubbles in the liquid stream, and wherein the output is relatively independent of variations in the flow rate of the liquid stream. Generally, this object is effected by a novel electrode chamber system comprising a short hollow cylinder closed at both ends and having at least a pair of sensing electrodes forming part of the two closed end walls. Inlet and outlet ports are provided in the circular walls of the cylinder. This system has the unique advantage of being effectively unaffected by any air bubbles in the liquid stream. This system has another advantage in substantially insuring that fresh solution will not move through while earlier solution remains behind.

The term "flow rate" as used herein is intended to mean the volume of liquid passing a given point per unit of time.

Other objects of the invention will in part be obvious and will in part appear hereinafter. The invention accordingly comprises the apparatus possessing the construction, combination of elements, and arrangement of parts, and the process including the several steps and the relation of one or more of such steps with respect to each of the others, all of which are exemplified in the following detailed disclosure and the scope of the application of which will be indicated in the claims.

For a fuller understanding of the nature and objects of the present invention, reference should be had to the following detailed description taken in connection with the accompanying drawings wherein;

FIG. 1 shows a preferred embodiment of the present invention, partly in cross-section and partly schematically; and

FIG. 2 is a cross-sectional view of the apparatus of FIG. 1 taken along line 2-2.

Referring to FIGS. 1 and 2 there is shown a first conduit 20 for conveying a stream of fluid 22 containing the ions of interest, and a second conduit 24 which is intended to convey a stream of fluid 26 containing a reagent or liquid having therein tag ions chosen so as to not interfere with the detection of the ions of interest by an appropriate electrochemical electrode. Reagent 26 may be supplied from a reservoir or the like (not shown). The supply of sample fluid 22 can be obtained from any source, such as from process or the like, which is to be monitored.

The device includes pump means 30, in its preferred form shown as a dual pump, capable of delivering an output of reagent and sample streams at a substantially adjustable ratio of pumped flow rates indicated respectively as V_R and V_S . Alternatively, pump means 30 can be two separate pumps or only one channel need be pumped, the other being gravity fed, for example. Pumping should be arranged to use as little reagent as practicable, typically in the order of one or two ml/minute. As an alternative embodiment, one or both of sample and reagent streams 22 and 26 may be gravity fed. Pump means 30 are disposed to pump the liquids in conduits 20 and 24 into a common conduit 32 wherein reagent stream 26 and sample stream 22 are intimately mixed. Conduit 32 is connected through inlet port 34 to sensing chamber 36. Chamber 36 is a hollow chamber preferably in the shape of a short cylinder formed of curved wall 38. The chamber is closed at both ends by end walls 40 and 42, respectively. Walls 40 and 42 preferably are flat, substantially parallel to one another and are substantially perpendicular to the cylindrical axis of chamber 36. In order to minimize electrical resistance and decrease sample hold-up volume, both the length and diameter of chamber 36 should be kept small. Preferably, in order to assure that fresh solvent will displace earlier solution and cause the latter to move through the chamber the length of the chamber should not be greater than about twice its diameter. Conduit 32 and inlet port 34 communicate with chamber 36 so that fluid passing through conduit 32 and out of port 34 is directed along a path initially substantially tangent to curved wall 38. An outlet port 46 is provided coupled to outlet conduit 48 which provides an outlet path for fluid directed substantially radially toward the cylindrical axis of chamber 36. Preferably inlet port 34 and outlet port 46 are also positioned substantially equidistant between walls 40 and 42. The positioning of inlet and outlet ports 34 and 46 relative

to one other around the interior surface of chamber 36 is also important, and the ports should be spaced approximately 180° apart as measured around the curved wall 38. For convenience in illustration however, the inlet and outlet ports are shown as being somewhat less than 180° apart. Inlet port 34 and outlet port 46 preferably each have a small cross-sectional area relative to the spacing between walls 40 and 42 so that any air which may enter chamber 36 will enter as relatively small bubbles.

Serving as at least part of one end wall such as 40 is electrode 49 which has a portion thereof sensitive to the ionic species of interest. Serving as at least part of the other end wall 42 is electrode 50 which has a portion thereof sensitive to the reference ionic species. Electrodes 49 and 50 are typically cemented in place on the ends of the cylinder as shown using an adhesive which is resistant to the solution being tested. It will be apparent however, that the electrodes may be held in place by mechanical means, e.g. springs, and sealed with O-rings or the like. The ion-sensitive portions 51 and 52 of sensing electrodes 49 and 50 respectively should form a large or significant fraction of the total wall area, since this will reduce the electrical resistance and reduce the sensitivity to any air bubbles. Typically the ion-sensitive portion of each sensing element should represent 10 to 100 percent of the corresponding side wall area. Ion-sensitive portions 51 and 52, as known, typically are coupled through a contact having a substantially constant (neglecting temperature effects) contact potential, to output lead wires 53 and 54 respectively. Electrode 49 should be sensitive to the ionic species of interest and relatively insensitive to the second ionic species to which electrode 50 is responsive. Similarly electrode 50 should be non-responsive to the ionic species of interest to which electrode 49 responds. The electrodes most useful in the present invention are generally those which provide an electrical signal which is a function of the logarithm of the activity of the ionic species to which the electrode is sensitive, i.e., exhibit a response which is substantially according to the well-known Nernst equation. Typically the electrode elements may be made of solid state ion-sensing materials such as lanthanum fluoride, silver chloride, or sodium-sensitive glass, or they may consist of a porous membrane material which has been saturated with an organic ion-exchanger or other electrodes known in the art. A large number of such electrodes are described in detail in the literature, as for example, R.A. Durst, "Ion Sensitive Electrodes", National Bureau of Standards, Special Publication 134, (1969). In operation, chamber 36 is oriented so that end walls 40 and 42 are substantially vertical with input 34 substantially at the six o'clock position and output port 46 substantially at the twelve o'clock position. The mixed reagent-sample stream in conduit 32 is fed into the cell through input port 34 along a flow stream tangent to wall 38. Once the chamber is filled with liquid, any additional liquid introduced thereto has the effect of stirring the liquid in the chamber as a result of the combination of the circular shape of the latter and the tangential entry of the liquid. The withdrawal of liquid is from the top of the chamber through outlet 46. The circular shape and tangential entry also has the effect of minimizing formation of eddies and the accumulation of old solution in the chamber.

The output leads 53 and 54 of each electrode 49 and 50 are connected to respective amplifiers (not shown) of appropriate input impedance which amplifiers, as explained hereinafter, may be inverting or non-inverting depending on the choice of tag ion used. The amplifiers may have variable gain if desired. The outputs of amplifiers are in turn connected to be summed as in a summing operational amplifier. One can assume that the reagent contains a fixed concentration R of tag ions which do not significantly interfere with the determination, and the sample contains a variable concentration S of the ionic species to be monitored. With respect to an arbitrary reference potential, then according to the Nernst equation:

$$E_s = B_s + \phi_s \log(q)/(1+q) + \phi_s \log S$$

and

$$E_R = [B_R + \phi_R \log R] + \phi \log(q)/(1+q)$$

where B_s , B_R are constants, ϕ_R and ϕ_s are the well-known values RT/nf of the respective Nernst equations, and q is equal to the ratio of sample flow rate to reagent flow rate, V_s/V_R .

If now one sets ϕ_R equal and opposite to ϕ_s as by proper choice of the tag ion species, and feeds the two signals E_s and E_R into an algebraic summing device such as the summing amplifier the output signal ΔE of the latter will be (remembering that the log R by definition is fixed)

$$\Delta E = \text{constant} + \phi_s \log [(q)/(q+1)]^2 + \phi_s \log S$$

The second term varies with the flow rate ratio, q . However, for flow rates of sample and reagent which are approximately equal, we have found that variations in q have little effect on the measured potentials. The potential ΔE actually measured between electrodes 49 and 50, will substantially follow the Nernst equation

$$\Delta E \approx \text{constant} + \phi \log S$$

where S is the concentration of the species of interest.

The tag ion should have a valence equal and opposite to the sample ion. For example, if one sample ion is a monovalent cation, the tag ion should only be a monovalent anion, e.g. Na^+ and Cl^- respectively.

However, one can employ a wide variety of tag ions and achieve proper flow compensation through the electronics employed. For example, if the tag ion is the same polarity as the sample ion and even of different charge (e.g. tag ion is Cl^- and sample ion is Ca^{++}) then to obtain a difference signal ΔE , by summation, one can invert one of the signals by an inverter, provided that the summing amplifier is connected to one of the streams by a conventional reference electrode. Further, where the slopes are different, one should provide a gain of two to the amplifier reading the signal responsive to the divalent ion in order to have the two signals track properly. Obviously one can employ a tag ion with a sample ion of the same polarity and charge (e.g. Na^+ and K^+) in which case, tracking can be achieved

merely by inversion of one of the signals and summation of the two against a common reference electrode. While, in principle, one can use any pair of ion-sensing electrodes to achieve flow compensation (provided that correct gains and senses are used in the respective electrode amplifiers), the need for a stable reference electrode can only be eliminated by employing a pair of electrodes which respond to ions of the same charge number but opposite sign.

It will be appreciated that any entrained air in the reagentsample stream which may be introduced into the chamber 36 will tend to rise directly to the top of the cell and to exit almost immediately through outlet port 46. Since chamber 36 is much wider than input port 34, any air bubbles which form will tend to be substantially smaller than the width of the cell and thus will tend not to affect a significant part of the ion-sensitive portions of the electrodes. In other words, any bubble will tend to displace a relatively insignificant amount of liquid from contact with the electrodes, and only relatively small fluctuations in electrical resistance for the cell should occur. For example, as an extreme, if through inadvertance, only air is introduced to the system after initial operations, the air will pass directly to the top of the chamber and exit through outlet port 46 without changing the nature of the solution still in the chamber. The cell formed by the electrodes will continue to function, reporting the concentration of the last solution which was run through it.

The following examples are illustrative of the monitoring system which can be achieved by the present invention.

EXAMPLE I

A monitoring system for fluoride was built as follows:

A cylindrically shaped hollow tube was constructed from an insulating, chemically inert polymeric material. The tube had an interior diameter of 1 cm. and a length of 1 cm. Completing the end walls of the tube were a sodium-sensitive electrode and a fluoride-sensitive electrode (respectively Model Nos. 94-11 and 94-09 available commercially from Orion Research Incorporated, Cambridge, Mass.) in which the ion-sensitive faces constituted approximately 90 percent of the respective end walls. The electrodes were held in place by springs and were sealed into the walls of the chamber with flat silicon-rubber washers.

A sixteenth inch inside diameter inlet tube was provided in the circular surface of the cylinder directed tangentially to the circular surface intermediate the end walls. A one eighth inch inside diameter outlet tube was provided in the circular surface of the cylinder radially to the circular surface, intermediate the end walls on the opposite side of the circular surface. The cylinder was oriented so that the end walls were substantially upright and the inlet tube was at or near the low point of the circular surface.

An aqueous sample stream comprising 1 ppm of potassium fluoride was taken up from a sample pool through a 1/16 inch inside diameter Tygon (plasticized polyvinyl chloride) tubing, and passed through one channel of four-channel peristaltic pump.

A separate channel of the same pump drew a stream of reagent known as TISAB (1 M KCl, 1 M acetate/acetic acid pH buffer and 1 g/l of a complexing agent for aluminum, EDTA). This reagent stream was mingled in a single conduit with the sample stream in a 1:1 ratio

by the pump. The reagent here was intended to fix the total ionic strength of the water at a uniformly measurable level, adjust the pH, and free fluoride in the sample stream from complexing agents. The mingled solution was then directed through a mixing chamber, which was formed of a small cylindrical section containing a magnetic stirrer, and thence into the cell formed of the two electrodes. From the cell, the mixed stream went to waste. Each electrode was connected to an electronic circuit serving as a differential amplifier and readout.

For the purposes of this experiment, each meter served as a high input impedance, unitary gain amplifier. In order to simplify the electronics, an ohmic connection was made to the mixed stream. The difference in output potential between the two meters was read out on a third similar meter.

The system was started up at a flow rate of about 1 ml/min into the electrode cell. After about 15 minutes a bucking or bias potential was applied and the difference between the electrode pair was arbitrarily set to read zero mv. Over a period of 10 to 15 minutes the potential difference between the electrode pair was observed to vary about 0.3 mv.

Next an additional channel of the pump was opened to introduce air into the stream as air bubbles. The amount of air bubbles in the stream amounted to about 33 percent of the total volume of the stream. No detectable potential change was observed in the meter reading over a period of 10 to 15 minutes.

EXAMPLE II

The same physical arrangement was used as in the preceding example, except that two channels of the pump were fed an aqueous solution of 1 ppm of potassium fluoride.

After an initial 15 minutes of operation, at a flow rate of about 1 ml/min., a bucking or bias potential was applied and the difference between the electrode pair was again arbitrarily set to read zero mv. Over a period of 10 to 15 minutes, the potential difference between the electrode pair was observed to vary by less than about 0.3 mv. Next the last channel of the pump was opened to introduce air into the stream as air bubbles. The amount of air bubbles in the stream amounted to about 25 percent of the total volume of the stream. Notwithstanding such 25 percent volume, no detectable potential change was observed in the meter reading over a period of 10 to 15 minutes.

It should be noted that the system of the present invention has unique advantages. First of all, the system allows reliable results even with extremely low flow rates and it minimizes time lapse for "on-line" monitoring. Also the presence of any air bubbles in the sample and/or reagent stream exhibit virtually no effect on the electrode reading. Additionally the output is unaffected by variations in the flow rate of the liquid stream. Finally the system insures that fresh solution will not move through while earlier solutions remain behind.

While the chamber has been described as being cylindrically shaped that is, as having a circular cross section, it will be apparent that the advantages of the present invention can be achieved with a chamber which has an oval or other more or less circular or round cross-section.

Since certain changes may be made in the above apparatus and made without departing from the scope of the invention herein involved it is intended that all matter contained in the above description or shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. An electrode cell comprising in combination:
hollow chamber means having a portion with a substantially circular cross-section bounded by two end walls;
means for introducing a stream of liquid into said cell through an inlet port along a path substantially tangent to the interior curved wall of said chamber;
means for permitting fluid flow from said cell through an outlet port along a path initially directed radially with respect to said cross-section; and
a pair of electrodes responsive to ionic species in said liquid, each forming a portion of a respective one of said end walls.
2. A cell as defined in claim 1 wherein said input and output ports are in opposite sides of said chamber in said curved wall.
3. A cell as defined in claim 2 wherein said ports are each disposed substantially halfway between said end walls.
4. A cell as defined in claim 1 wherein said side walls are substantially parallel to each other.
5. A cell as defined in claim 1 having the shape of a right cylinder with a length not greater than about twice its cross-sectional radius.
6. A cell as defined in claim 1 wherein each of said electrodes includes an ion-sensitive surface and said surface comprises at least about 10 percent of the surface area of the corresponding one of said end walls.
7. Apparatus for electrochemical monitoring of a first ionic species of interest in a first liquid flow stream comprising in combination;

- means for mixing a second flow stream containing a second species of ion at a substantially fixed concentration, intimately into said first flow stream;
- an electrode cell comprising a hollow chamber having a substantially circular cross-section portion bounded by two end walls;
- means for introducing said mixed flow streams into said cell through an inlet port along a path substantially at least partially tangentially to the interior curved wall of said chamber;
- means for permitting said stream to flow out of said cell through an outlet port along a path initially directly radially to said curved wall;
- a first electrochemical electrode for providing an electrical signal as a function of the activity of said first ionic species in said stream, said first electrode forming at least a portion of one of said end walls; and
- a second electrochemical electrode for providing an electrical signal as a function of the activity of said second species of ion, said second electrode forming at least a portion of the other of said end walls.
8. Apparatus according to claim 7 wherein said first electrode is substantially non-responsive to said second species, and said second electrode is substantially non-responsive to said first species.
9. Apparatus according to claim 7 wherein said input and output ports are on opposite sides of said chamber in said curved wall and disposed substantially halfway between said end walls.
10. Apparatus according to claim 7 wherein said cell is oriented with respect to gravity so that said side walls are substantially vertical and said inlet port is positioned in the bottom portion of said chamber.
11. Apparatus according to claim 7 including pump means for impelling both of said flow streams at an approximately fixed ratio of flow rates.
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